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TABLES OF THE CLASSICAL ORBITAL INTEGRALS IN COULOMB EXCITATION

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CONTENTS

Synopsis.

In the classical description of the Coulomb excitation process one is led to some non-elementary definite integrals. These integrals can also be used in a more refined treatment, which is related to the WBK method, for the calculation of the quantum mechanical corrections. This paper contains a collection of formulae, mathematical properties, and asymptotic expansions of these integrals. An explicit tabulation of the integrals for a large range of the interesting parameters is given.

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I. Introduction.

In a Coulomb excitation process, the amplitude for excitation of the nucleus depends on the nuclear properties only through matrix elements identical to those which determine the corresponding radiative transitions. The dependence of the cross section on the various parameters of the process, such as velocity and charge of the projectile, is given through numerical functions (e. g., f and a) of dimensionless combinations of these quantities (e. g., η, ξ, and ϑ).[1]

In the classical description of the excitation process, these functions (cf. eqs. (24—26)) are simply related to the orbital integrals $I_{\lambda\mu}(\vartheta, \xi)$ defined by

$$I_{\lambda\mu}(\vartheta, \xi) = \int_{-\infty}^{+\infty} e^{i\xi[\varepsilon \sinh w + w]} \frac{[\cosh w + \varepsilon + i\sqrt{\varepsilon^2 - 1} \sinh w]^{\mu} dw}{[\varepsilon \cosh w + 1]^{\lambda + \mu}}, \tag{1}$$

where ϑ is the deflection angle of the projectile and is connected with the eccentricity ε of the hyperbolic orbit through

$$\varepsilon = (\sin \vartheta/2)^{-1}. \tag{2}$$

The classical approximation is valid only when the parameter η, defined by

$$\eta = \frac{Z_1 Z_2 e^2}{\hbar v}, \tag{3}$$

is much larger than unity. By a proper symmetrization of the classical expressions for the cross sections, introducing a symmetrized adiabaticity parameter ξ through

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[1] For a discussion of the theory and experimental data concerning Coulomb excitation, the reader is referred to a review article by K. Alder, A. Bohr, T. Huus, B. Mottelson, and A. Winther (Rev. Mod. Phys., in press). This article contains references to the original papers in which the theoretical relations employed here are derived.

$$\xi = \eta_f - \eta_i = \frac{Z_1 Z_2 e^2}{\hbar}\left(\frac{1}{v_f} - \frac{1}{v_i}\right), \tag{4}$$

one obtains, however, results for the total cross sections which differ only slightly from the quantum mechanical expressions, even for η of the order of unity. The angular distributions of the γ-rays following a Coulomb excitation have proved to be more sensitive to quantal corrections. Also the differential cross sections which have so far been evaluated only in the classical approximation are expected to be more sensitive to quantum effects.

In the quantum mechanical treatment of Coulomb excitation, the f- and a-functions are expressed as sums of radial matrix elements between Coulomb wave functions of different angular momenta. As is seen, for instance, from a *WKB* approximation, these radial matrix elements can for large values of η or l be expressed in terms of the classical orbital integrals by the relation

$$M_{l,\, l+\mu}^{-\lambda-1} \approx \frac{k^{\lambda-2}}{4\,\eta^{\lambda}} I_{\lambda\mu}(\vartheta,\ \xi), \tag{5}$$

where

$$\varepsilon = \frac{1}{\sin \vartheta/2} = \eta^{-1}\left[\eta^2 + \left(l + \frac{\mu}{2}\right)\left(l + \frac{\mu}{2} + 1\right)\right]^{1/2} \tag{6}$$

and where η and k are the geometric mean values of the classical parameter and wave numbers, respectively, in the initial and final state. Employing the relation (6) between the angular momenta involved in the radial matrix elements, and the deflection angle entering in the $I_{\lambda\mu}$, one may in this way obtain a very good approximation of the radial matrix elements, even for η and l of the order of unity. In turn, the study of the radial matrix elements has proved fruitful in the development of the theory of the classical integrals. The exact expressions which one has obtained for the matrix elements reduce, in the limit of $|l + i\eta| \gg 1$, to functions which provide series forms of the $I_{\lambda\mu}$. Also recursion relations for the $I_{\lambda\mu}$ can easily be obtained from recursion formulae for the radial matrix elements.

In the theory of Coulomb excitation enter only the orbital integrals with $\mu = -\lambda, -\lambda + 2, -\lambda + 4, \ldots \lambda$. With these integrals one may easily evaluate the f-functions entering in the differential and total excitation cross sections. Tables of these functions are also included in this paper. Furthermore, one can calculate the a-coefficients for the angular distribution of the de-excitation γ-rays. The coefficients for the distribution, irrespective of the scattering angle of the projectile, are given in ref. 1. The γ-ray angular distribution for a fixed scattering angle is expressed as a simple polynomial in the $I_{\lambda\mu}$ and is thus readily evaluated from the present tables (loc. cit., eq. (II A. 66)). Also the cross sections for higher order excitation processes may be evaluated from the $I_{\lambda\mu}$ (loc. cit., eqs. (II D 10 and 11)).

Besides these applications of the orbital integrals in the classical theory of Coulomb excitation, one obtains by means of the relation (5) an extension of the applicability of the $I_{\lambda\mu}$ in the domain where quantum mechanics must be used.

The present paper contains a tabulation of the $I_{\lambda\mu}(\vartheta, \xi)$ for $\lambda = 1, 2, 3$, and 4. Before we give the tables, we quote some mathematical properties of these functions.

II. Some Properties of the $I_{\lambda\mu}$.

For the numerical evaluation of the orbital integrals (1), it is convenient to translate the path of integration by an amount $i\pi/2$, whereby the integral takes the form

$$I_{\lambda\mu}(\vartheta, \xi) = e^{-\frac{\pi}{2}\xi} \int_{-\infty}^{+\infty} e^{-\xi\varepsilon \cosh w}\, e^{i\xi w} \frac{[i \sinh w + \varepsilon - \sqrt{\varepsilon^2 - 1} \cosh w]^{\mu}\, dw}{[i\varepsilon \sinh w + 1]^{\lambda+\mu}}. \qquad (7)$$

While the integral forms (1) and (7) are convenient for a discussion of different limiting cases, it may especially for small values of ξ be convenient to use a series form. As mentioned before, this was obtained from the series expression for the radial matrix elements in the limit $|l + i\eta| \gg 1$. For $\mu = \pm\lambda$ the result may be written

$$\left.\begin{aligned} I_{\lambda,-\lambda}(\vartheta, \xi) &= 2^{\lambda} \sin^{\lambda} \vartheta/2\, e^{-\xi(\cot\vartheta/2 + \vartheta/2 - \pi/2)} \\ &\times \left\{ \frac{|\Gamma(\lambda + i\xi)|^2}{(2\lambda - 1)!} \psi_2(-2\lambda + 1, -\lambda + 1 - i\xi, -\lambda + 1 + i\xi, z, z^*) \right. \\ &\qquad + 2\, Re\, [e^{-\pi\xi}\, \Gamma(-\lambda - i\xi)\, z^{\lambda + i\xi} \\ &\qquad \left. \psi_2(-\lambda + 1 + i\xi, \lambda + 1 + i\xi, -\lambda + 1 + i\xi, z, z^*) \right\} \end{aligned}\right\} \qquad (8)$$

with

$$z = \xi/2\,(\cot\vartheta/2 - i) = e^{-i\vartheta/2} \frac{\xi}{2 \sin\vartheta/2} \qquad (9)$$

and

$$\left.\begin{aligned} I_{\lambda,\lambda}(\vartheta,\xi) &= 2^{\lambda}\sin^{\lambda}\vartheta/2\,(-1)^{\lambda}\,e^{\xi\,[\cot\vartheta/2+\vartheta/2-\pi/2]} \\ &\left\{\frac{|\Gamma(\lambda+i\xi)|^{2}}{(2\lambda-1)!}\,\psi_2(-2\lambda+1,\,-\lambda+1-i\xi,\,-\lambda+1+i\xi,\,-z^{*},\,-z)\right. \\ &\quad+2\,Re\,[\Gamma(-\lambda-i\xi)\,(z^{*})^{\lambda+i\xi}\,(-1)^{\lambda} \\ &\left.\psi_2(-\lambda+1+i\xi,\,\lambda+1+i\xi,\,-\lambda+1+i\xi,\,-z^{*},\,-z)\right\} \\ &= e^{-\pi\xi}\,(-1)^{\lambda}\,I_{\lambda,-\lambda}(-\vartheta,\xi). \end{aligned}\right\} \quad (10)$$

The function ψ_2 is a generalized confluent hypergeometric function of two variables, and is defined by the power series

$$\psi_2(\alpha,\beta,\beta';x,y)=\sum_{m,n}\frac{\alpha_{m+n}}{\beta_m\beta'_n}\frac{x^m}{m!}\frac{y^n}{n!} \quad (11)$$

with

$$a_m=\frac{\Gamma(a+m)}{\Gamma(a)} \quad (12)$$

which is convergent for all x and y.

The first ψ_2 function in (8) and (10) is, according to (11), a polynomial which for the lowest multipole orders is given by

$$\left.\begin{aligned} &\psi_2\,(-2\lambda+1,\,-\lambda+1-i\xi,\,-\lambda+1+i\xi,\,z,\,z^{*}) \\ &=\begin{cases} 0 & \lambda=1 \\ \dfrac{1}{(1+\xi^2)} & \lambda=2 \\ \dfrac{2}{(1+\xi^2)(4+\xi^2)}(5\,\xi\cot\vartheta/2+4) & \lambda=3. \end{cases} \end{aligned}\right\} \quad (13)$$

In the dipole ($\lambda=1$) case, (8) and (10) may be expressed in terms of Hankel functions, as may be seen directly from (1) or (7). One finds

$$I_{1,\pm1}(\vartheta,\xi)=-2\,\xi\,e^{-\frac{\pi}{2}\xi}\left[K'_{i\xi}(\xi\varepsilon)\pm\frac{\sqrt{\varepsilon^2-1}}{\varepsilon}K_{i\xi}(\xi\varepsilon)\right], \quad (14)$$

where K is the Hankel function of imaginary argument, and where K' means the derivative with respect to the argument.

The integrals $I_{\lambda\mu}$ with $|\mu|\neq\lambda$ are most easily obtained from the recursion relations. There exist a large number of such relations which may be derived from the recursion formulae for the radial matrix elements. We shall here give the following three examples of such relations:

$$(\lambda+1)\, I_{\lambda+1,\,1} = -\frac{\partial}{\partial\varepsilon} I_{\lambda,\,0} - \xi\,\frac{\sqrt{\varepsilon^2-1}}{\varepsilon}\, I_{\lambda,\,0} \tag{15}$$

$$\left.\begin{aligned} 2(\lambda-1)\, I_{\lambda+1,\,0} = {} & -\frac{\partial}{\partial\varepsilon}(I_{\lambda,\,1}+I_{\lambda,\,-1}) + \frac{\sqrt{\varepsilon^2-1}}{\varepsilon}(I_{\lambda,\,1}+I_{\lambda,\,-1}) \\ & + \xi\,(I_{\lambda,\,1}-I_{\lambda,\,-1}), \end{aligned}\right\} \tag{16}$$

$$\left.\begin{aligned} \frac{2\,\xi}{3}\, I_{2,\,0} = {} & \frac{\varepsilon}{\sqrt{\varepsilon^2-1}}\,\frac{\partial}{\partial\varepsilon}(I_{2,\,-2}-I_{2,\,2}) + \xi\,(I_{2,\,-2}+I_{2,\,2}) \\ & + [3\,(\varepsilon^2-1)^{-1/2} - (\varepsilon^2-1)^{-3/2}]\,(I_{2,\,-2}-I_{2,\,2}). \end{aligned}\right\} \tag{17}$$

The series form of the $I_{\lambda\mu}$ is especially convenient for small values of ξ and not too small values of ϑ.

For small values of ϑ (and arbitrary ξ) it is convenient to use the asymptotic formula

$$I_{\lambda\mu}(\vartheta,\,\xi) \approx (-1)^{\frac{\lambda+\mu}{2}}\,\varepsilon^{-1}\left(\frac{\xi}{2\,\varepsilon}\right)^{\frac{\lambda-1}{2}}\,\Gamma\!\left(\frac{-\lambda+\mu+1}{2}\right) e^{-\frac{\pi}{2}\xi}\, W_{-\frac{\mu}{2},\,-\frac{\lambda}{2}}(2\,\xi\varepsilon). \tag{18}$$

The function W is the Whittaker function, which in this case may be expressed in terms of Hankel functions of integer order.

For $\xi\cdot\varepsilon$ large, one may use the asymptotic expansion of W which leads to

$$I_{\lambda\mu}(\vartheta,\,\xi) \approx \frac{2\,\pi}{\Gamma\!\left(\frac{\lambda-\mu+1}{2}\right)}\, e^{-\xi\left(\varepsilon+\frac{\pi}{2}\right)}\, \xi^{\frac{\lambda-\mu-1}{2}}\,(2\,\varepsilon)^{-\frac{\lambda+\mu+1}{2}}. \tag{19}$$

For large values of ξ and arbitrary values of ε, one may employ the method of steepest descent leading to

$$I_{\lambda,\,\mu}(\vartheta,\,\xi) = e^{-\xi\,(\pi+\zeta-\operatorname{arctg}\zeta)} \int_{-\infty-i\delta}^{+\infty-i\delta} dx\, \frac{\exp\left\{-\frac{\zeta\xi}{2}x^2 - \frac{i\,\xi}{6}x^3\right\}}{x^{\lambda-\mu}\,(x-2\,i\,\zeta)^{\lambda+\mu}} \tag{20}$$

with $\zeta = \sqrt{\varepsilon^2-1} = \cot\vartheta/2$. For the evaluation of the integral, a series development in ζ may be employed.

For $\xi = 0$, the orbital integrals may be reduced to elementary functions. Thus, one obtains

$$I_{\lambda,\,\mu}(\vartheta, 0) = \sqrt{2\pi}\,(\lambda-1)!\,\varepsilon^{-1/2}\,(\varepsilon^2-1)^{-\frac{\lambda}{2}+\frac{1}{4}}\,P_{\mu-1/2}^{-\lambda+1/2}(1/\varepsilon), \tag{21}$$

where P is the Legendre function. For the lowest multipole orders, one finds the following explicit expressions in terms of elementary functions.

$$\left.\begin{aligned}
I_{1\pm1} &= 2\sin\vartheta/2\\
I_{2\pm2} &= \frac{2}{3}\sin^2\vartheta/2\\
I_{20} &= 2\,\mathrm{tg}^2\,\vartheta/2\left[1-\frac{\pi-\vartheta}{2}\,\mathrm{tg}\,\vartheta/2\right]\\
I_{3\pm3} &= \frac{4}{15}\sin^3\vartheta/2\\
I_{3\pm1} &= \frac{2\sin^3\vartheta/2}{\cos^4\vartheta/2}\left[\frac{2+\sin^2\vartheta/2}{3}-\mathrm{tg}\,\vartheta/2\cdot\frac{\pi-\vartheta}{2}\right]\\
I_{4\pm4} &= \frac{4}{35}\sin^4\vartheta/2\\
I_{4\pm2} &= \frac{2\sin^4\vartheta/2}{\cos^6\vartheta/2}\left[\frac{8+9\sin^2\vartheta/2-2\sin^4\vartheta/2}{20}-\frac{\pi-\vartheta}{2}\cdot\frac{3}{4}\,\mathrm{tg}\,\vartheta/2\right]\\
I_{40} &= 2\,\mathrm{tg}^6\,\vartheta/2\left[\frac{2}{3\sin^2\vartheta/2}+\frac{11}{6}-\frac{5\,\mathrm{tg}^2\,\vartheta/2+3}{2\,\mathrm{tg}\,\vartheta/2}\cdot\frac{\pi-\vartheta}{2}\right].
\end{aligned}\right\} \tag{22}$$

The orbital integrals for negative values of ξ can be found from the following symmetry relation:

$$I_{\lambda,\,\mu}(\vartheta, -\xi) = I_{\lambda,\,-\mu}(\vartheta, \xi). \tag{23}$$

III. Tables of $I_{\lambda\mu}(\vartheta, \xi)$.

The following tables of the orbital integrals were obtained from the integral form (7) by numerical integration. This calculation was performed on the high speed electronic computor Besk in Stockholm and the tables are directly reproduced from the output of the machine.

Besides the $I_{\lambda\mu}$, the tables contain the differential and total cross section functions $df_\lambda(\vartheta, \xi)/d\Omega$ and $f_\lambda(\xi)$, entering in the classical theory of Coulomb excitation. These functions are defined in terms of the orbital integrals by

$$df_{E\lambda}(\vartheta, \xi)/d\Omega = \frac{4\pi^2}{(2\lambda+1)^3} \sum_\mu \left| Y_{\lambda\mu}\left(\frac{\pi}{2}, 0\right)\right|^2 \left| I_{\lambda\mu}(\vartheta, \xi)\right|^2 \sin^{-4}\vartheta/2, \quad (24)$$

$$\left.\begin{aligned} df_{M\lambda}(\vartheta, \xi)/d\Omega = \frac{4\pi^2}{(2\lambda+1)^2} \sum_\mu \frac{(\lambda+1)^2-\mu^2}{\lambda^2(2\lambda+3)} \left| Y_{\lambda+1,\,\mu}\left(\frac{\pi}{2}, 0\right)\right|^2 \\ \left| I_{\lambda+1,\,\mu}(\vartheta, \xi)\right|^2 \cdot \cot^2\vartheta/2 \cdot \sin^{-4}\vartheta/2, \end{aligned}\right\} \quad (25)$$

$$f_\lambda(\xi) = 2\pi \int_0^\pi \frac{df_\lambda(\vartheta, \xi)}{d\Omega} \sin\vartheta \, d\vartheta. \quad (26)$$

The table contains the f-functions

$$df_{E\lambda}(\vartheta, \xi)/d\Omega \text{ and } f_{E\lambda}(\xi) \text{ for } \lambda = 1, 2, 3, \text{ and } 4$$
$$df_{M\lambda}(\vartheta, \xi)/d\Omega \text{ and } f_{M\lambda}(\xi) \text{ for } \lambda = 1 \text{ and } 2$$

and the following orbital integrals necessary for the evaluation of these functions

$$I_{\lambda\mu}(\vartheta, \xi) \text{ for } \lambda = 1, 2, 3, \text{ and } 4$$
$$\text{and } \mu = -\lambda, -\lambda+2, \ldots, \lambda.$$

All integrals were calculated for the following values of the parameters

$$\vartheta = 10^\circ\,(10^\circ)\,180^\circ$$

and

$$\xi = 0.0\ (0.1)\ 1.0\ (0.2)\ 2.0,\ 4.0 \quad \text{for } \lambda = 1 \text{ and } 2$$
$$\xi = 0.2\ (0.2)\ 1.0\ (0.5)\ 2.0,\ 4.0 \quad \text{for } \lambda = 3 \text{ and } 4\,.$$

The table is expected to be accurate with the number of decimals given, except for small angles (10°), where a strong cancellation in the integral (7) diminishes the accuracy especially for the higher multipoles. More accurate values may here be obtained by means of (18).

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Explanation of the Tables.

Column 1	$10\,\xi$.
Column 2	angle ϑ in degrees.
Column 3	λ, μ.
Columns 4-5	$I_{\lambda\mu}(\vartheta, \xi)$ as a decimal fraction (decimal point in front of the number) and the power of ten by which it should be multiplied, e. g.,

$$298559 - 02 = 0.00298559.$$

The last line for each value of ϑ and ξ (indicated by DF in the third column) gives the $df_{E\lambda}(\vartheta, \xi)/d\Omega$ for the λ, ϑ, ξ in question. For each value of ξ, the table concludes with the value of $f_{E\lambda}(\xi)$, indicated by F. In this line, the first and second columns give λ and $10\,\xi$, respectively.

The tables 5 and 6 contain only the $df_{M\lambda}(\vartheta, \xi)/d\Omega$ and $f_{M\lambda}(\xi)$, since the $I_{\lambda\mu}$ necessary are the same as those for the electric excitations.

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Table 1. $I_{1\mu}(\vartheta, \xi)$, $df_{E1}(\vartheta, \xi)/d\Omega$ and $f_{E1}(\xi)$.

00	180	1.+1	200000	01
		1.-1	200000	01
		1 DF	139626	01
00	170	1.+1	199238	01
		1.-1	199238	01
		1 DF	140695	01
00	160	1.+1	196961	01
		1.-1	196961	01
		1 DF	143967	01
00	150	1.+1	193185	01
		1.-1	193185	01
		1 DF	149651	01
00	140	1.+1	187938	01
		1.-1	187938	01
		1 DF	158123	01
00	130	1.+1	181261	01
		1.-1	181261	01
		1 DF	169987	01
00	120	1.+1	173205	01
		1.-1	173205	01
		1 DF	186168	01
00	110	1.+1	163830	01
		1.-1	163830	01
		1 DF	208083	01
00	100	1.+1	153208	01
		1.-1	153208	01
		1 DF	237935	01
00	090	1.+1	141421	01
		1.-1	141421	01
		1 DF	279252	01
00	080	1.+1	128557	01
		1.-1	128557	01
		1 DF	337934	01
00	070	1.+1	114715	01
		1.-1	114715	01
		1 DF	424409	01
00	060	1.+1	100000	01
		1.-1	100000	01
		1 DF	055850	02
00	050	1.+1	084523	01
		1.-1	084523	01
		1 DF	078175	02
00	040	1.+1	068404	01
		1.-1	068404	01
		1 DF	119361	02
00	030	1.+1	051763	01
		1.-1	051763	01
		1 DF	208437	02
00	020	1.+1	347296	00
		1.-1	347296	00
		1 DF	463048	02
00	010	1.+1	174311	00
		1.-1	174311	00
		1 DF	183812	03
1	000	F	113945	03
01	180	1.+1	162146	01
		1.-1	162146	01
		1 DF	091774	01
01	170	1.+1	157978	01
		1.-1	165081	01
		1 DF	092522	01
01	160	1.+1	152638	01
		1.-1	166726	01
		1 DF	094811	01
01	150	1.+1	146200	01
		1.-1	167034	01
		1 DF	098793	01
01	140	1.+1	138739	01
		1.-1	165965	01
		1 DF	104741	01
01	130	1.+1	130344	01
		1.-1	163490	01
		1 DF	113095	01

TABLE 1 (cont.).

01	120	1.+1	121106	01	02	180	1.+1	126875	01
		1.−1	159584	01			1.−1	126875	01
		1 DF	124528	01			1 DF	056190	01
01	110	1.+1	111125	01	02	170	1.+1	122133	01
		1.−1	154231	01			1.−1	130653	01
		1 DF	140075	01			1 DF	056685	01
01	100	1.+1	100507	01	02	160	1.+1	116509	01
		1.−1	147419	01			1.−1	133383	01
		1 DF	161345	01			1 DF	058200	01
01	090	1.+1	089366	01	02	150	1.+1	110093	01
		1.−1	139142	01			1.−1	134989	01
		1 DF	190917	01			1 DF	060835	01
01	080	1.+1	077824	01	02	140	1.+1	102977	01
		1.−1	129391	01			1.−1	135398	01
		1 DF	233087	01			1 DF	064772	01
01	070	1.+1	066015	01	02	130	1.+1	095257	01
		1.−1	118154	01			1.−1	134542	01
		1 DF	295395	01			1 DF	070300	01
01	060	1.+1	054088	01	02	120	1.+1	087030	01
		1.−1	105405	01			1.−1	132357	01
		1 DF	391957	01			1 DF	077858	01
01	050	1.+1	422186	00	02	110	1.+1	078399	01
		1.−1	091087	01			1.−1	128780	01
		1 DF	055146	02			1 DF	088112	01
01	040	1.+1	306259	00	02	100	1.+1	069469	01
		1.−1	075082	01			1.−1	123752	01
		1 DF	083865	02			1 DF	102079	01
01	030	1.+1	196251	00	02	090	1.+1	060350	01
		1.−1	057156	01			1.−1	117215	01
		1 DF	142045	02			1 DF	121346	01
01	020	1.+1	097539	00	02	080	1.+1	051158	01
		1.−1	368676	00			1.−1	109106	01
		1 DF	279170	02			1 DF	148462	01
01	010	1.+1	222266	−01	02	070	1.+1	420200	00
		1.−1	138437	00			1.−1	099357	01
		1 DF	059464	03			1 DF	187661	01
1	01	F	060419	03					

TABLE 1 (cont.).

02	060	1.+1	330777	00
		1.-1	087886	01
		1 DF	246251	01
02	050	1.+1	245018	00
		1.-1	074594	01
		1 DF	337287	01
02	040	1.+1	165127	00
		1.-1	059364	01
		1 DF	484278	01
02	030	1.+1	094291	00
		1.-1	421108	00
		1 DF	072431	02
02	020	1.+1	037718	00
		1.-1	230991	00
		1 DF	105152	02
02	010	1.+1	046571	-01
		1.-1	050675	00
		1 DF	078333	02
1	02	F	272124	02
03	180	1.+1	097783	01
		1.-1	097783	01
		1 DF	333762	00
03	170	1.+1	093277	01
		1.-1	101544	01
		1 DF	336921	00
03	160	1.+1	088117	01
		1.-1	104471	01
		1 DF	346596	00
03	150	1.+1	082394	01
		1.-1	106474	01
		1 DF	363412	00
03	140	1.+1	076199	01
		1.-1	107468	01
		1 DF	388487	00
03	130	1.+1	069622	01
		1.-1	107364	01
		1 DF	423585	00
03	120	1.+1	062757	01
		1.-1	106078	01
		1 DF	471351	00
03	110	1.+1	055694	01
		1.-1	103526	01
		1 DF	053569	01
03	100	1.+1	485281	00
		1.-1	099625	01
		1 DF	062239	01
03	090	1.+1	413534	00
		1.-1	094291	01
		1 DF	074009	01
03	080	1.+1	342707	00
		1.-1	087443	01
		1 DF	090180	01
03	070	1.+1	273880	00
		1.-1	078997	01
		1 DF	112727	01
03	060	1.+1	208271	00
		1.-1	068877	01
		1 DF	144594	01
03	050	1.+1	147338	00
		1.-1	057027	01
		1 DF	189811	01
03	040	1.+1	092965	00
		1.-1	434640	00
		1 DF	251975	01
03	030	1.+1	047772	00
		1.-1	284464	00
		1 DF	323614	01
03	020	1.+1	155923	-01
		1.-1	131024	00
		1 DF	334203	01
03	010	1.+1	106667	-02
		1.-1	165056	-01
		1 DF	082750	01
1	03	F	134950	02

TABLE 1 (cont.).

04	180	1.+1	074673	01
		1.-1	074673	01
		1 DF	194642	00
04	170	1.+1	070704	01
		1.-1	078072	01
		1 DF	196611	00
04	160	1.+1	066254	01
		1.-1	080815	01
		1 DF	202639	00
04	150	1.+1	061406	01
		1.-1	082811	01
		1 DF	213095	00
04	140	1.+1	056246	01
		1.-1	083968	01
		1 DF	228636	00
04	130	1.+1	050853	01
		1.-1	084197	01
		1 DF	250286	00
04	120	1.+1	453087	00
		1.-1	083404	01
		1 DF	279538	00
04	110	1.+1	396907	00
		1.-1	081499	01
		1 DF	318534	00
04	100	1.+1	340776	00
		1.-1	078390	01
		1 DF	370305	00
04	090	1.+1	285484	00
		1.-1	073990	01
		1 DF	439094	00
04	080	1.+1	231849	00
		1.-1	068216	01
		1 DF	053070	01
04	070	1.+1	180748	00
		1.-1	060997	01
		1 DF	065266	01
04	060	1.+1	133164	00
		1.-1	052291	01
		1 DF	081309	01
04	050	1.+1	090266	00
		1.-1	421157	00
		1 DF	101502	01
04	040	1.+1	053527	00
		1.-1	306430	00
		1 DF	123420	01
04	030	1.+1	248684	-01
		1.-1	184358	00
		1 DF	134601	01
04	020	1.+1	066629	-01
		1.-1	070989	00
		1 DF	097587	01
04	010	1.+1	254773	-03
		1.-1	051067	-01
		1 DF	079080	00
1	04	F	069261	02
05	180	1.+1	056667	01
		1.-1	056667	01
		1 DF	112091	00
05	170	1.+1	053314	01
		1.-1	059588	01
		1 DF	113296	00
05	160	1.+1	496091	00
		1.-1	061995	01
		1 DF	116982	00
05	150	1.+1	456266	00
		1.-1	063803	01
		1 DF	123358	00
05	140	1.+1	414398	00
		1.-1	064927	01
		1 DF	132799	00
05	130	1.+1	371185	00
		1.-1	065276	01
		1 DF	145868	00

TABLE 1 (cont.).

05	120	1.+1	327297	00
		1.-1	064761	01
		1 DF	163371	00
05	110	1.+1	283384	00
		1.-1	063292	01
		1 DF	186412	00
05	100	1.+1	240079	00
		1.-1	060782	01
		1 DF	216458	00
05	090	1.+1	198014	00
		1.-1	057147	01
		1 DF	255372	00
05	080	1.+1	157838	00
		1.-1	052318	01
		1 DF	305311	00
05	070	1.+1	120238	00
		1.-1	462451	00
		1 DF	368175	00
05	060	1.+1	085981	00
		1.-1	389263	00
		1 DF	443784	00
05	050	1.+1	055960	00
		1.-1	304530	00
		1 DF	052452	01
05	040	1.+1	031258	00
		1.-1	211184	00
		1 DF	058130	01
05	030	1.+1	131657	-01
		1.-1	116583	00
		1 DF	053539	01
05	020	1.+1	290526	-02
		1.-1	037451	00
		1 DF	270857	00
05	010	1.+1	062375	-03
		1.-1	153467	-02
		1 DF	071358	-01
1	05	F	359110	01
06	180	1.+1	428044	00
		1.-1	428044	00
		1 DF	063956	00
06	170	1.+1	400462	00
		1.-1	452363	00
		1 DF	064684	00
06	160	1.+1	370309	00
		1.-1	472691	00
		1 DF	066904	00
06	150	1.+1	338238	00
		1.-1	488262	00
		1 DF	070735	00
06	140	1.+1	304865	00
		1.-1	498285	00
		1 DF	076380	00
06	130	1.+1	270770	00
		1.-1	050193	01
		1 DF	084140	00
06	120	1.+1	236503	00
		1.-1	498396	00
		1 DF	094428	00
06	110	1.+1	202584	00
		1.-1	486828	00
		1 DF	107778	00
06	100	1.+1	169518	00
		1.-1	466444	00
		1 DF	124835	00
06	090	1.+1	137799	00
		1.-1	436530	00
		1 DF	146292	00
06	080	1.+1	107929	00
		1.-1	396535	00
		1 DF	172667	00
06	070	1.+1	080437	00
		1.-1	346214	00
		1 DF	203720	00

TABLE 1 (cont.).

06	060	1.+1	055901	00
		1.-1	285907	00
		1 DF	236995	00
06	050	1.+1	034982	00
		1.-1	217071	00
		1 DF	264498	00
06	040	1.+1	184358	-01
		1.-1	143339	00
		1 DF	266395	00
06	030	1.+1	070516	-01
		1.-1	072533	00
		1 DF	206563	00
06	020	1.+1	128428	-02
		1.-1	194162	-01
		1 DF	072681	00
06	010	1.+1	155231	-04
		1.-1	045261	-02
		1 DF	062037	-02
1	06	F	187172	01
07	180	1.+1	322178	00
		1.-1	322178	00
		1 DF	036232	00
07	170	1.+1	299898	00
		1.-1	342000	00
		1 DF	036666	00
07	160	1.+1	275753	00
		1.-1	358735	00
		1 DF	037988	00
07	150	1.+1	250290	00
		1.-1	371714	00
		1 DF	040262	00
07	140	1.+1	224022	00
		1.-1	380237	00
		1 DF	043596	00
07	130	1.+1	197421	00
		1.-1	383577	00
		1 DF	048143	00
07	120	1.+1	170927	00
		1.-1	380996	00
		1 DF	054105	00
07	110	1.+1	144956	00
		1.-1	371767	00
		1 DF	061720	00
07	100	1.+1	119897	00
		1.-1	355205	00
		1 DF	071232	00
07	090	1.+1	096134	00
		1.-1	330724	00
		1 DF	082812	00
07	080	1.+1	074049	00
		1.-1	297936	00
		1 DF	096357	00
07	070	1.+1	054039	00
		1.-1	256806	00
		1 DF	111055	00
07	060	1.+1	036534	00
		1.-1	207946	00
		1 DF	124481	00
07	050	1.+1	220049	-01
		1.-1	153133	00
		1 DF	130949	00
07	040	1.+1	109530	-01
		1.-1	096228	00
		1 DF	119638	00
07	030	1.+1	038093	-01
		1.-1	044605	00
		1 DF	077952	00
07	020	1.+1	057340	-02
		1.-1	099426	-01
		1 DF	190390	-01
07	010	1.+1	039085	-04
		1.-1	131741	-03
		1 DF	052544	-03
1	07	F	097952	01

TABLE 1 (cont.).

08	180	1.+1	241805	00
		1.-1	241805	00
		1 DF	204098	-01
08	170	1.+1	224049	00
		1.-1	257716	00
		1 DF	206661	-01
08	160	1.+1	204943	00
		1.-1	271248	00
		1 DF	214459	-01
08	150	1.+1	184941	00
		1.-1	281830	00
		1 DF	227825	-01
08	140	1.+1	164460	00
		1.-1	288858	00
		1 DF	247310	-01
08	130	1.+1	143880	00
		1.-1	291702	00
		1 DF	273670	-01
08	120	1.+1	123551	00
		1.-1	289728	00
		1 DF	307821	-01
08	110	1.+1	103794	00
		1.-1	282311	00
		1 DF	035070	00
08	100	1.+1	084913	00
		1.-1	268881	00
		1 DF	040296	00
08	090	1.+1	067198	00
		1.-1	248977	00
		1 DF	046429	00
08	080	1.+1	050937	00
		1.-1	222354	00
		1 DF	053200	00
08	070	1.+1	036426	00
		1.-1	189141	00
		1 DF	059827	00
08	060	1.+1	239742	-01
		1.-1	150118	00
		1 DF	064535	00
08	050	1.+1	139090	-01
		1.-1	107182	00
		1 DF	063912	00
08	040	1.+1	065444	-01
		1.-1	064068	00
		1 DF	052902	00
08	030	1.+1	207144	-02
		1.-1	271929	-01
		1 DF	289279	-01
08	020	1.+1	257957	-03
		1.-1	050448	-01
		1 DF	048981	-01
08	010	1.+1	099274	-05
		1.-1	037975	-03
		1 DF	043651	-04
1	08	F	051430	01
09	180	1.+1	181061	00
		1.-1	181061	00
		1 DF	114434	-01
09	170	1.+1	167054	00
		1.-1	193685	00
		1 DF	115936	-01
09	160	1.+1	152074	00
		1.-1	204482	00
		1 DF	120498	-01
09	150	1.+1	136491	00
		1.-1	212971	00
		1 DF	128290	-01
09	140	1.+1	120640	00
		1.-1	218642	00
		1 DF	139582	-01
09	130	1.+1	104823	00
		1.-1	220963	00
		1 DF	154728	-01

TABLE 1 (cont.).

09	120	1.+1	089315	00	10	180	1.+1	135312	00
		1.-1	219394	00			1.-1	135312	00
		1 DF	174102	-01			1 DF	063912	-01
09	110	1.+1	074364	00	10	170	1.+1	124353	00
		1.-1	213416	00			1.-1	145238	00
		1 DF	197989	-01			1 DF	064786	-01
09	100	1.+1	060202	00	10	160	1.+1	112693	00
		1.-1	202563	00			1.-1	153765	00
		1 DF	226331	-01			1 DF	067437	-01
09	090	1.+1	047047	00	10	150	1.+1	100632	00
		1.-1	186490	00			1.-1	160493	00
		1 DF	258252	-01			1 DF	071947	-01
09	080	1.+1	035114	00	10	140	1.+1	088437	00
		1.-1	165063	00			1.-1	164998	00
		1 DF	291161	-01			1 DF	078445	-01
09	070	1.+1	246200	-01	10	130	1.+1	076345	00
		1.-1	138524	00			1.-1	166835	00
		1 DF	031920	00			1 DF	087081	-01
09	060	1.+1	157841	-01	10	120	1.+1	064571	00
		1.-1	107734	00			1.-1	165557	00
		1 DF	033107	00			1 DF	097982	-01
09	050	1.+1	088262	-01	10	110	1.+1	053304	00
		1.-1	074557	00			1.-1	160736	00
		1 DF	308396	-01			1 DF	111163	-01
09	040	1.+1	039281	-01	10	100	1.+1	042720	00
		1.-1	042381	00			1.-1	152004	00
		1 DF	231069	-01			1 DF	126354	-01
09	030	1.+1	113230	-02	10	090	1.+1	032982	00
		1.-1	164655	-01			1.-1	139107	00
		1.DF	105948	-01			1 DF	142689	-01
09	020	1.+1	116741	-03	10	080	1.+1	242500	-01
		1.-1	254160	-02			1.-1	122001	00
		1 DF	124259	-02			1 DF	158184	-01
09	010	1.+1	253874	-06	10	070	1.+1	166779	-01
		1.-1	108653	-04			1.-1	100991	00
		1 DF	035728	-05			1 DF	168954	-01
1	09	F	270749	00					

TABLE 1 (cont.).

10	060	1.+1	104203	-01
		1.-1	076948	00
		1 DF	168379	-01
10	050	1.+1	056188	-01
		1.-1	051604	00
		1 DF	147429	-01
10	040	1.+1	236663	-02
		1.-1	278898	-01
		1 DF	099926	-01
10	030	1.+1	062159	-02
		1.-1	099159	-01
		1 DF	038394	-01
10	020	1.+1	053088	-03
		1.-1	127321	-02
		1 DF	311714	-03
10	010	1.+1	065277	-06
		1.-1	309033	-05
		1 DF	289000	-07
1	10	F	142827	00
12	180	1.+1	075217	00
		1.-1	075217	00
		1 DF	197488	-02
12	170	1.+1	068630	00
		1.-1	081228	00
		1 DF	200399	-02
12	160	1.+1	061684	00
		1.-1	086424	00
		1 DF	209196	-02
12	150	1.+1	054568	00
		1.-1	090538	00
		1 DF	224052	-02
12	140	1.+1	047448	00
		1.-1	093286	00
		1 DF	245187	-02
12	130	1.+1	040469	00
		1.-1	094370	00
		1 DF	272747	-02
12	120	1.+1	033756	00
		1.-1	093491	00
		1 DF	306564	-02
12	110	1.+1	274202	-01
		1.-1	090375	00
		1 DF	034575	-01
12	100	1.+1	215592	-01
		1.-1	084798	00
		1 DF	038801	-01
12	090	1.+1	162631	-01
		1.-1	076643	00
		1 DF	042856	-01
12	080	1.+1	116155	-01
		1.-1	065965	00
		1 DF	045867	-01
12	070	1.+1	076950	-01
		1.-1	053104	00
		1 DF	046430	-01
12	060	1.+1	045715	-01
		1.-1	038816	00
		1 DF	042660	-01
12	050	1.+1	229489	-02
		1.-1	244355	-01
		1 DF	032956	-01
12	040	1.+1	086671	-02
		1.-1	119320	-01
		1 DF	182551	-02
12	030	1.+1	189223	-03
		1.-1	035512	-01
		1 DF	049190	-02
12	020	1.+1	111033	-04
		1.-1	031535	-02
		1 DF	191134	-04
12	010	1.+1	043705	-07
		1.-1	246611	-06
		1 DF	184016	-09
1	12	F	039924	00

Table 1 (cont.).

14	180	1.+1	041603	00
		1.-1	041603	00
		1 DF	060419	-02
14	170	1.+1	037717	00
		1.-1	045171	00
		1 DF	061371	-02
14	160	1.+1	033648	00
		1.-1	048267	00
		1 DF	064238	-02
14	150	1.+1	295137	-01
		1.-1	050720	00
		1 DF	069042	-02
14	140	1.+1	254143	-01
		1.-1	052344	00
		1 DF	075788	-02
14	130	1.+1	214359	-01
		1.-1	052948	00
		1 DF	084409	-02
14	120	1.+1	176514	-01
		1.-1	052340	00
		1 DF	094668	-02
14	110	1.+1	141232	-01
		1.-1	050350	00
		1 DF	106002	-02
14	100	1.+1	109056	-01
		1.-1	046852	00
		1 DF	117284	-02
14	090	1.+1	080467	-01
		1.-1	041802	00
		1 DF	126516	-02
14	080	1.+1	055893	-01
		1.-1	035292	00
		1 DF	130539	-02
14	070	1.+1	035708	-01
		1.-1	276185	-01
		1 DF	125058	-02
14	060	1.+1	201951	-02
		1.-1	193589	-01
		1 DF	105794	-02
14	050	1.+1	094488	-02
		1.-1	114343	-01
		1 DF	072021	-02
14	040	1.+1	032035	-02
		1.-1	050426	-01
		1 DF	032563	-02
14	030	1.+1	058202	-03
		1.-1	125577	-02
		1 DF	061467	-03
14	020	1.+1	234915	-05
		1.-1	077090	-03
		1 DF	114181	-05
14	010	1.+1	296367	-09
		1.-1	194141	-07
		1 DF	114033	-11
1	14	F	112058	-01
16	180	1.+1	229229	-01
		1.-1	229229	-01
		1 DF	183420	-03
16	170	1.+1	206605	-01
		1.-1	250097	-01
		1 DF	186491	-03
16	160	1.+1	183061	-01
		1.-1	268249	-01
		1 DF	195702	-03
16	150	1.+1	159308	-01
		1.-1	282607	-01
		1 DF	211012	-03
16	140	1.+1	135947	-01
		1.-1	292004	-01
		1 DF	232227	-03
16	130	1.+1	113479	-01
		1.-1	295222	-01
		1 DF	258774	-03

TABLE 1 (cont.).

16	120	1.+1	092320	-01
		1.-1	291080	-01
		1 DF	289339	-03
16	110	1.+1	072819	-01
		1.-1	278554	-01
		1 DF	032132	-02
16	100	1.+1	055269	-01
		1.-1	256967	-01
		1 DF	035015	-02
16	090	1.+1	039922	-01
		1.-1	226255	-01
		1 DF	036851	-02
16	080	1.+1	269929	-02
		1.-1	187319	-01
		1 DF	036618	-02
16	070	1.+1	166451	-02
		1.-1	142452	-01
		1 DF	033169	-02
16	060	1.+1	089691	-02
		1.-1	095722	-01
		1 DF	258122	-03
16	050	1.+1	039146	-02
		1.-1	053033	-01
		1 DF	154717	-03
16	040	1.+1	119245	-03
		1.-1	211166	-02
		1 DF	057056	-03
16	030	1.+1	180436	-04
		1.-1	043989	-02
		1 DF	075392	-04
16	020	1.+1	050132	-05
		1.-1	186629	-04
		1 DF	066906	-06
16	010	1.+1	202870	-10
		1.-1	151315	-08
		1 DF	069268	-13
1	16	F	031536	-01
18	180	1.+1	125911	-01
		1.-1	125911	-01
		1 DF	055339	-03
18	170	1.+1	112875	-01
		1.-1	137980	-01
		1 DF	056317	-03
18	160	1.+1	099380	-01
		1.-1	148495	-01
		1 DF	059242	-03
18	150	1.+1	085853	-01
		1.-1	156790	-01
		1 DF	064066	-03
18	140	1.+1	072646	-01
		1.-1	162138	-01
		1 DF	070658	-03
18	130	1.+1	060049	-01
		1.-1	163791	-01
		1 DF	078727	-03
18	120	1.+1	048295	-01
		1.-1	161029	-01
		1 DF	087694	-03
18	110	1.+1	037577	-01
		1.-1	153254	-01
		1 DF	096516	-03
18	100	1.+1	280533	-02
		1.-1	140123	-01
		1 DF	103501	-03
18	090	1.+1	198515	-02
		1.-1	121723	-01
		1 DF	106189	-03
18	080	1.+1	130739	-02
		1.-1	098800	-01
		1 DF	101547	-03
18	070	1.+1	077870	-02
		1.-1	072999	-01
		1 DF	086910	-03

TABLE 1 (cont.).

18	060	1.+1	040006	-02
		1.-1	047016	-01
		1 DF	062175	-03
18	050	1.+1	162991	-03
		1.-1	244284	-02
		1 DF	032794	-03
18	040	1.+1	044634	-03
		1.-1	087805	-02
		1 DF	098589	-04
18	030	1.+1	056283	-04
		1.-1	152979	-03
		1 DF	091148	-05
18	020	1.+1	107708	-06
		1.-1	044845	-04
		1 DF	038626	-07
18	010	1.+1	139885	-11
		1.-1	117035	-09
		1 DF	041436	-15
1	18	F	088918	-02
20	180	1.+1	068984	-01
		1.-1	068984	-01
		1 DF	166116	-04
20	170	1.+1	061534	-01
		1.-1	075905	-01
		1 DF	169206	-04
20	160	1.+1	053858	-01
		1.-1	081939	-01
		1 DF	178406	-04
20	150	1.+1	046207	-01
		1.-1	086681	-01
		1 DF	193451	-04
20	140	1.+1	038788	-01
		1.-1	089688	-01
		1 DF	213734	-04
20	130	1.+1	031765	-01
		1.-1	090506	-01
		1 DF	238003	-04
20	120	1.+1	252696	-02
		1.-1	088703	-01
		1 DF	263949	-04
20	110	1.+1	194061	-02
		1.-1	083939	-01
		1 DF	287716	-04
20	100	1.+1	142577	-02
		1.-1	076050	-01
		1 DF	303439	-04
20	090	1.+1	098895	-02
		1.-1	065167	-01
		1 DF	303309	-04
20	080	1.+1	063477	-02
		1.-1	051849	-01
		1 DF	278972	-04
20	070	1.+1	036538	-02
		1.-1	037214	-01
		1 DF	225481	-04
20	060	1.+1	179074	-03
		1.-1	229693	-02
		1 DF	148227	-04
20	050	1.+1	068137	-03
		1.-1	111905	-02
		1 DF	068769	-04
20	040	1.+1	167831	-04
		1.-1	036304	-02
		1 DF	168470	-05
20	030	1.+1	176442	-05
		1.-1	052893	-03
		1 DF	108938	-06
20	020	1.+1	232662	-07
		1.-1	107123	-05
		1 DF	220381	-09
20	010	1.+1	097015	-12
		1.-1	089973	-10
		1 DF	244893	-18
1	20	F	251066	-03

TABLE 1 (cont.).

40	180	1.+1	155192 -04
		1.-1	155192 -04
		1 DF	084071 -09
40	170	1.+1	133306 -04
		1.-1	175867 -04
		1 DF	086303 -09
40	160	1.+1	111449 -04
		1.-1	193770 -04
		1 DF	092717 -09
40	150	1.+1	090551 -04
		1.-1	207052 -04
		1 DF	102392 -09
40	140	1.+1	071271 -04
		1.-1	213700 -04
		1 DF	113592 -09
40	130	1.+1	054063 -04
		1.-1	211796 -04
		1 DF	123602 -09
40	120	1.+1	039215 -04
		1.-1	199903 -04
		1 DF	128764 -09
40	110	1.+1	268908 -05
		1.-1	177612 -04
		1 DF	125085 -09
40	100	1.+1	171420 -05
		1.-1	146123 -04
		1 DF	109707 -09
40	090	1.+1	099105 -05
		1.-1	108687 -04
		1 DF	083155 -09
40	080	1.+1	050052 -05
		1.-1	070513 -04
		1 DF	051089 -09
40	070	1.+1	208191 -06
		1.-1	037719 -04
		1 DF	230123 -10
40	060	1.+1	064681 -06
		1.-1	151517 -05
		1 DF	064226 -10
40	050	1.+1	126043 -07
		1.-1	038652 -05
		1 DF	081827 -11
40	040	1.+1	108996 -08
		1.-1	044843 -06
		1 DF	256636 -13
40	030	1.+1	188087 -10
		1.-1	108891 -08
		1 DF	046132 -15
40	020	1.+1	060463 -13
		1.-1	054459 -11
		1 DF	056937 -21
40	010	1.+1	296282 -24
		1.-1	054357 -21
		1 DF	089377 -40
1	40	F	083914 -08

Table 2. $I_{2\mu}(\vartheta, \xi)$, $df_{E2}(\vartheta, \xi)/d\Omega$ and $f_{E2}(\xi)$.

00	180	2.+2	066666	01
		2. 0	066666	01
		2.-2	066666	01
		2 DF	055850	00
00	170	2.+2	066160	01
		2. 0	066362	01
		2.-2	066160	01
		2 DF	055935	00
00	160	2.+2	064656	01
		2. 0	065449	01
		2.-2	064656	01
		2 DF	056195	00
00	150	2.+2	062200	01
		2. 0	063934	01
		2.-2	062200	01
		2 DF	056639	00
00	140	2.+2	058868	01
		2. 0	061822	01
		2.-2	058868	01
		2 DF	057287	00
00	130	2.+2	054759	01
		2. 0	059125	01
		2.-2	054759	01
		2 DF	058165	00
00	120	2.+2	050000	01
		2. 0	055860	01
		2.-2	050000	01
		2 DF	059315	00
00	110	2.+2	447340	00
		2. 0	052048	01
		2.-2	447340	00
		2 DF	060789	00
00	100	2.+2	391216	00
		2. 0	477210	00
		2.-2	391216	00
		2 DF	062663	00
00	090	2.+2	333333	00
		2. 0	429203	00
		2.-2	333333	00
		2 DF	065037	00
00	080	2.+2	275450	00
		2. 0	377035	00
		2.-2	275450	00
		2 DF	068048	00
00	070	2.+2	219326	00
		2. 0	321482	00
		2.-2	219326	00
		2 DF	071886	00
00	060	2.+2	166666	00
		2. 0	263600	00
		2.-2	166666	00
		2 DF	076814	00
00	050	2.+2	119070	00
		2. 0	204827	00
		2.-2	119070	00
		2 DF	083205	00
00	040	2.+2	077985	00
		2. 0	147133	00
		2.-2	077985	00
		2 DF	091588	00
00	030	2.+2	044658	00
		2. 0	093228	00
		2.-2	044658	00
		2 DF	102738	00
00	020	2.+2	201024	-01
		2. 0	046873	00
		2.-2	201024	-01
		2 DF	117801	00
00	010	2.+2	050640	-01
		2. 0	133216	-01
		2.-2	050640	-01
		2 DF	138510	00
2	00	F	089539	01

TABLE 2 (cont.).

01	180	2.+2	062881	01
		2. 0	062881	01
		2.-2	062881	01
		2 DF	049688	00
01	170	2.+2	061012	01
		2. 0	062584	01
		2.-2	063825	01
		2 DF	049797	00
01	160	2.+2	058284	01
		2. 0	061696	01
		2.-2	063808	01
		2 DF	050130	00
01	150	2.+2	054785	01
		2. 0	060220	01
		2.-2	062820	01
		2 DF	050698	00
01	140	2.+2	050627	01
		2. 0	058165	01
		2.-2	060883	01
		2 DF	051524	00
01	130	2.+2	459390	00
		2. 0	055541	01
		2.-2	058048	01
		2 DF	052639	00
01	120	2.+2	408633	00
		2. 0	052364	01
		2.-2	054394	01
		2 DF	054090	00
01	110	2.+2	355524	00
		2. 0	486597	00
		2.-2	050025	01
		2 DF	055941	00
01	100	2.+2	301626	00
		2. 0	444570	00
		2.-2	450715	00
		2 DF	058279	00
01	090	2.+2	248499	00
		2. 0	397998	00
		2.-2	396812	00
		2 DF	061226	00
01	080	2.+2	197651	00
		2. 0	347469	00
		2.-2	340188	00
		2 DF	064947	00
01	070	2.+2	150493	00
		2. 0	293779	00
		2.-2	282588	00
		2 DF	069680	00
01	060	2.+2	108292	00
		2. 0	238017	00
		2.-2	225805	00
		2 DF	075763	00
01	050	2.+2	072137	00
		2. 0	181673	00
		2.-2	171619	00
		2 DF	083700	00
01	040	2.+2	042896	00
		2. 0	126804	00
		2.-2	121719	00
		2 DF	094274	00
01	030	2.+2	211746	-01
		2. 0	076278	00
		2.-2	077632	00
		2 DF	108734	00
01	020	2.+2	072506	-01
		2. 0	034174	00
		2.-2	040632	00
		2 DF	128642	00
01	010	2.+2	086749	-02
		2. 0	065051	-01
		2.-2	119526	-01
		2 DF	140331	00
2	01	F	086382	01

TABLE 2 (cont.).

02	180	2.+2	055614	01
		2. 0	055614	01
		2.-2	055614	01
		2 DF	038868	00
02	170	2.+2	053028	01
		2. 0	055338	01
		2.-2	057430	01
		2 DF	039005	00
02	160	2.+2	497638	00
		2. 0	054510	01
		2.-2	058403	01
		2 DF	039420	00
02	150	2.+2	459291	00
		2. 0	053136	01
		2.-2	058488	01
		2 DF	040127	00
02	140	2.+2	416472	00
		2. 0	051222	01
		2.-2	057662	01
		2 DF	041148	00
02	130	2.+2	370502	00
		2. 0	487808	00
		2.-2	055932	01
		2 DF	042518	00
02	120	2.+2	322749	00
		2. 0	458291	00
		2.-2	053331	01
		2 DF	044285	00
02	110	2.+2	274589	00
		2. 0	423908	00
		2.-2	499236	00
		2 DF	046514	00
02	100	2.+2	227362	00
		2. 0	384987	00
		2.-2	457967	00
		2 DF	049296	00
02	090	2.+2	182332	00
		2. 0	341975	00
		2.-2	410649	00
		2 DF	052749	00
02	080	2.+2	140649	00
		2. 0	295484	00
		2.-2	358637	00
		2 DF	057032	00
02	070	2.+2	103320	00
		2. 0	246349	00
		2.-2	303462	00
		2 DF	062357	00
02	060	2.+2	071169	00
		2. 0	195713	00
		2.-2	246788	00
		2 DF	068993	00
02	050	2.+2	044821	00
		2. 0	145146	00
		2.-2	190355	00
		2 DF	077243	00
02	040	2.+2	246615	-01
		2. 0	096829	00
		2.-2	135942	00
		2 DF	087262	00
02	030	2.+2	107972	-01
		2. 0	053815	00
		2.-2	085379	00
		2 DF	098053	00
02	020	2.+2	295693	-02
		2. 0	204034	-01
		2.-2	040918	00
		2 DF	101614	00
02	010	2.+2	189515	-03
		2. 0	228018	-02
		2.-2	077651	-01
		2 DF	052104	00
2	02	F	072889	01

TABLE 2 (cont.).

03	180	2.+2	474507	00
		2. 0	474507	00
		2.-2	474507	00
		2 DF	282940	-01
03	170	2.+2	446003	00
		2. 0	472014	00
		2.-2	496880	00
		2 DF	284380	-01
03	160	2.+2	412401	00
		2. 0	464550	00
		2.-2	051223	01
		2 DF	288740	-01
03	150	2.+2	374832	00
		2. 0	452159	00
		2.-2	051985	01
		2 DF	296138	-01
03	140	2.+2	334493	00
		2. 0	434920	00
		2.-2	051924	01
		2 DF	306777	-01
03	130	2.+2	292603	00
		2. 0	412954	00
		2.-2	051011	01
		2 DF	032095	00
03	120	2.+2	250369	00
		2. 0	386434	00
		2.-2	492468	00
		2 DF	033909	00
03	110	2.+2	208945	00
		2. 0	355604	00
		2.-2	466539	00
		2 DF	036172	00
03	100	2.+2	169403	00
		2. 0	320798	00
		2.-2	432853	00
		2 DF	038954	00
03	090	2.+2	132700	00
		2. 0	282477	00
		2.-2	392199	00
		2 DF	042341	00
03	080	2.+2	099656	00
		2. 0	241269	00
		2.-2	345624	00
		2 DF	046428	00
03	070	2.+2	070929	00
		2. 0	198031	00
		2.-2	294411	00
		2 DF	051311	00
03	060	2.+2	046998	00
		2. 0	153937	00
		2.-2	240063	00
		2 DF	057029	00
03	050	2.+2	281455	-01
		2. 0	110595	00
		2.-2	184298	00
		2 DF	063391	00
03	040	2.+2	144327	-01
		2. 0	070216	00
		2.-2	129098	00
		2 DF	069432	00
03	030	2.+2	056582	-01
		2. 0	035822	00
		2.-2	076985	00
		2 DF	071561	00
03	020	2.+2	125689	-02
		2. 0	113714	-01
		2.-2	032064	00
		2 DF	057835	00
03	010	2.+2	044254	-03
		2. 0	073107	-02
		2.-2	036372	-01
		2 DF	110973	-01
2	03	F	056084	01

TABLE 2 (cont.).

04	180	2.+2	395284	00
		2. 0	395284	00
		2.-2	395284	00
		2 DF	196349	-01
04	170	2.+2	367024	00
		2. 0	393092	00
		2.-2	418822	00
		2 DF	197676	-01
04	160	2.+2	335077	00
		2. 0	386529	00
		2.-2	436683	00
		2 DF	201687	-01
04	150	2.+2	300524	00
		2. 0	375640	00
		2.-2	448031	00
		2 DF	208477	-01
04	140	2.+2	264454	00
		2. 0	360503	00
		2.-2	452186	00
		2 DF	218205	-01
04	130	2.+2	227931	00
		2. 0	341237	00
		2.-2	448652	00
		2 DF	231098	-01
04	120	2.+2	191964	00
		2. 0	318017	00
		2.-2	437151	00
		2 DF	247452	-01
04	110	2.+2	157478	00
		2. 0	291083	00
		2.-2	417643	00
		2 DF	267630	-01
04	100	2.+2	125289	00
		2. 0	260773	00
		2.-2	390353	00
		2 DF	292036	-01
04	090	2.+2	096090	00
		2. 0	227546	00
		2.-2	355774	00
		2 DF	032105	00
04	080	2.+2	070428	00
		2. 0	192028	00
		2.-2	314685	00
		2 DF	035490	00
04	070	2.+2	048698	00
		2. 0	155075	00
		2.-2	268159	00
		2 DF	039321	00
04	060	2.+2	311342	-01
		2. 0	117848	00
		2.-2	217581	00
		2 DF	043406	00
04	050	2.+2	177915	-01
		2. 0	081924	00
		2.-2	164712	00
		2 DF	047154	00
04	040	2.+2	085379	-01
		2. 0	049418	00
		2.-2	111866	00
		2 DF	048953	00
04	030	2.+2	301281	-02
		2. 0	230851	-01
		2.-2	062416	00
		2 DF	044738	00
04	020	2.+2	054666	-02
		2. 0	061113	-01
		2.-2	221719	-01
		2 DF	267841	-01
04	010	2.+2	106908	-04
		2. 0	224451	-03
		2.-2	146820	-02
		2 DF	178800	-02
2	04	F	404593	00

TABLE 2 (cont.).

05	180	2.+2	323662	00
		2. 0	323662	00
		2.-2	323662	00
		2 DF	131642	-01
05	170	2.+2	297321	00
		2. 0	321772	00
		2.-2	346451	00
		2 DF	132756	-01
05	160	2.+2	268405	00
		2. 0	316115	00
		2.-2	364745	00
		2 DF	136121	-01
05	150	2.+2	237893	00
		2. 0	306735	00
		2.-2	377671	00
		2 DF	141804	-01
05	140	2.+2	206733	00
		2. 0	293706	00
		2.-2	384463	00
		2 DF	149918	-01
05	130	2.+2	175819	00
		2. 0	277145	00
		2.-2	384495	00
		2 DF	160613	-01
05	120	2.+2	145966	00
		2. 0	257221	00
		2.-2	377319	00
		2 DF	174073	-01
05	110	2.+2	117887	00
		2. 0	234168	00
		2.-2	362694	00
		2 DF	190483	-01
05	100	2.+2	092186	00
		2. 0	208314	00
		2.-2	340622	00
		2 DF	209989	-01
05	090	2.+2	069338	00
		2. 0	180105	00
		2.-2	311377	00
		2 DF	232582	-01
05	080	2.+2	049688	00
		2. 0	150150	00
		2.-2	275531	00
		2 DF	257867	-01
05	070	2.+2	033444	00
		2. 0	119272	00
		2.-2	234001	00
		2 DF	284564	-01
05	060	2.+2	206737	-01
		2. 0	088580	00
		2.-2	188104	00
		2 DF	309446	-01
05	050	2.+2	112998	-01
		2. 0	059551	00
		2.-2	139691	00
		2 DF	032507	00
05	040	2.+2	050885	-01
		2. 0	034103	00
		2.-2	091420	00
		2 DF	031541	00
05	030	2.+2	162149	-02
		2. 0	145704	-01
		2.-2	047373	00
		2 DF	250826	-01
05	020	2.+2	241324	-03
		2. 0	032108	-01
		2.-2	142263	-01
		2 DF	108484	-01
05	010	2.+2	263715	-05
		2. 0	067156	-03
		2.-2	054419	-02
		2 DF	244322	-03
2	05	F	278098	00

TABLE 2 (cont.).

06	180	2.+2	261573	00
		2. 0	261573	00
		2.-2	261573	00
		2 DF	085980	-01
06	170	2.+2	238000	00
		2. 0	259970	00
		2.-2	282528	00
		2 DF	086855	-01
06	160	2.+2	212691	00
		2. 0	255172	00
		2.-2	299980	00
		2 DF	089495	-01
06	150	2.+2	186502	00
		2. 0	247220	00
		2.-2	313076	00
		2 DF	093946	-01
06	140	2.+2	160236	00
		2. 0	236185	00
		2.-2	321030	00
		2 DF	100279	-01
06	130	2.+2	134622	00
		2. 0	222178	00
		2.-2	323157	00
		2 DF	108583	-01
06	120	2.+2	110299	00
		2. 0	205357	00
		2.-2	318913	00
		2 DF	118950	-01
06	110	2.+2	087806	00
		2. 0	185947	00
		2.-2	307932	00
		2 DF	131435	-01
06	100	2.+2	067571	00
		2. 0	164257	00
		2.-2	290067	00
		2 DF	146001	-01
06	090	2.+2	049908	00
		2. 0	140709	00
		2.-2	265435	00
		2 DF	162381	-01
06	080	2.+2	035015	00
		2. 0	115878	00
		2.-2	234466	00
		2 DF	179846	-01
06	070	2.+2	229750	-01
		2. 0	090534	00
		2.-2	197967	00
		2 DF	196721	-01
06	060	2.+2	137537	-01
		2. 0	065699	00
		2.-2	157224	00
		2 DF	209503	-01
06	050	2.+2	072028	-01
		2. 0	042704	00
		2.-2	114176	00
		2 DF	211301	-01
06	040	2.+2	304961	-02
		2. 0	232090	-01
		2.-2	071738	00
		2 DF	189916	-01
06	030	2.+2	087952	-02
		2. 0	090635	-01
		2.-2	034379	00
		2 DF	129956	-01
06	020	2.+2	107661	-03
		2. 0	166102	-02
		2.-2	086848	-01
		2 DF	040050	-01
06	010	2.+2	065982	-05
		2. 0	197523	-04
		2.-2	190847	-03
		2 DF	299588	-04
2	06	F	184375	00

TABLE 2 (cont.).

07	180	2.+2	209230	00
		2. 0	209230	00
		2.-2	209230	00
		2 DF	055012	-01
07	170	2.+2	188733	00
		2. 0	207887	00
		2.-2	227830	00
		2 DF	055665	-01
07	160	2.+2	167115	00
		2. 0	203871	00
		2.-2	243734	00
		2 DF	057636	-01
07	150	2.+2	145105	00
		2. 0	197218	00
		2.-2	256144	00
		2 DF	060952	-01
07	140	2.+2	123367	00
		2. 0	187996	00
		2.-2	264300	00
		2 DF	065655	-01
07	130	2.+2	102482	00
		2. 0	176304	00
		2.-2	267508	00
		2 DF	071791	-01
07	120	2.+2	082943	00
		2. 0	162292	00
		2.-2	265186	00
		2 DF	079388	-01
07	110	2.+2	065146	00
		2. 0	146167	00
		2.-2	256899	00
		2 DF	088422	-01
07	100	2.+2	049385	00
		2. 0	128216	00
		2.-2	242414	00
		2 DF	098750	-01
07	090	2.+2	035855	00
		2. 0	108829	00
		2.-2	221747	00
		2 DF	109993	-01
07	080	2.+2	246560	-01
		2. 0	088534	00
		2.-2	195232	00
		2 DF	121316	-01
07	070	2.+2	157884	-01
		2. 0	068031	00
		2.-2	163605	00
		2 DF	131058	-01
07	060	2.+2	091643	-01
		2. 0	048238	00
		2.-2	128130	00
		2 DF	136113	-01
07	050	2.+2	046045	-01
		2. 0	303125	-01
		2.-2	090797	00
		2 DF	131148	-01
07	040	2.+2	183563	-02
		2. 0	156311	-01
		2.-2	054641	00
		2 DF	108544	-01
07	030	2.+2	047992	-02
		2. 0	055778	-01
		2.-2	241519	-01
		2 DF	063459	-01
07	020	2.+2	048411	-03
		2. 0	084965	-02
		2.-2	051169	-01
		2 DF	138207	-02
07	010	2.+2	166802	-06
		2. 0	057391	-04
		2.-2	064380	-03
		2 DF	034029	-04
2	07	F	118941	00

TABLE 2 (cont.).

08	180	2.+2	165971	00
		2. 0	165971	00
		2.-2	165971	00
		2 DF	034616	-01
08	170	2.+2	148530	00
		2. 0	164860	00
		2.-2	182063	00
		2 DF	035085	-01
08	160	2.+2	130405	00
		2. 0	161535	00
		2.-2	196099	00
		2 DF	036500	-01
08	150	2.+2	112205	00
		2. 0	156031	00
		2.-2	207359	00
		2 DF	038877	-01
08	140	2.+2	094468	00
		2. 0	148408	00
		2.-2	215133	00
		2 DF	042239	-01
08	130	2.+2	077652	00
		2. 0	138757	00
		2.-2	218757	00
		2 DF	046601	-01
08	120	2.+2	062129	00
		2. 0	127214	00
		2.-2	217648	00
		2 DF	051957	-01
08	110	2.+2	048182	00
		2. 0	113968	00
		2.-2	211350	00
		2 DF	058243	-01
08	100	2.+2	036010	00
		2. 0	099278	00
		2.-2	199585	00
		2 DF	065276	-01
08	090	2.+2	257221	-01
		2. 0	083499	00
		2.-2	182312	00
		2 DF	072660	-01
08	080	2.+2	173512	-01
		2. 0	067104	00
		2.-2	159806	00
		2 DF	079612	-01
08	070	2.+2	108536	-01
		2. 0	050716	00
		2.-2	132751	00
		2 DF	084707	-01
08	060	2.+2	061145	-01
		2. 0	035136	00
		2.-2	102386	00
		2 DF	085526	-01
08	050	2.+2	295058	-02
		2. 0	213449	-01
		2.-2	070694	00
		2 DF	078443	-01
08	040	2.+2	110879	-02
		2. 0	104427	-01
		2.-2	040680	00
		2 DF	059537	-01
08	030	2.+2	263126	-03
		2. 0	034044	-01
		2.-2	165545	-01
		2 DF	295986	-02
08	020	2.+2	219029	-04
		2. 0	043090	-02
		2.-2	293566	-02
		2 DF	045309	-02
08	010	2.+2	042499	-06
		2. 0	165236	-05
		2.-2	211021	-04
		2 DF	036516	-05
2	08	F	075113	00

TABLE 2 (cont.).

09	180	2.+2	130753	00
		2. 0	130753	00
		2.-2	130753	00
		2 DF	214839	-02
09	170	2.+2	116158	00
		2. 0	129841	00
		2.-2	144403	00
		2 DF	218112	-02
09	160	2.+2	101182	00
		2. 0	127114	00
		2.-2	156500	00
		2 DF	227965	-02
09	150	2.+2	086324	00
		2. 0	122603	00
		2.-2	166407	00
		2 DF	244490	-02
09	140	2.+2	072016	00
		2. 0	116361	00
		2.-2	173481	00
		2 DF	267785	-02
09	130	2.+2	058612	00
		2. 0	108470	00
		2.-2	177107	00
		2 DF	297865	-02
09	120	2.+2	046389	00
		2. 0	099050	00
		2.-2	176730	00
		2 DF	033448	-01
09	110	2.+2	035546	00
		2. 0	088271	00
		2.-2	171903	00
		2 DF	037687	-01
09	100	2.+2	262085	-01
		2. 0	076365	00
		2.-2	162335	00
		2 DF	042322	-01
09	090	2.+2	184312	-01
		2. 0	063645	00
		2.-2	147959	00
		2 DF	046996	-01
09	080	2.+2	122055	-01
		2. 0	050531	00
		2.-2	129013	00
		2 DF	051055	-01
09	070	2.+2	074638	-01
		2. 0	037565	00
		2.-2	106140	00
		2 DF	053388	-01
09	060	2.+2	040843	-01
		2. 0	254295	-01
		2.-2	080537	00
		2 DF	052281	-01
09	050	2.+2	189452	-02
		2. 0	149340	-01
		2.-2	054124	00
		2 DF	045525	-01
09	040	2.+2	067170	-02
		2. 0	069316	-01
		2.-2	297469	-01
		2 DF	031591	-01
09	030	2.+2	144822	-03
		2. 0	206436	-02
		2.-2	111302	-01
		2 DF	133103	-02
09	020	2.+2	099586	-04
		2. 0	217070	-03
		2.-2	164975	-02
		2 DF	142691	-03
09	010	2.+2	108957	-07
		2. 0	047236	-05
		2.-2	067651	-04
		2 DF	037499	-06
2	09	F	046634	00

TABLE 2 (cont.).

10	180	2.+2	1024 12	00
		2. 0	1024 12	00
		2.-2	1024 12	00
		2 DF	131799	-02
10	170	2.+2	090362	00
		2. 0	101669	00
		2.-2	113813	00
		2 DF	134023	-02
10	160	2.+2	078132	00
		2. 0	099451	00
		2.-2	124050	00
		2 DF	140715	-02
10	150	2.+2	066130	00
		2. 0	095784	00
		2.-2	132568	00
		2 DF	151920	-02
10	140	2.+2	054695	00
		2. 0	090713	00
		2.-2	138800	00
		2 DF	167668	-02
10	130	2.+2	044098	00
		2. 0	084313	00
		2.-2	142190	00
		2 DF	187898	-02
10	120	2.+2	034544	00
		2. 0	076688	00
		2.-2	142229	00
		2 DF	212315	-02
10	110	2.+2	261685	-01
		2. 0	067988	00
		2.-2	138496	00
		2 DF	240171	-02
10	100	2.+2	190456	-01
		2. 0	058416	00
		2.-2	130710	00
		2 DF	269897	-02
10	090	2.+2	131946	-01
		2. 0	048249	00
		2.-2	118798	00
		2 DF	298559	-02
10	080	2.+2	085832	-01
		2. 0	037847	00
		2.-2	102972	00
		2 DF	032108	-01
10	070	2.+2	051344	-01
		2. 0	276758	-01
		2.-2	083842	00
		2 DF	032944	-01
10	060	2.+2	273104	-02
		2. 0	183068	-01
		2.-2	062540	00
		2 DF	312314	-02
10	050	2.+2	121853	-02
		2. 0	103937	-01
		2.-2	040875	00
		2 DF	257673	-02
10	040	2.+2	040791	-02
		2. 0	045768	-01
		2.-2	214372	-01
		2 DF	163126	-02
10	030	2.+2	079966	-03
		2. 0	124512	-02
		2.-2	073681	-01
		2 DF	058104	-02
10	020	2.+2	045463	-04
		2. 0	108756	-03
		2.-2	091190	-02
		2 DF	043508	-03
10	010	2.+2	280731	-08
		2. 0	134270	-06
		2.-2	213102	-05
		2 DF	037186	-07
2	10	F	285521	-01

TABLE 2 (cont.).

12	180	2.+2	061942	00
		2. 0	061942	00
		2.-2	061942	00
		2 DF	048215	-02
12	170	2.+2	053980	00
		2. 0	061460	00
		2.-2	069620	00
		2 DF	049184	-02
12	160	2.+2	046047	00
		2. 0	060022	00
		2.-2	076654	00
		2 DF	052094	-02
12	150	2.+2	038405	00
		2. 0	057646	00
		2.-2	082645	00
		2 DF	056952	-02
12	140	2.+2	031261	00
		2. 0	054367	00
		2.-2	087170	00
		2 DF	063739	-02
12	130	2.+2	247687	-01
		2. 0	050241	00
		2.-2	089803	00
		2 DF	072367	-02
12	120	2.+2	190323	-01
		2. 0	045345	00
		2.-2	090145	00
		2 DF	082596	-02
12	110	2.+2	141105	-01
		2. 0	039791	00
		2.-2	087855	00
		2 DF	093914	-02
12	100	2.+2	100214	-01
		2. 0	033730	00
		2.-2	082704	00
		2 DF	105356	-02
12	090	2.+2	067476	-01
		2. 0	273656	-01
		2.-2	074635	00
		2 DF	115268	-02
12	080	2.+2	042420	-01
		2. 0	209570	-01
		2.-2	063834	00
		2 DF	121059	-02
12	070	2.+2	243222	-02
		2. 0	148307	-01
		2.-2	050827	00
		2 DF	119120	-02
12	060	2.+2	122428	-02
		2. 0	093684	-01
		2.-2	036579	00
		2 DF	105409	-02
12	050	2.+2	050628	-02
		2. 0	049717	-01
		2.-2	225714	-01
		2 DF	077732	-02
12	040	2.+2	151351	-03
		2. 0	197064	-02
		2.-2	107589	-01
		2 DF	040762	-02
12	030	2.+2	245727	-04
		2. 0	044733	-02
		2.-2	311408	-02
		2 DF	103247	-03
12	020	2.+2	095671	-05
		2. 0	269554	-04
		2.-2	268148	-03
		2 DF	037517	-04
12	010	2.+2	188555	-09
		2. 0	107070	-07
		2.-2	203058	-06
		2 DF	033736	-09
2	12	F	103532	-01

TABLE 2 (cont.).

14	180	2.+2	036905	00
		2. 0	036905	00
		2.-2	036905	00
		2 DF	171156	-03
14	170	2.+2	031806	00
		2. 0	036599	00
		2.-2	041897	00
		2 DF	175128	-03
14	160	2.+2	268033	-01
		2. 0	035686	00
		2.-2	046540	00
		2 DF	187046	-03
14	150	2.+2	220590	-01
		2. 0	034181	00
		2.-2	050558	00
		2 DF	206880	-03
14	140	2.+2	176955	-01
		2. 0	032107	00
		2.-2	053652	00
		2 DF	234431	-03
14	130	2.+2	137974	-01
		2. 0	295039	-01
		2.-2	055514	00
		2 DF	269081	-03
14	120	2.+2	104150	-01
		2. 0	264283	-01
		2.-2	055848	00
		2 DF	309400	-03
14	110	2.+2	075687	-01
		2. 0	229596	-01
		2.-2	054404	00
		2 DF	035256	-02
14	100	2.+2	052535	-01
		2. 0	192057	-01
		2.-2	051015	00
		2 DF	039357	-02
14	090	2.+2	034434	-01
		2. 0	153085	-01
		2.-2	045647	00
		2 DF	042445	-02
14	080	2.+2	209562	-02
		2. 0	114483	-01
		2.-2	038467	00
		2 DF	043380	-02
14	070	2.+2	115358	-02
		2. 0	078422	-01
		2.-2	299078	-01
		2 DF	040787	-02
14	060	2.+2	055045	-02
		2. 0	047317	-01
		2.-2	207335	-01
		2 DF	033560	-02
14	050	2.+2	211344	-03
		2. 0	234761	-02
		2.-2	120588	-01
		2 DF	220306	-03
14	040	2.+2	056520	-03
		2. 0	083768	-02
		2.-2	052150	-01
		2 DF	095282	-03
14	030	2.+2	076132	-04
		2. 0	158670	-03
		2.-2	126884	-02
		2 DF	170840	-04
14	020	2.+2	203351	-06
		2. 0	065953	-04
		2.-2	075870	-03
		2 DF	299845	-06
14	010	2.+2	128157	-10
		2. 0	084259	-08
		2.-2	185820	-07
		2 DF	282382	-12
2	14	F	036276	-01

TABLE 2 (cont.).

16	180	2.+2	217313	-01	16	090	2.+2	175469	-02
		2. 0	217313	-01			2. 0	084733	-01
		2.-2	217313	-01			2.-2	273501	-01
		2 DF	059345	-03			2 DF	150603	-03
16	170	2.+2	185408	-01	16	080	2.+2	103507	-02
		2. 0	215406	-01			2. 0	061892	-01
		2.-2	248942	-01			2.-2	226857	-01
		2 DF	060901	-03			2 DF	149406	-03
16	160	2.+2	154511	-01	16	070	2.+2	054776	-02
		2. 0	209714	-01			2. 0	041047	-01
		2.-2	278711	-01			2.-2	172038	-01
		2 DF	065567	-03			2 DF	133884	-03
16	150	2.+2	125612	-01	16	060	2.+2	248108	-03
		2. 0	200334	-01			2. 0	236614	-02
		2.-2	304777	-01			2.-2	114760	-01
		2 DF	073309	-03			2 DF	102159	-03
16	140	2.+2	099415	-01	16	050	2.+2	088560	-03
		2. 0	187440	-01			2. 0	109769	-02
		2.-2	032509	00			2.-2	062840	-01
		2 DF	084000	-03			2 DF	059533	-03
16	130	2.+2	076369	-01	16	040	2.+2	212154	-04
		2. 0	171302	-01			2. 0	035265	-02
		2.-2	033750	00			2.-2	246281	-02
		2 DF	097300	-03			2 DF	211750	-04
16	120	2.+2	056697	-01	16	030	2.+2	237389	-05
		2. 0	152313	-01			2. 0	055743	-03
		2.-2	033996	00			2.-2	050307	-02
		2 DF	112476	-03			2 DF	267961	-05
16	110	2.+2	040435	-01	16	020	2.+2	043553	-06
		2. 0	131024	-01			2. 0	159829	-05
		2.-2	033070	00			2.-2	208635	-04
		2 DF	128150	-03			2 DF	226481	-07
16	100	2.+2	274649	-02	16	010	2.+2	087883	-11
		2. 0	108176	-01			2. 0	065661	-09
		2.-2	308582	-01			2.-2	165057	-08
		2 DF	142015	-03			2 DF	222734	-14
					2	16	F	123845	-02

TABLE 2 (cont.).

18	180	2.+2	126758	-01
		2. 0	126758	-01
		2.-2	126758	-01
		2 DF	201914	-04
18	170	2.+2	107150	-01
		2. 0	125585	-01
		2.-2	146404	-01
		2 DF	207804	-04
18	160	2.+2	088379	-01
		2. 0	122086	-01
		2.-2	165077	-01
		2 DF	225439	-04
18	150	2.+2	071035	-01
		2. 0	116326	-01
		2.-2	181570	-01
		2 DF	254616	-04
18	140	2.+2	055517	-01
		2. 0	108422	-01
		2.-2	194519	-01
		2 DF	294670	-04
18	130	2.+2	042056	-01
		2. 0	098558	-01
		2.-2	202483	-01
		2 DF	034394	-03
18	120	2.+2	307382	-02
		2. 0	086999	-01
		2.-2	204060	-01
		2 DF	039903	-03
18	110	2.+2	215349	-02
		2. 0	074117	-01
		2.-2	198067	-01
		2 DF	045377	-03
18	100	2.+2	143280	-02
		2. 0	060407	-01
		2.-2	183778	-01
		2 DF	049828	-03
18	090	2.+2	089317	-02
		2. 0	046506	-01
		2.-2	161222	-01
		2 DF	051863	-03
18	080	2.+2	051123	-02
		2. 0	033185	-01
		2.-2	131523	-01
		2 DF	049849	-03
18	070	2.+2	260368	-03
		2. 0	213127	-02
		2.-2	097212	-01
		2 DF	042493	-03
18	060	2.+2	112066	-03
		2. 0	117392	-02
		2.-2	062348	-01
		2 DF	300115	-04
18	050	2.+2	037226	-03
		2. 0	050931	-02
		2.-2	032116	-01
		2 DF	154949	-04
18	040	2.+2	079963	-04
		2. 0	147342	-03
		2.-2	113971	-02
		2 DF	045233	-04
18	030	2.+2	074399	-05
		2. 0	194374	-04
		2.-2	195292	-03
		2 DF	040317	-05
18	020	2.+2	093847	-07
		2. 0	038444	-05
		2.-2	056124	-04
		2 DF	163764	-08
18	010	2.+2	060683	-12
		2. 0	050783	-10
		2.-2	143304	-09
		2 DF	167858	-16
2	18	F	041427	-02

TABLE 2 (cont.).

20	180	2.+2	073366	-01
		2. 0	073366	-01
		2.-2	073366	-01
		2 DF	067639	-04
20	170	2.+2	061486	-01
		2. 0	072652	-01
		2.-2	085379	-01
		2 DF	069806	-04
20	160	2.+2	050230	-01
		2. 0	070527	-01
		2.-2	096891	-01
		2 DF	076287	-04
20	150	2.+2	039944	-01
		2. 0	067031	-01
		2.-2	107127	-01
		2 DF	086978	-04
20	140	2.+2	308513	-02
		2. 0	062243	-01
		2.-2	115200	-01
		2 DF	101568	-04
20	130	2.+2	230646	-02
		2. 0	056284	-01
		2.-2	120161	-01
		2 DF	119315	-04
20	120	2.+2	166090	-02
		2. 0	049331	-01
		2.-2	121087	-01
		2 DF	138735	-04
20	110	2.+2	114402	-02
		2. 0	041627	-01
		2.-2	117206	-01
		2 DF	157237	-04
20	100	2.+2	074623	-02
		2. 0	033497	-01
		2.-2	108075	-01
		2 DF	170836	-04
20	090	2.+2	045428	-02
		2. 0	253511	-02
		2.-2	093788	-01
		2 DF	174269	-04
20	080	2.+2	252524	-03
		2. 0	176753	-02
		2.-2	075206	-01
		2 DF	162055	-04
20	070	2.+2	123879	-03
		2. 0	109942	-02
		2.-2	054146	-01
		2 DF	131223	-04
20	060	2.+2	050710	-03
		2. 0	057873	-02
		2.-2	033368	-01
		2 DF	085657	-04
20	050	2.+2	156900	-04
		2. 0	234857	-03
		2.-2	161602	-02
		2 DF	039125	-04
20	040	2.+2	302435	-05
		2. 0	061188	-03
		2.-2	051894	-02
		2 DF	093603	-05
20	030	2.+2	234150	-06
		2. 0	067373	-04
		2.-2	074545	-03
		2 DF	058676	-06
20	020	2.+2	203203	-08
		2. 0	091925	-06
		2.-2	148364	-05
		2 DF	114374	-09
20	010	2.+2	042134	-13
		2. 0	039042	-11
		2.-2	122189	-10
		2 DF	122017	-18
2	20	F	136330	-03

TABLE 2 (cont.).

40	180	2.+2	242113	-04
		2. 0	242113	-04
		2.-2	242113	-04
		2 DF	073662	-09
40	170	2.+2	190282	-04
		2. 0	238763	-04
		2.-2	297649	-04
		2 DF	077900	-09
40	160	2.+2	144444	-04
		2. 0	228823	-04
		2.-2	035321	-03
		2 DF	090445	-09
40	150	2.+2	105725	-04
		2. 0	212642	-04
		2.-2	040365	-03
		2 DF	110574	-09
40	140	2.+2	074367	-04
		2. 0	190858	-04
		2.-2	044257	-03
		2 DF	136397	-09
40	130	2.+2	050001	-04
		2. 0	164470	-04
		2.-2	046291	-03
		2 DF	164013	-09
40	120	2.+2	031877	-04
		2. 0	134906	-04
		2.-2	045820	-03
		2 DF	186903	-09
40	110	2.+2	190442	-05
		2. 0	104041	-04
		2.-2	042433	-03
		2 DF	196382	-09
40	100	2.+2	104789	-05
		2. 0	074131	-04
		2.-2	036172	-03
		2 DF	184219	-09
40	090	2.+2	051767	-05
		2. 0	047574	-04
		2.-2	277190	-04
		2 DF	147724	-09
40	080	2.+2	220858	-06
		2. 0	264706	-05
		2.-2	184244	-04
		2 DF	095007	-09
40	070	2.+2	076548	-06
		2. 0	120318	-05
		2.-2	100430	-04
		2 DF	044337	-09
40	060	2.+2	194741	-07
		2. 0	040491	-05
		2.-2	040895	-04
		2 DF	126925	-10
40	050	2.+2	303428	-08
		2. 0	084679	-06
		2.-2	105219	-05
		2 DF	164254	-11
40	040	2.+2	202522	-09
		2. 0	077798	-07
		2.-2	122520	-06
		2 DF	051834	-12
40	030	2.+2	254587	-11
		2. 0	141087	-09
		2.-2	297239	-08
		2 DF	092922	-15
40	020	2.+2	053421	-14
		2. 0	047089	-12
		2.-2	147898	-11
		2 DF	113443	-21
40	010	2.+2	129364	-25
		2. 0	236159	-23
		2.-2	146365	-21
		2 DF	174987	-40
2	40	F	124705	-08

Table 3. $I_{3\mu}(\vartheta,\xi)$, $df_{E3}(\vartheta,\xi)/d\Omega$ and $f_{E3}(\xi)$.

02	180	3.+3	242049	00
		3.+1	242049	00
		3.-1	242049	00
		3.-3	242049	00
		3 DF	037563	-01
02	170	3.+3	229876	00
		3.+1	237097	00
		3.-1	243528	00
		3.-3	249100	00
		3 DF	037474	-01
02	160	3.+3	213265	00
		3.+1	228829	00
		3.-1	241450	00
		3.-3	250597	00
		3 DF	037207	-01
02	150	3.+3	193103	00
		3.+1	217468	00
		3.-1	235805	00
		3.-3	246395	00
		3 DF	036765	-01
02	140	3.+3	170419	00
		3.+1	203304	00
		3.-1	226663	00
		3.-3	236651	00
		3 DF	036146	-01
02	130	3.+3	146315	00
		3.+1	186691	00
		3.-1	214179	00
		3.-3	221821	00
		3 DF	035353	-01
02	120	3.+3	121897	00
		3.+1	168049	00
		3.-1	198601	00
		3.-3	202635	00
		3 DF	034383	-01
02	110	3.+3	098204	00
		3.+1	147857	00
		3.-1	180276	00
		3.-3	180056	00
		3 DF	033232	-01
02	100	3.+3	076150	00
		3.+1	126661	00
		3.-1	159656	00
		3.-3	155212	00
		3 DF	031889	-01
02	090	3.+3	056470	00
		3.+1	105068	00
		3.-1	137310	00
		3.-3	129333	00
		3 DF	303358	-02
02	080	3.+3	039688	00
		3.+1	083746	00
		3.-1	113927	00
		3.-3	103658	00
		3 DF	285381	-02
02	070	3.+3	260904	-01
		3.+1	063415	00
		3.-1	090322	00
		3.-3	079355	00
		3 DF	264450	-02
02	060	3.+3	157249	-01
		3.+1	044833	00
		3.-1	067432	00
		3.-3	057439	00
		3 DF	239815	-02
02	050	3.+3	084119	-01
		3.+1	287677	-01
		3.-1	046307	00
		3.-3	038693	00
		3 DF	210473	-02
02	040	3.+3	037711	-01
		3.+1	159324	-01
		3.-1	280645	-01
		3.-3	236132	-01
		3 DF	175217	-02
02	030	3.+3	126157	-02
		3.+1	068802	-01
		3.-1	138111	-01
		3.-3	123726	-01
		3 DF	132843	-02

TABLE 3 (cont.).

02	020	3.+3	235291	-03
		3.+1	179359	-02
		3.-1	044727	-01
		3.-3	048329	-01
		3 DF	082293	-02
02	010	3.+3	077688	-04
		3.+1	102117	-03
		3.-1	040499	-02
		3.-3	073394	-02
		3 DF	223411	-03
3	02	F	035323	00
04	180	3.+3	192022	00
		3.+1	192022	00
		3.-1	192022	00
		3.-3	192022	00
		3 DF	236404	-02
04	170	3.+3	176622	00
		3.+1	186033	00
		3.-1	195169	00
		3.-3	203955	00
		3 DF	236826	-02
04	160	3.+3	158603	00
		3.+1	177419	00
		3.-1	195318	00
		3.-3	211712	00
		3 DF	238044	-02
04	150	3.+3	138884	00
		3.+1	166446	00
		3.-1	192373	00
		3.-3	214767	00
		3 DF	239920	-02
04	140	3.+3	118402	00
		3.+1	153431	00
		3.-1	186310	00
		3.-3	212830	00
		3 DF	242227	-02
04	130	3.+3	098053	00
		3.+1	138731	00
		3.-1	177188	00
		3.-3	205869	00
		3 DF	244643	-02
04	120	3.+3	078640	00
		3.+1	122749	00
		3.-1	165152	00
		3.-3	194128	00
		3 DF	246753	-02
04	110	3.+3	060833	00
		3.+1	105927	00
		3.-1	150449	00
		3.-3	178121	00
		3 DF	248041	-02
04	100	3.+3	045137	00
		3.+1	088743	00
		3.-1	133442	00
		3.-3	158612	00
		3 DF	247882	-02
04	090	3.+3	031879	00
		3.+1	071712	00
		3.-1	114619	00
		3.-3	136563	00
		3 DF	245510	-02
04	080	3.+3	212006	-01
		3.+1	055378	00
		3.-1	094606	00
		3.-3	113086	00
		3 DF	239987	-02
04	070	3.+3	130638	-01
		3.+1	040305	00
		3.-1	074180	00
		3.-3	089360	00
		3 DF	230139	-02
04	060	3.+3	072764	-01
		3.+1	270566	-01
		3.-1	054272	00
		3.-3	066561	00
		3 DF	214457	-02

TABLE 3 (cont.).

04	050	3.+3	035162	-01
		3.+1	161602	-01
		3.-1	035959	00
		3.-3	045777	00
		3 DF	190967	-02
04	040	3.+3	136833	-02
		3.+1	080411	-01
		3.-1	204245	-01
		3.-3	279584	-01
		3 DF	157054	-02
04	030	3.+3	036701	-02
		3.+1	290268	-02
		3.-1	088489	-01
		3.-3	139029	-01
		3 DF	109599	-02
04	020	3.+3	045064	-03
		3.+1	052638	-02
		3.-1	213131	-02
		3.-3	043778	-01
		3 DF	048608	-02
04	010	3.+3	044968	-05
		3.+1	098568	-04
		3.-1	069483	-03
		3.-3	257358	-03
		3 DF	240245	-04
3	04	F	272275	-01
06	180	3.+3	140477	00
		3.+1	140477	00
		3.-1	140477	00
		3.-3	140477	00
		3 DF	126521	-02
06	170	3.+3	125892	00
		3.+1	134869	00
		3.-1	143933	00
		3.-3	153028	00
		3 DF	127372	-02
06	160	3.+3	110052	00
		3.+1	127334	00
		3.-1	145058	00
		3.-3	162809	00
		3 DF	129875	-02
06	150	3.+3	093722	00
		3.+1	118127	00
		3.-1	143721	00
		3.-3	169169	00
		3 DF	133880	-02
05	140	3.+3	077612	00
		3.+1	107539	00
		3.-1	139851	00
		3.-3	171603	00
		3 DF	139130	-02
06	130	3.+3	062338	00
		3.+1	095886	00
		3.-1	133445	00
		3.-3	169789	00
		3 DF	145261	-02
06	120	3.+3	048399	00
		3.+1	083508	00
		3.-1	124579	00
		3.-3	163628	00
		3 DF	151783	-02
06	110	3.+3	036155	00
		3.+1	070767	00
		3.-1	113429	00
		3.-3	153267	00
		3 DF	158070	-02

TABLE 3 (cont.).

06	100	3.+3	258237	-01
		3.+1	058043	00
		3.-1	100276	00
		3.-3	139109	00
		3 DF	163332	-02
06	090	3.+3	174801	-01
		3.+1	045731	00
		3.-1	085530	00
		3.-3	121800	00
		3 DF	166577	-02
06	080	3.+3	110734	-01
		3.+1	034236	00
		3.-1	069743	00
		3.-3	102211	00
		3 DF	166558	-02
06	070	3.+3	064431	-01
		3.+1	239557	-01
		3.-1	053620	00
		3.-3	081391	00
		3 DF	161705	-02
06	060	3.+3	033438	-01
		3.+1	152656	-01
		3.-1	038024	00
		3.-3	060518	00
		3 DF	150058	-02
06	050	3.+3	147340	-02
		3.+1	084787	-01
		3.-1	239602	-01
		3.-3	040853	00
		3 DF	129304	-02
06	040	3.+3	050328	-02
		3.+1	037822	-01
		3.-1	125059	-01
		3.-3	237061	-01
		3 DF	097318	-02
06	030	3.+3	109745	-03
		3.+1	113656	-02
		3.-1	046384	-01
		3.-3	104393	-01
		3 DF	054774	-02
06	020	3.+3	090392	-04
		3.+1	142251	-03
		3.-1	079657	-02
		3.-3	241800	-02
		3 DF	137495	-03
06	010	3.+3	280755	-07
		3.+1	086187	-05
		3.-1	087327	-04
		3.-3	048868	-03
		3 DF	084526	-05
3	06	F	173639	-01
08	180	3.+3	097409	00
		3.+1	097409	00
		3.-1	097409	00
		3.-3	097409	00
		3 DF	060835	-02
08	170	3.+3	085404	00
		3.+1	092806	00
		3.-1	100469	00
		3.-3	108366	00
		3 DF	061562	-02
08	160	3.+3	072970	00
		3.+1	086856	00
		3.-1	101817	00
		3.-3	117635	00
		3 DF	063709	-02
08	150	3.+3	060671	00
		3.+1	079782	00
		3.-1	101320	00
		3.-3	124600	00
		3 DF	067171	-02
08	140	3.+3	048991	00
		3.+1	071820	00
		3.-1	098892	00
		3.-3	128712	00
		3 DF	071767	-02

TABLE 3 (cont.).

08	130	3.+3	038313	00
		3.+1	063226	00
		3.-1	094502	00
		3.-3	129535	00
		3 DF	077222	-02
08	120	3.+3	289092	-01
		3.+1	054265	00
		3.-1	088189	00
		3.-3	126792	00
		3 DF	083153	-02
08	110	3.+3	209381	-01
		3.+1	045211	00
		3.-1	080075	00
		3.-3	120405	00
		3 DF	089039	-02
08	100	3.+3	144544	-01
		3.+1	036345	00
		3.-1	070379	00
		3.-3	110520	00
		3 DF	094186	-02
08	090	3.+3	094173	-01
		3.+1	279498	-01
		3.-1	059439	00
		3.-3	097534	00
		3 DF	097694	-02
08	080	3.+3	057087	-01
		3.+1	203041	-01
		3.-1	047720	00
		3.-3	082090	00
		3 DF	098410	-02
08	070	3.+3	031516	-01
		3.+1	136702	-01
		3.-1	035827	00
		3.-3	065079	00
		3 DF	094917	-02
08	060	3.+3	153190	-02
		3.+1	082748	-01
		3.-1	245037	-01
		3.-3	047614	00
		3 DF	085620	-02
08	050	3.+3	061904	-02
		3.+1	042754	-01
		3.-1	145928	-01
		3.-3	310122	-01
		3 DF	069143	-02
08	040	3.+3	186800	-03
		3.+1	170973	-02
		3.-1	069433	-01
		3.-3	167499	-01
		3 DF	045576	-02
08	030	3.+3	033362	-03
		3.+1	042737	-02
		3.-1	218121	-02
		3.-3	063740	-01
		3 DF	194647	-03
08	020	3.+3	186012	-05
		3.+1	036842	-03
		3.-1	263169	-03
		3.-3	105560	-02
		3 DF	254878	-04
08	010	3.+3	182037	-08
		3.+1	071897	-06
		3.-1	094980	-05
		3.-3	071060	-04
		3 DF	177230	-07
3	08	F	095574	-01

TABLE 3 (cont.).

10	180	3.+3	065031	00	10	100	3.+3	079715	-01
		3.+1	065031	00			3.+1	220840	-01
		3.-1	065031	00			3.-1	047117	00
		3.-3	065031	00			3.-3	082034	00
		3 DF	271143	-03			3 DF	048976	-02
10	170	3.+3	055944	00	10	090	3.+3	050145	-01
		3.+1	061544	00			3.+1	165917	-01
		3.-1	067452	00			3.-1	039336	00
		3.-3	073658	00			3.-3	072573	00
		3 DF	275817	-03			3 DF	051176	-02
10	160	3.+3	046853	00	10	080	3.+3	291819	-02
		3.+1	057153	00			3.+1	117065	-01
		3.-1	068666	00			3.-1	310349	-01
		3.-3	081327	00			3.-3	060892	00
		3 DF	289657	-03			3 DF	051365	-02
10	150	3.+3	038142	00	10	070	3.+3	153382	-02
		3.+1	052031	00			3.+1	075903	-01
		3.-1	068558	00			3.-1	227042	-01
		3.-3	087522	00			3.-3	047732	00
		3 DF	312085	-03			3 DF	048585	-02
10	140	3.+3	301180	-01	10	060	3.+3	070082	-02
		3.+1	046362	00			3.+1	043677	-01
		3.-1	067046	00			3.-1	149372	-01
		3.-3	091747	00			3.-3	034098	00
		3 DF	034204	-02			3 DF	041946	-02
10	130	3.+3	229979	-01	10	050	3.+3	260730	-03
		3.+1	040337	00			3.+1	210065	-02
		3.-1	064092	00			3.-1	083806	-01
		3.-3	093565	00			3.-3	212382	-01
		3 DF	037786	-02			3 DF	311474	-03
10	120	3.+3	169126	-01	10	040	3.+3	069797	-03
		3.+1	034151	00			3.+1	075338	-02
		3.-1	059714	00			3.-1	036206	-01
		3.-3	092644	00			3.-3	105696	-01
		3 DF	041704	-02			3 DF	175597	-03
10	110	3.+3	119110	-01	10	030	3.+3	102575	-04
		3.+1	280014	-01			3.+1	156662	-03
		3.-1	053999	00			3.-1	095846	-02
		3.-3	088800	00			3.-3	034365	-01
		3 DF	045599	-02			3 DF	055257	-03

TABLE 3 (cont.).

10	020	3.+3	038916	-05
		3.+1	092976	-04
		3.-1	080700	-03
		3.-3	040187	-02
		3 DF	036460	-04
10	010	3.+3	120762	-09
		3.+1	058342	-07
		3.-1	095007	-06
		3.-3	088939	-05
		3 DF	276559	-09
3	10	F	047217	-01
15	180	3.+3	212135	-01
		3.+1	212135	-01
		3.-1	212135	-01
		3.-3	212135	-01
		3 DF	288522	-04
15	170	3.+3	175504	-01
		3.+1	197972	-01
		3.-1	222476	-01
		3.-3	249106	-01
		3 DF	297156	-04
15	160	3.+3	141000	-01
		3.+1	180842	-01
		3.-1	228409	-01
		3.-3	284412	-01
		3 DF	032312	-03
15	150	3.+3	109804	-01
		3.+1	161487	-01
		3.-1	229302	-01
		3.-3	031555	00
		3 DF	036555	-03
15	140	3.+3	082682	-01
		3.+1	140693	-01
		3.-1	224704	-01
		3.-3	033987	00
		3 DF	042274	-03
15	130	3.+3	059987	-01
		3.+1	119238	-01
		3.-1	214368	-01
		3.-3	035469	00
		3 DF	049149	-03
15	120	3.+3	041730	-01
		3.+1	097883	-01
		3.-1	198325	-01
		3.-3	035762	00
		3 DF	056629	-03
15	110	3.+3	276459	-02
		3.+1	077360	-01
		3.-1	176965	-01
		3.-3	034689	00
		3 DF	063847	-03
15	100	3.+3	172776	-02
		3.+1	058357	-01
		3.-1	151118	-01
		3.-3	032169	00
		3 DF	069547	-03
15	090	3.+3	100492	-02
		3.+1	041497	-01
		3.-1	122126	-01
		3.-3	282610	-01
		3 DF	072089	-03
15	080	3.+3	053324	-02
		3.+1	273088	-02
		3.-1	091865	-01
		3.-3	231946	-01
		3 DF	069642	-03
15	070	3.+3	250395	-03
		3.+1	161655	-02
		3.-1	062693	-01
		3.-3	174012	-01
		3 DF	060720	-03
15	060	3.+3	099043	-03
		3.+1	082201	-02
		3.-1	037229	-01
		3.-3	115095	-01
		3 DF	045265	-03

TABLE 3 (cont.).

15	050	3.+3	302943 -04
		3.+1	033137 -02
		3.-1	178783 -02
		3.-3	062911 -01
		3 DF	261050 -04
15	040	3.+3	060798 -04
		3.+1	090717 -03
		3.-1	060199 -02
		3.-3	249949 -02
		3 DF	094731 -04
15	030	3.+3	055525 -05
		3.+1	119241 -04
		3.-1	102861 -03
		3.-3	053623 -02
		3 DF	131264 -05
15	020	3.+3	081470 -07
		3.+1	278340 -06
		3.-1	034791 -04
		3.-3	256630 -04
		3 DF	146734 -07
15	010	3.+3	145122 -12
		3.+1	102191 -10
		3.-1	244787 -09
		3.-3	034370 -07
		3 DF	041144 -13
3	15	F	059321 -02

20	180	3.+3	062533 -01
		3.+1	062533 -01
		3.-1	062533 -01
		3.-3	062533 -01
		3 DF	250713 -05
20	170	3.+3	050160 -01
		3.+1	057720 -01
		3.-1	066163 -01
		3.-3	075560 -01
		3 DF	261434 -05
20	160	3.+3	038962 -01
		3.+1	052009 -01
		3.-1	068338 -01
		3.-3	088505 -01
		3 DF	293449 -05
20	150	3.+3	292553 -02
		3.+1	045687 -01
		3.-1	068819 -01
		3.-3	100427 -01
		3 DF	034606 -04
20	140	3.+3	211755 -02
		3.+1	039038 -01
		3.-1	067422 -01
		3.-3	110226 -01
		3 DF	041729 -04
20	130	3.+3	147162 -02
		3.+1	032329 -01
		3.-1	064045 -01
		3.-3	116724 -01
		3 DF	050273 -04
20	120	3.+3	097643 -02
		3.+1	258169 -02
		3.-1	058704 -01
		3.-3	118798 -01
		3 DF	059398 -04
20	110	3.+3	061367 -02
		3.+1	197334 -02
		3.-1	051568 -01
		3.-3	115556 -01
		3 DF	067727 -04

TABLE 3 (cont.).

20	100	3.+3	036127 -02
		3.+1	142866 -02
		3.-1	042995 -01
		3.-3	106550 -01
		3 DF	073295 -04
20	090	3.+3	196024 -03
		3.+1	096487 -02
		3.-1	033550 -01
		3.-3	092018 -01
		3 DF	073751 -04
20	080	3.+3	095714 -03
		3.+1	059423 -02
		3.-1	239958 -02
		3.-3	073089 -01
		3 DF	067010 -04
20	070	3.+3	040527 -03
		3.+1	032221 -02
		3.-1	152300 -02
		3.-3	051888 -01
		3 DF	052534 -04
20	060	3.+3	140097 -04
		3.+1	145248 -03
		3.-1	081351 -02
		3.-3	031395 -01
		3 DF	032912 -04
20	050	3.+3	035568 -04
		3.+1	049221 -03
		3.-1	033302 -02
		3.-3	148681 -02
		3 DF	143114 -05
20	040	3.+3	054028 -05
		3.+1	103121 -04
		3.-1	086977 -03
		3.-3	046521 -02
		3 DF	032363 -05
20	030	3.+3	309530 -07
		3.+1	085849 -05
		3.-1	095355 -04
		3.-3	064929 -03
		3 DF	190689 -07
20	020	3.+3	177277 -09
		3.+1	078905 -07
		3.-1	128595 -06
		3.-3	125334 -05
		3 DF	034834 -09
20	010	3.+3	182981 -15
		3.+1	169426 -13
		3.-1	053552 -11
		3.-3	100147 -10
		3 DF	034885 -18
3	20	F	056542 -03
40	180	3.+3	295043 -04
		3.+1	295043 -04
		3.-1	295043 -04
		3.-3	295043 -04
		3 DF	055811 -09
40	170	3.+3	216114 -04
		3.+1	262894 -04
		3.-1	031838 -03
		3.-3	038398 -03
		3 DF	060305 -09
40	160	3.+3	152302 -04
		3.+1	227366 -04
		3.-1	033332 -03
		3.-3	048080 -03
		3 DF	074990 -09
40	150	3.+3	102708 -04
		3.+1	189847 -04
		3.-1	033661 -03
		3.-3	057618 -03
		3 DF	099462 -09
40	140	3.+3	066031 -04
		3.+1	152464 -04
		3.-1	032653 -03
		3.-3	065847 -03
		3 DF	132557 -09

Table 3 (cont.).

40	130	3.+3	040234 -04
		3.+1	117063 -04
		3.-1	302419 -04
		3.-3	071376 -03
		3 DF	170507 -09
40	120	3.+3	230352 -05
		3.+1	085182 -04
		3.-1	265056 -04
		3.-3	072810 -03
		3 DF	205584 -09
40	110	3.+3	122383 -05
		3.+1	058001 -04
		3.-1	217136 -04
		3.-3	069119 -03
		3 DF	226143 -09
40	100	3.+3	059251 -05
		3.+1	036289 -04
		3.-1	163358 -04
		3.-3	060085 -03
		3 DF	219849 -09
40	090	3.+3	254520 -06
		3.+1	203140 -05
		3.-1	110020 -04
		3.-3	046717 -03
		3 DF	180938 -09
40	080	3.+3	093155 -06
		3.+1	097751 -05
		3.-1	063848 -04
		3.-3	031354 -03
		3 DF	118316 -09
40	070	3.+3	272599 -07
		3.+1	037988 -05
		3.-1	300810 -05
		3.-3	171757 -04
		3 DF	055631 -09
40	060	3.+3	057400 -07
		3.+1	107581 -06
		3.-1	104269 -05
		3.-3	069969 -04
		3 DF	159056 -10
40	050	3.+3	072108 -08
		3.+1	184969 -07
		3.-1	223150 -06
		3.-3	179328 -05
		3 DF	203870 -11
40	040	3.+3	037370 -09
		3.+1	134813 -08
		3.-1	208432 -07
		3.-3	207178 -06
		3 DF	063230 -12
40	030	3.+3	034355 -11
		3.+1	182746 -10
		3.-1	038168 -08
		3.-3	049690 -07
		3 DF	110639 -15
40	020	3.+3	047155 -15
		3.+1	040716 -13
		3.-1	127735 -12
		3.-3	243739 -11
		3 DF	131126 -21
40	010	3.+3	056473 -26
		3.+1	102603 -24
		3.-1	063763 -22
		3.-3	237418 -21
		3 DF	195811 -40
3	40	F	139778 -08

Table 4. $I_{4u}(\vartheta, \xi)$, $df_{E4}(\vartheta, \xi)/d\Omega$ and $f_{E4}(\xi)$.

02	180	4.+4	107360	00
		4.+2	107360	00
		4. 0	107360	00
		4.-2	107360	00
		4.-4	107360	00
		4 DF	044704	-02
02	170	4.+4	101651	00
		4.+2	104190	00
		4. 0	106438	00
		4.-2	108376	00
		4.-4	109987	00
		4 DF	044334	-02
02	160	4.+4	093304	00
		4.+2	099023	00
		4. 0	103697	00
		4.-2	107167	00
		4.-4	109307	00
		4 DF	043239	-02
02	150	4.+4	082936	00
		4.+2	092093	00
		4. 0	099210	00
		4.-2	103753	00
		4.-4	105345	00
		4 DF	041465	-02
02	140	4.+4	071273	00
		4.+2	083703	00
		4. 0	093104	00
		4.-2	098250	00
		4.-4	098371	00
		4 DF	039082	-02
02	130	4.+4	059078	00
		4.+2	074208	00
		4. 0	085554	00
		4.-2	090864	00
		4.-4	088883	00
		4 DF	036184	-02
02	120	4.+4	047084	00
		4.+2	064003	00
		4. 0	076790	00
		4.-2	081892	00
		4.-4	077552	00
		4 DF	032875	-02
02	110	4.+4	035925	00
		4.+2	053507	00
		4. 0	067093	00
		4.-2	071710	00
		4.-4	065162	00
		4 DF	292688	-03
02	100	4.+4	260881	-01
		4.+2	043141	00
		4. 0	056797	00
		4.-2	060757	00
		4.-4	052526	00
		4 DF	254742	-03
02	090	4.+4	178870	-01
		4.+2	033312	00
		4. 0	046285	00
		4.-2	049526	00
		4.-4	040415	00
		4 DF	215961	-03
02	080	4.+4	114498	-01
		4.+2	243931	-01
		4. 0	035979	00
		4.-2	038529	00
		4.-4	294776	-01
		4 DF	177304	-03
02	070	4.+4	067321	-01
		4.+2	166944	-01
		4. 0	263254	-01
		4.-2	282788	-01
		4.-4	201857	-01
		4 DF	139670	-03

Table 4 (cont.).

02	060	4.+4	035472	-01
		4.+2	104454	-01
		4. 0	177697	-01
		4.-2	192447	-01
		4.-4	128016	-01
		4 DF	103989	-03
02	050	4.+4	160987	-02
		4.+2	057649	-01
		4. 0	107137	-01
		4.-2	118143	-01
		4.-4	073682	-01
		4 DF	071366	-03
02	040	4.+4	058699	-02
		4.+2	263521	-02
		4. 0	054535	-01
		4.-2	062405	-01
		4.-4	037307	-01
		4 DF	043231	-03
02	030	4.+4	149669	-03
		4.+2	087965	-02
		4. 0	209637	-02
		4.-2	258655	-02
		4.-4	158395	-02
		4 DF	214045	-04
02	020	4.+4	189397	-04
		4.+2	157118	-03
		4. 0	046300	-02
		4.-2	067265	-02
		4.-4	055008	-02
		4 DF	079996	-04
02	010	4.+4	032039	-05
		4.+2	045564	-04
		4. 0	205367	-04
		4.-2	045943	-03
		4.-4	283788	-03
		4 DF	150660	-04
4	02	F	272938	-02
04	180	4.+4	090829	00
		4.+2	090829	00
		4. 0	090829	00
		4.-2	090829	00
		4.-4	090829	00
		4 DF	031997	-02
04	170	4.+4	083077	00
		4.+2	086616	00
		4. 0	090018	00
		4.-2	093256	00
		4.-4	096307	00
		4 DF	031875	-02
04	160	4.+4	073632	00
		4.+2	080838	00
		4. 0	087606	00
		4.-2	093746	00
		4.-4	099069	00
		4 DF	031501	-02
04	150	4.+4	063155	00
		4.+2	073769	00
		4. 0	083663	00
		4.-2	092222	00
		4.-4	098855	00
		4 DF	308596	-03
04	140	4.+4	052317	00
		4.+2	065725	00
		4. 0	078303	00
		4.-2	088698	00
		4.-4	095629	00
		4 DF	299223	-03
04	130	4.+4	041744	00
		4.+2	057050	00
		4. 0	071688	00
		4.-2	083275	00
		4.-4	089585	00
		4 DF	286614	-03

TABLE 4 (cont.).

04	120	4.+4	031964	00
		4.+2	048100	00
		4. 0	064026	00
		4.-2	076151	00
		4.-4	081134	00
		4 DF	270527	-03
04	110	4.+4	233716	-01
		4.+2	039229	00
		4. 0	055577	00
		4.-2	067615	00
		4.-4	070867	00
		4 DF	250823	-03
04	100	4.+4	162090	-01
		4.+2	307723	-01
		4. 0	046646	00
		4.-2	058042	00
		4.-4	059499	00
		4 DF	227532	-03
04	090	4.+4	105641	-01
		4.+2	230310	-01
		4. 0	037581	00
		4.-2	047879	00
		4.-4	047800	00
		4 DF	200900	-03
04	080	4.+4	063860	-01
		4.+2	162589	-01
		4. 0	287664	-01
		4.-2	037628	00
		4.-4	036511	00
		4 DF	171435	-03
04	070	4.+4	035124	-01
		4.+2	106445	-01
		4. 0	206045	-01
		4.-2	278212	-01
		4.-4	262775	-01
		4 DF	139944	-03
04	060	4.+4	170678	-02
		4.+2	062950	-01
		4. 0	134901	-01
		4.-2	189798	-01
		4.-4	175792	-01
		4 DF	107584	-03
04	050	4.+4	069816	-02
		4.+2	032198	-01
		4. 0	077680	-01
		4.-2	115726	-01
		4.-4	106961	-01
		4 DF	075926	-03
04	040	4.+4	220440	-03
		4.+2	131690	-02
		4. 0	036700	-01
		4.-2	059544	-01
		4.-4	056925	-01
		4 DF	046991	-03
04	030	4.+4	044939	-03
		4.+2	036609	-02
		4. 0	123198	-02
		4.-2	229323	-02
		4.-4	243920	-02
		4 DF	231944	-04
04	020	4.+4	037303	-04
		4.+2	045356	-03
		4. 0	201723	-03
		4.-2	048012	-02
		4.-4	067130	-02
		4 DF	070507	-04
04.	010	4.+4	189553	-07
		4.+2	043255	-05
		4. 0	032637	-04
		4.-2	132920	-04
		4.-4	049843	-03
		4 DF	047621	-05
4	04	F	233022	-02

TABLE 4 (cont.).

06	180	4.+4	071211	00
		4.+2	071211	00
		4. 0	071211	00
		4.-2	071211	00
		4.-4	071211	00
		4 DF	196681	-03
06	170	4.+4	063224	00
		4.+2	066887	00
		4. 0	070543	00
		4.-2	074172	00
		4.-4	077750	00
		4 DF	197082	-03
06	160	4.+4	054360	00
		4.+2	061435	00
		4. 0	068561	00
		4.-2	075582	00
		4.-4	082330	00
		4 DF	198126	-03
06	150	4.+4	045193	00
		4.+2	055122	00
		4. 0	065323	00
		4.-2	075313	00
		4.-4	084550	00
		4 DF	199350	-03
06	140	4.+4	036248	00
		4.+2	048234	00
		4. 0	060928	00
		4.-2	073306	00
		4.-4	084169	00
		4 DF	200045	-03
06	130	4.+4	279648	-01
		4.+2	041064	00
		4. 0	055517	00
		4.-2	069585	00
		4.-4	081137	00
		4 DF	199330	-03
06	120	4.+4	206657	-01
		4.+2	033901	00
		4. 0	049271	00
		4.-2	064261	00
		4.-4	075613	00
		4 DF	196258	-03
06	110	4.+4	145480	-01
		4.+2	270137	-01
		4. 0	042415	00
		4.-2	057536	00
		4.-4	067957	00
		4 DF	189934	-03
06	100	4.+4	096827	-01
		4.+2	206436	-01
		4. 0	035211	00
		4.-2	049708	00
		4.-4	058699	00
		4 DF	179622	-03
06	090	4.+4	060298	-01
		4.+2	149928	-01
		4. 0	279612	-01
		4.-2	041160	00
		4.-4	048491	00
		4 DF	164868	-03
06	080	4.+4	034615	-01
		4.+2	102141	-01
		4. 0	209912	-01
		4.-2	032348	00
		4.-4	038045	00
		4 DF	145592	-03
06	070	4.+4	179213	-02
		4.+2	064010	-01
		4. 0	146398	-01
		4.-2	237815	-01
		4.-4	280540	-01
		4 DF	122192	-03

TABLE 4 (cont.).

06	060	4.+4	080875	-02
		4.+2	035786	-01
		4. 0	092292	-01
		4.-2	159852	-01
		4.-4	191256	-01
		4 DF	095632	-03
06	050	4.+4	300641	-03
		4.+2	169562	-02
		4. 0	050239	-01
		4.-2	094536	-01
		4.-4	117216	-01
		4 DF	067547	-03
06	040	4.+4	083025	-03
		4.+2	061953	-02
		4. 0	217026	-02
		4.-2	045795	-01
		4.-4	061206	-01
		4 DF	040374	-03
06	030	4.+4	137080	-04
		4.+2	142931	-03
		4. 0	062168	-02
		4.-2	155666	-02
		4.-4	241135	-02
		4 DF	175127	-04
06	020	4.+4	076010	-05
		4.+2	121933	-04
		4. 0	072606	-03
		4.-2	241652	-03
		4.-4	050214	-02
		4 DF	033629	-04
06	010	4.+4	119578	-08
		4.+2	037601	-06
		4. 0	039834	-05
		4.-2	236381	-05
		4.-4	102927	-04
		4 DF	200736	-07
4	06	F	175975	-02
08	180	4.+4	052800	00
		4.+2	052800	00
		4. 0	052800	00
		4.-2	052800	00
		4.-4	052800	00
		4 DF	108130	-03
08	170	4.+4	045682	00
		4.+2	048944	00
		4. 0	052280	00
		4.-2	055677	00
		4.-4	059120	00
		4 DF	109061	-03
08	160	4.+4	038245	00
		4.+2	044324	00
		4. 0	050735	00
		4.-2	057385	00
		4.-4	064160	00
		4 DF	111707	-03
08	150	4.+4	309312	-01
		4.+2	039170	00
		4. 0	048215	00
		4.-2	057780	00
		4.-4	067491	00
		4 DF	115638	-03
08	140	4.+4	241070	-01
		4.+2	033719	00
		4. 0	044801	00
		4.-2	056769	00
		4.-4	068779	00
		4 DF	120171	-03
08	130	4.+4	180458	-01
		4.+2	282025	-01
		4. 0	040610	00
		4.-2	054325	00
		4.-4	067829	00
		4 DF	124422	-03

TABLE 4 (cont.).

08	120	4.+4	129164	-01
		4.+2	228332	-01
		4. 0	035790	00
		4.-2	050497	00
		4.-4	064617	00
		4 DF	127378	-03
08	110	4.+4	087863	-01
		4.+2	178034	-01
		4. 0	305286	-01
		4.-2	045422	00
		4.-4	059304	00
		4 DF	127983	-03
08	100	4.+4	056333	-01
		4.+2	132736	-01
		4. 0	250400	-01
		4.-2	039325	00
		4.-4	052233	00
		4 DF	125248	-03
08	090	4.+4	033652	-01
		4.+2	093677	-01
		4. 0	195696	-01
		4.-2	032519	00
		4.-4	043904	00
		4 DF	118368	-03
08	080	4.+4	184233	-02
		4.+2	061666	-01
		4. 0	143811	-01
		4.-2	254013	-01
		4.-4	034929	00
		4 DF	106865	-03
08	070	4.+4	090187	-02
		4.+2	037035	-01
		4. 0	097409	-01
		4.-2	184284	-01
		4.-4	259729	-01
		4 DF	090744	-03
08	060	4.+4	037986	-02
		4.+2	195938	-02
		4. 0	058927	-01
		4.-2	120894	-01
		4.-4	176877	-01
		4 DF	070685	-03
08	050	4.+4	129037	-03
		4.+2	086059	-02
		4. 0	301799	-02
		4.-2	068502	-01
		4.-4	106451	-01
		4 DF	048291	-03
08	040	4.+4	031366	-03
		4.+2	280979	-03
		4. 0	118416	-02
		4.-2	307382	-02
		4.-4	052801	-01
		4 DF	263869	-04
08	030	4.+4	042261	-04
		4.+2	053772	-03
		4. 0	286650	-03
		4.-2	090196	-02
		4.-4	183848	-02
		4 DF	091908	-04
08	020	4.+4	158029	-06
		4.+2	031528	-04
		4. 0	235225	-04
		4.-2	100637	-03
		4.-4	279284	-03
		4 DF	098066	-05
08	010	4.+4	078009	-09
		4.+2	031284	-07
		4. 0	042681	-06
		4.-2	033286	-05
		4.-4	181632	-05
		4 DF	061816	-08
4	08	F	117557	-02

TABLE 4 (cont.).

10	180	4.+4	037535	00
		4.+2	037535	00
		4. 0	037535	00
		4.-2	037535	00
		4.-4	037535	00
		4 DF	054645	-03
10	170	4.+4	031742	00
		4.+2	034390	00
		4. 0	037147	00
		4.-2	040006	00
		4.-4	042962	00
		4 DF	055494	-03
10	160	4.+4	259528	-01
		4.+2	307515	-01
		4. 0	035993	00
		4.-2	041637	00
		4.-4	047624	00
		4 DF	057942	-03
10	150	4.+4	204772	-01
		4.+2	268053	-01
		4. 0	034114	00
		4.-2	042288	00
		4.-4	051129	00
		4 DF	061699	-03
10	140	4.+4	155516	-01
		4.+2	227330	-01
		4. 0	031573	00
		4.-2	041858	00
		4.-4	053131	00
		4 DF	066344	-03
10	130	4.+4	113277	-01
		4.+2	187046	-01
		4. 0	284644	-01
		4.-2	040297	00
		4.-4	053374	00
		4 DF	071075	-03
10	120	4.+4	078753	-01
		4.+2	148713	-01
		4. 0	249047	-01
		4.-2	037618	00
		4.-4	051729	00
		4 DF	075264	-03
10	110	4.+4	051915	-01
		4.+2	113612	-01
		4. 0	210402	-01
		4.-2	033908	00
		4.-4	048221	00
		4 DF	077980	-03
10	100	4.+4	032159	-01
		4.+2	082750	-01
		4. 0	170412	-01
		4.-2	293342	-01
		4.-4	043043	00
		4 DF	078324	-03
10	090	4.+4	184854	-02
		4.+2	056821	-01
		4. 0	130981	-01
		4.-2	241459	-01
		4.-4	036552	00
		4 DF	075480	-03
10	080	4.+4	096821	-02
		4.+2	036187	-01
		4. 0	094129	-01
		4.-2	186731	-01
		4.-4	292443	-01
		4 DF	068861	-03
10	070	4.+4	044969	-02
		4.+2	208521	-02
		4. 0	061841	-01
		4.-2	133079	-01
		4.-4	217151	-01
		4 DF	058311	-03

TABLE 4 (cont.).

10	060	4.+4	177428 -03	15	180	4.+4	140552 -01
		4.+2	104507 -02			4.+2	140552 -01
		4. 0	035834 -01			4. 0	140552 -01
		4.-2	084733 -01			4.-2	140552 -01
		4.-4	146006 -01			4.-4	140552 -01
		4 DF	044366 -03			4 DF	076619 -04
10	050	4.+4	055297 -03	15	170	4.+4	113342 -01
		4.+2	042589 -02			4.+2	125667 -01
		4. 0	172263 -02			4. 0	138918 -01
		4.-2	045686 -01			4.-2	153122 -01
		4.-4	085093 -01			4.-4	168304 -01
		4 DF	285805 -04			4 DF	079168 -04
10	040	4.+4	118839 -04	15	160	4.+4	088149 -01
		4.+2	124343 -03			4.+2	109380 -01
		4. 0	061185 -02			4. 0	134078 -01
		4.-2	188257 -02			4.-2	162466 -01
		4.-4	039434 -01			4.-4	194712 -01
		4 DF	137778 -04			4 DF	086646 -04
10	030	4.+4	131308 -05	15	150	4.+4	065983 -01
		4.+2	197461 -04			4.+2	092555 -01
		4. 0	124563 -03			4. 0	126219 -01
		4.-2	047156 -02			4.-2	167734 -01
		4.-4	119055 -02			4.-4	217601 -01
		4 DF	036696 -04			4 DF	098521 -04
10	020	4.+4	033303 -06	15	140	4.+4	047397 -01
		4.+2	079546 -05			4.+2	075967 -01
		4. 0	071309 -04			4. 0	115656 -01
		4.-2	037267 -03			4.-2	168219 -01
		4.-4	129474 -03			4.-4	234692 -01
		4 DF	205094 -06			4 DF	113807 -04
10	010	4.+4	051961 -10	15	130	4.+4	032537 -01
		4.+2	253526 -09			4.+2	060275 -01
		4. 0	042317 -07			4. 0	102831 -01
		4.-2	040887 -06			4.-2	163447 -01
		4.-4	273850 -06			4.-4	243860 -01
		4 DF	139609 -10			4 DF	130948 -04
4	10	F	070503 -02				

TABLE 4 (cont.).

15	120	4.+4	212253	-02
		4.+2	046009	-01
		4. 0	088315	-01
		4.-2	153263	-01
		4.-4	243425	-01
		4 DF	147719	-04
15	110	4.+4	130558	-02
		4.+2	033556	-01
		4. 0	072802	-01
		4.-2	137931	-01
		4.-4	232456	-01
		4 DF	161220	-04
15	100	4.+4	074914	-02
		4.+2	231600	-02
		4. 0	057087	-01
		4.-2	118208	-01
		4.-4	211048	-01
		4 DF	168042	-04
15	090	4.+4	039493	-02
		4.+2	149176	-02
		4. 0	042036	-01
		4.-2	095387	-01
		4.-4	180518	-01
		4 DF	164754	-04
15	080	4.+4	187091	-03
		4.+2	087853	-02
		4. 0	285217	-02
		4.-2	071271	-01
		4.-4	143475	-01
		4 DF	148808	-04
15	070	4.+4	077006	-03
		4.+2	045844	-02
		4. 0	173206	-02
		4.-2	048053	-01
		4.-4	103693	-01
		4 DF	119921	-04
15	060	4.+4	260935	-04
		4.+2	201511	-03
		4. 0	089836	-02
		4.-2	280346	-02
		4.-4	065745	-01
		4 DF	081711	-04
15	050	4.+4	066342	-04
		4.+2	068356	-03
		4. 0	036690	-02
		4.-2	131496	-02
		4.-4	034296	-01
		4 DF	042628	-04
15	040	4.+4	106097	-05
		4.+2	151396	-04
		4. 0	100948	-03
		4.-2	042987	-02
		4.-4	129571	-02
		4 DF	138718	-05
15	030	4.+4	072350	-06
		4.+2	151158	-05
		4. 0	132071	-04
		4.-2	070871	-03
		4.-4	263756	-03
		4 DF	171414	-06
15	020	4.+4	070527	-08
		4.+2	238479	-07
		4. 0	303201	-06
		4.-2	229884	-05
		4.-4	119802	-04
		4 DF	170985	-08
15	010	4.+4	062815	-13
		4.+2	044354	-11
		4. 0	107814	-10
		4.-2	154289	-09
		4.-4	153699	-08
		4 DF	043670	-14
4	15	F	137004	-03

TABLE 4 (cont.).

20	180	4.+4	046509	-01
		4.+2	046509	-01
		4. 0	046509	-01
		4.-2	046509	-01
		4.-4	046509	-01
		4 DF	083898	-05
20	170	4.+4	036092	-01
		4.+2	040768	-01
		4. 0	045911	-01
		4.-2	051553	-01
		4.-4	057724	-01
		4 DF	088163	-05
20	160	4.+4	269427	-02
		4.+2	034700	-01
		4. 0	044142	-01
		4.-2	055504	-01
		4.-4	069032	-01
		4 DF	100820	-05
20	150	4.+4	193050	-02
		4.+2	286372	-02
		4. 0	041279	-01
		4.-2	057977	-01
		4.-4	079510	-01
		4 DF	121344	-05
20	140	4.+4	132338	-02
		4.+2	228550	-02
		4. 0	037453	-01
		4.-2	058628	-01
		4.-4	088083	-01
		4 DF	148499	-05
20	130	4.+4	086392	-02
		4.+2	175705	-02
		4. 0	032847	-01
		4.-2	057206	-01
		4.-4	093634	-01
		4 DF	179875	-05
20	120	4.+4	053364	-02
		4.+2	129383	-02
		4. 0	276947	-02
		4.-2	053600	-01
		4.-4	095151	-01
		4 DF	211429	-05
20	110	4.+4	309141	-03
		4.+2	090525	-02
		4. 0	222772	-02
		4.-2	047896	-01
		4.-4	091928	-01
		4 DF	237267	-05
20	100	4.+4	165875	-03
		4.+2	059493	-02
		4. 0	169111	-02
		4.-2	040424	-01
		4.-4	083757	-01
		4 DF	250045	-05
20	090	4.+4	080985	-03
		4.+2	036120	-02
		4. 0	119268	-02
		4.-2	031772	-01
		4.-4	071115	-01
		4 DF	242462	-05
20	080	4.+4	035048	-03
		4.+2	197659	-03
		4. 0	076357	-02
		4.-2	227746	-02
		4.-4	055263	-01
		4 DF	210149	-05
20	070	4.+4	129165	-04
		4.+2	093847	-03
		4. 0	042819	-02
		4.-2	144122	-02
		4.-4	038203	-01
		4 DF	155612	-05

Table 4 (cont.).

20	060	4.+4	037988	-04
		4.+2	036342	-03
		4. 0	198474	-03
		4.-2	076352	-02
		4.-4	224092	-02
		4 DF	091220	-05
20	050	4.+4	079651	-05
		4.+2	103050	-04
		4. 0	068701	-03
		4.-2	308332	-03
		4.-4	102473	-02
		4 DF	036799	-05
20	040	4.+4	095839	-06
		4.+2	173795	-05
		4. 0	145900	-04
		4.-2	079001	-03
		4.-4	308584	-03
		4 DF	076651	-06
20	030	4.+4	040784	-07
		4.+2	109432	-06
		4. 0	122022	-05
		4.-2	084497	-04
		4.-4	041357	-03
		4 DF	041407	-07
20	020	4.+4	154509	-10
		4.+2	067749	-08
		4. 0	111460	-07
		4.-2	110568	-06
		4.-4	076633	-05
		4 DF	069320	-10
20	010	4.+4	079460	-16
		4.+2	073528	-14
		4. 0	234677	-13
		4.-2	044463	-11
		4.-4	059043	-10
		4 DF	064283	-19
4	20	F	186996	-04
40	180	4.+4	303399	-04
		4.+2	303399	-04
		4. 0	303399	-04
		4.-2	303399	-04
		4.-4	303399	-04
		4 DF	035702	-09
40	170	4.+4	211188	-04
		4.+2	251338	-04
		4. 0	298127	-04
		4.-2	035250	-03
		4.-4	041552	-03
		4 DF	039850	-09
40	160	4.+4	139991	-04
		4.+2	200293	-04
		4. 0	282638	-04
		4.-2	039381	-03
		4.-4	054233	-03
		4 DF	052582	-09
40	150	4.+4	088146	-04
		4.+2	153227	-04
		4. 0	257913	-04
		4.-2	042203	-03
		4.-4	067342	-03
		4 D	074398	-09
40	140	4.+4	052495	-04
		4.+2	112092	-04
		4. 0	225587	-04
		4.-2	043206	-03
		4.-4	079290	-03
		4 D	104932	-09
40	130	4.+4	293803	-05
		4.+2	077934	-04
		4. 0	187926	-04
		4.-2	041997	-03
		4.-4	088066	-03
		4 DF	141289	-09

TABLE 4 (cont.).

40	120	4.+4	153089	-05
		4.+2	051033	-04
		4. 0	147738	-04
		4.-2	038421	-03
		4.-4	091565	-03
		4 DF	176419	-09
40	110	4.+4	073280	-05
		4.+2	310631	-05
		4. 0	108180	-04
		4.-2	032675	-03
		4.-4	088143	-03
		4 DF	198928	-09
40	100	4.+4	031611	-05
		4.+2	172453	-05
		4. 0	072419	-04
		4.-2	253821	-04
		4.-4	077316	-03
		4 DF	196321	-09
40	090	4.+4	119473	-06
		4.+2	084930	-05
		4. 0	043137	-04
		4.-2	175559	-04
		4.-4	060368	-03
		4 DF	162491	-09
40	080	4.+4	037921	-06
		4.+2	035586	-05
		4. 0	219595	-05
		4.-2	104070	-04
		4.-4	040498	-03
		4 DF	105891	-09
40	070	4.+4	094594	-07
		4.+2	118867	-06
		4. 0	089716	-05
		4.-2	049816	-04
		4.-4	220773	-04
		4 DF	049189	-09
40	060	4.+4	166222	-08
		4.+2	284338	-07
		4. 0	265304	-06
		4.-2	174506	-05
		4.-4	089123	-04
		4 DF	137797	-10
40	050	4.+4	169474	-09
		4.+2	040296	-07
		4. 0	047289	-06
		4.-2	037540	-05
		4.-4	225470	-05
		4 DF	171724	-11
40	040	4.+4	068538	-10
		4.+2	233354	-09
		4. 0	035454	-07
		4.-2	035058	-06
		4.-4	256221	-06
		4 DF	051429	-12
40	030	4.+4	046235	-12
		4.+2	236637	-11
		4. 0	049017	-09
		4.-2	063849	-08
		4.-4	060273	-07
		4 DF	086413	-15
40	020	4.+4	041591	-16
		4.+2	035205	-14
		4. 0	110329	-13
		4.-2	211414	-12
		4.-4	289426	-11
		4 DF	098003	-21
40	010	4.+4	246533	-28
		4.+2	044578	-25
		4. 0	277783	-24
		4.-2	103923	-22
		4.-4	276001	-21
		4 DF	140124	-40
4	40	F	120367	-08

Table 5. $df_{M1}(\vartheta, \xi)/d\Omega$ and $f_{M1}(\xi)$.

01	180	1	DF	000000	-27
01	170	1	DF	106260	-02
01	160	1	DF	043919	-01
01	150	1	DF	104407	-01
01	140	1	DF	200642	-01
01	130	1	DF	034703	00
01	120	1	DF	056721	00
01	110	1	DF	090000	00
01	100	1	DF	141058	00
01	090	1	DF	221172	00
01	080	1	DF	350625	00
01	070	1	DF	056771	01
01	060	1	DF	094921	01
01	050	1	DF	166093	01
01	040	1	DF	309626	01
01	030	1	DF	063040	02
01	020	1	DF	144206	02
01	010	1	DF	334450	02
1	01	F		222970	02

02	180	1	DF	000000	-27
02	170	1	DF	083078	-02
02	160	1	DF	034285	-01
02	150	1	DF	081286	-01
02	140	1	DF	155601	-01
02	130	1	DF	267700	-01
02	120	1	DF	043445	00
02	110	1	DF	068304	00
02	100	1	DF	105781	00
02	090	1	DF	163289	00
02	080	1	DF	253560	00
02	070	1	DF	399202	00
02	060	1	DF	064178	01
02	050	1	DF	106018	01
02	040	1	DF	180545	01
02	030	1	DF	313784	01
02	020	1	DF	051403	02
02	010	1	DF	410923	01
1	02	F		082765	02

TABLE 5 (cont.).

03	180	1 DF	000000	-27
03	170	1 DF	060442	-02
03	160	1 DF	249003	-02
03	150	1 DF	058860	-01
03	140	1 DF	112180	-01
03	130	1 DF	191846	-01
03	120	1 DF	308898	-01
03	110	1 DF	048065	00
03	100	1 DF	073448	00
03	090	1 DF	111412	00
03	080	1 DF	169049	00
03	070	1 DF	257962	00
03	060	1 DF	397040	00
03	050	1 DF	061551	01
03	040	1 DF	094939	01
03	030	1 DF	139036	01
03	020	1 DF	159669	01
03	010	1 DF	422415	00
1	03	F	371930	01
04	180	1 DF	000000	-27
04	170	1 DF	041920	-02
04	160	1 DF	172387	-02
04	150	1 DF	040623	-01
04	140	1 DF	077075	-01
04	130	1 DF	130997	-01
04	120	1 DF	209201	-01
04	110	1 DF	032206	00
04	100	1 DF	048534	00
04	090	1 DF	072294	00
04	080	1 DF	107088	00
04	070	1 DF	158188	00
04	060	1 DF	232701	00
04	050	1 DF	337749	00
04	040	1 DF	470261	00
04	030	1 DF	057740	01
04	020	1 DF	461165	00
04	010	1 DF	039816	00
1	04	F	180858	01

TABLE 5 (cont.).

05	180	1	DF	000000	-27
05	170	1	DF	280887	-03
05	160	1	DF	115300	-02
05	150	1	DF	270872	-02
05	140	1	DF	051159	-01
05	130	1	DF	086410	-01
05	120	1	DF	136860	-01
05	110	1	DF	208429	-01
05	100	1	DF	309711	-01
05	090	1	DF	045291	00
05	080	1	DF	065472	00
05	070	1	DF	093576	00
05	060	1	DF	131468	00
05	050	1	DF	178463	00
05	040	1	DF	223957	00
05	030	1	DF	230018	00
05	020	1	DF	127299	00
05	010	1	DF	035644	-01
1	05	F		090523	01

06	180	1	DF	000000	-27
06	170	1	DF	183350	-03
06	160	1	DF	075128	-02
06	150	1	DF	175956	-02
06	140	1	DF	033082	-01
06	130	1	DF	055533	-01
06	120	1	DF	087233	-01
06	110	1	DF	131426	-01
06	100	1	DF	192560	-01
06	090	1	DF	276449	-01
06	080	1	DF	038995	00
06	070	1	DF	053915	00
06	060	1	DF	072322	00
06	050	1	DF	091775	00
06	040	1	DF	103724	00
06	030	1	DF	089005	00
06	020	1	DF	034067	00
06	010	1	DF	308359	-03
1	06	F		460313	00

TABLE 5 (cont.).

07	180	1 DF	000000	-27	08	180	1 DF	000000	-27
07	170	1 DF	117243	-03	08	170	1 DF	073733	-03
07	160	1 DF	047956	-02	08	160	1 DF	301074	-03
07	150	1 DF	111978	-02	08	150	1 DF	070090	-02
07	140	1 DF	209601	-02	08	140	1 DF	130620	-02
07	130	1 DF	034968	-01	08	130	1 DF	216602	-02
07	120	1 DF	054483	-01	08	120	1 DF	033476	-01
07	110	1 DF	081209	-01	08	110	1 DF	049370	-01
07	100	1 DF	117328	-01	08	100	1 DF	070344	-01
07	090	1 DF	165371	-01	08	090	1 DF	097348	-01
07	080	1 DF	227632	-01	08	080	1 DF	130770	-01
07	070	1 DF	304448	-01	08	070	1 DF	169197	-01
07	060	1 DF	038987	00	08	060	1 DF	206856	-01
07	050	1 DF	046239	00	08	050	1 DF	229276	-01
07	040	1 DF	047049	00	08	040	1 DF	209991	-01
07	030	1 DF	033709	00	08	030	1 DF	125577	-01
07	020	1 DF	089140	-01	08	020	1 DF	229276	-02
07	010	1 DF	260324	-04	08	010	1 DF	215790	-05
1	07	F	236791	00	1	08	F	122911	00

TABLE 5 (cont.).

09	180	1 DF	000000	-27	10	180	1 DF	000000	-27
09	170	1 DF	045736	-03	10	170	1 DF	280426	-04
09	160	1 DF	186436	-03	10	160	1 DF	114120	-03
09	150	1 DF	043275	-02	10	150	1 DF	264133	-03
09	140	1 DF	080299	-02	10	140	1 DF	048802	-02
09	130	1 DF	132363	-02	10	130	1 DF	079972	-02
09	120	1 DF	202944	-02	10	120	1 DF	121653	-02
09	110	1 DF	296171	-02	10	110	1 DF	175700	-02
09	100	1 DF	041620	-01	10	100	1 DF	243554	-02
09	090	1 DF	056559	-01	10	090	1 DF	032504	-01
09	080	1 DF	074154	-01	10	080	1 DF	041598	-01
09	070	1 DF	092824	-01	10	070	1 DF	050383	-01
09	060	1 DF	108348	-01	10	060	1 DF	056153	-01
09	050	1 DF	112234	-01	10	050	1 DF	054364	-01
09	040	1 DF	092522	-01	10	040	1 DF	040337	-01
09	030	1 DF	046173	-01	10	030	1 DF	167975	-02
09	020	1 DF	058182	-02	10	020	1 DF	146050	-03
09	010	1 DF	176349	-06	10	010	1 DF	142489	-07
1	09	F	064248	00	1	10	F	033766	00

TABLE 5 (cont.).

12	180	1 DF	000000	-27	14	180	1 DF	000000	-27
12	170	1 DF	102478	-04	14	170	1 DF	036340	-04
12	160	1 DF	041568	-03	14	160	1 DF	146946	-04
12	150	1 DF	095671	-03	14	150	1 DF	033636	-03
12	140	1 DF	175300	-03	14	140	1 DF	061136	-03
12	130	1 DF	283969	-03	14	130	1 DF	097928	-03
12	120	1 DF	042533	-02	14	120	1 DF	144478	-03
12	110	1 DF	060184	-02	14	110	1 DF	200370	-03
12	100	1 DF	081203	-02	14	100	1 DF	263257	-03
12	090	1 DF	104562	-02	14	090	1 DF	032721	-02
12	080	1 DF	127547	-02	14	080	1 DF	038062	-02
12	070	1 DF	144682	-02	14	070	1 DF	040454	-02
12	060	1 DF	147056	-02	14	060	1 DF	037514	-02
12	050	1 DF	124390	-02	14	050	1 DF	277347	-03
12	040	1 DF	074779	-02	14	040	1 DF	135122	-03
12	030	1 DF	216808	-03	14	030	1 DF	272777	-04
12	020	1 DF	089718	-04	14	020	1 DF	053711	-05
12	010	1 DF	090607	-09	14	010	1 DF	056111	-11
1	12	F	094358	-01	1	14	F	266399	-02

TABLE 5 (cont.).

16	180	1 DF	000000	-27
16	170	1 DF	125878	-05
16	160	1 DF	050745	-04
16	150	1 DF	115544	-04
16	140	1 DF	208363	-04
16	130	1 DF	033012	-03
16	120	1 DF	047988	-03
16	110	1 DF	065254	-03
16	100	1 DF	083518	-03
16	090	1 DF	100247	-03
16	080	1 DF	111245	-03
16	070	1 DF	110831	-03
16	060	1 DF	093805	-03
16	050	1 DF	060636	-03
16	040	1 DF	239476	-04
16	030	1 DF	033666	-04
16	020	1 DF	031543	-06
16	010	1 DF	034075	-13
1	16	F	075696	-02
18	180	1 DF	000000	-27
18	170	1 DF	042787	-05
18	160	1 DF	171978	-05
18	150	1 DF	038957	-04
18	140	1 DF	069716	-04
18	130	1 DF	109279	-04
18	120	1 DF	156567	-04
18	110	1 DF	208807	-04
18	100	1 DF	260438	-04
18	090	1 DF	301990	-04
18	080	1 DF	031982	-03
18	070	1 DF	298792	-04
18	060	1 DF	230902	-04
18	050	1 DF	130541	-04
18	040	1 DF	041804	-04
18	030	1 DF	040935	-05
18	020	1 DF	182500	-08
18	010	1 DF	203828	-16
1	18	F	215998	-03

TABLE 5 (cont.).

20	180	1 DF	000000	-27	40	180	1 DF	000000	-27
20	170	1 DF	143199	-06	40	170	1 DF	154657	-11
20	160	1 DF	057391	-05	40	160	1 DF	060414	-10
20	150	1 DF	129357	-05	40	150	1 DF	130177	-10
20	140	1 DF	229764	-05	40	140	1 DF	216031	-10
20	130	1 DF	035639	-04	40	130	1 DF	304317	-10
20	120	1 DF	050338	-04	40	120	1 DF	037646	-09
20	110	1 DF	065864	-04	40	110	1 DF	041144	-09
20	100	1 DF	080081	-04	40	100	1 DF	039221	-09
20	090	1 DF	089734	-04	40	090	1 DF	031601	-09
20	080	1 DF	090729	-04	40	080	1 DF	203488	-10
20	070	1 DF	079509	-04	40	070	1 DF	095224	-10
20	060	1 DF	056119	-04	40	060	1 DF	274716	-11
20	050	1 DF	277573	-05	40	050	1 DF	036084	-11
20	040	1 DF	072095	-05	40	040	1 DF	116550	-13
20	030	1 DF	049180	-06	40	030	1 DF	215673	-16
20	020	1 DF	104341	-09	40	020	1 DF	273796	-22
20	010	1 DF	120473	-18	40	010	1 DF	044078	-40
1	20	F	061814	-03	1	40	F	240355	-09

Table 6. $df_{M2}(\vartheta, \xi)/d\Omega$ and $f_{M2}(\xi)$.

02	180	2 DF	000000	-27	04	180	2 DF	000000	-27
02	170	2 DF	042308	-03	04	170	2 DF	266256	-04
02	160	2 DF	172372	-03	04	160	2 DF	108455	-03
02	150	2 DF	039991	-02	04	150	2 DF	251510	-03
02	140	2 DF	074225	-02	04	140	2 DF	046638	-02
02	130	2 DF	122602	-02	04	130	2 DF	076912	-02
02	120	2 DF	189007	-02	04	120	2 DF	118243	-02
02	110	2 DF	278950	-02	04	110	2 DF	173727	-02
02	100	2 DF	040017	-01	04	100	2 DF	247450	-02
02	090	2 DF	056348	-01	04	090	2 DF	034457	-01
02	080	2 DF	078383	-01	04	080	2 DF	047113	-01
02	070	2 DF	108157	-01	04	070	2 DF	063291	-01
02	060	2 DF	148321	-01	04	060	2 DF	083185	-01
02	050	2 DF	201904	-01	04	050	2 DF	105591	-01
02	040	2 DF	270735	-01	04	040	2 DF	125253	-01
02	030	2 DF	034824	00	04	030	2 DF	126858	-01
02	020	2 DF	038710	00	04	020	2 DF	080340	-01
02	010	2 DF	186133	-01	04	010	2 DF	052549	-02
2	02	F	123315	00	2	04	F	057738	00

TABLE 6 (cont.).

06	180	2 DF	000000	-27
06	170	2 DF	142492	-04
06	160	2 DF	058032	-03
06	150	2 DF	134516	-03
06	140	2 DF	249181	-03
06	130	2 DF	041008	-02
06	120	2 DF	062814	-02
06	110	2 DF	091719	-02
06	100	2 DF	129344	-02
06	090	2 DF	177316	-02
06	080	2 DF	236653	-02
06	070	2 DF	306279	-02
06	060	2 DF	037976	-01
06	050	2 DF	043885	-01
06	040	2 DF	044376	-01
06	030	2 DF	033359	-01
06	020	2 DF	109145	-02
06	010	2 DF	082161	-04
2	06	F	239060	-01

08	180	2 DF	000000	-27
08	170	2 DF	068513	-04
08	160	2 DF	278989	-04
08	150	2 DF	064637	-03
08	140	2 DF	119596	-03
08	130	2 DF	196348	-03
08	120	2 DF	299419	-03
08	110	2 DF	043391	-02
08	100	2 DF	060452	-02
08	090	2 DF	081321	-02
08	080	2 DF	105440	-02
08	070	2 DF	130582	-02
08	060	2 DF	151303	-02
08	050	2 DF	157089	-02
08	040	2 DF	132924	-02
08	030	2 DF	072262	-02
08	020	2 DF	117712	-03
08	010	2 DF	096807	-06
2	08	F	091953	-01

TABLE 6 (cont.).

10	180	2 DF	000000	-27	15	180	2 DF	000000	-27
10	170	2 DF	305357	-05	15	170	2 DF	032481	-05
10	160	2 DF	124326	-04	15	160	2 DF	132205	-05
10	150	2 DF	287902	-04	15	150	2 DF	305712	-05
10	140	2 DF	053199	-03	15	140	2 DF	056273	-04
10	130	2 DF	087099	-03	15	130	2 DF	091384	-04
10	120	2 DF	132146	-03	15	120	2 DF	136593	-04
10	110	2 DF	189862	-03	15	110	2 DF	191408	-04
10	100	2 DF	260891	-03	15	100	2 DF	252846	-04
10	090	2 DF	034356	-02	15	090	2 DF	031359	-03
10	080	2 DF	043134	-02	15	080	2 DF	036010	-03
10	070	2 DF	050891	-02	15	070	2 DF	037224	-03
10	060	2 DF	054783	-02	15	060	2 DF	032880	-03
10	050	2 DF	050712	-02	15	050	2 DF	224609	-04
10	040	2 DF	035553	-02	15	040	2 DF	096348	-04
10	030	2 DF	137960	-03	15	030	2 DF	156840	-05
10	020	2 DF	110003	-04	15	020	2 DF	203064	-07
10	010	2 DF	096673	-08	15	010	2 DF	064045	-13
2	10	F	033775	-01	2	15	F	243260	-03

TABLE 6 (cont.).

20	180	2 DF	000000	-27	40	180	2 DF	000000	-27
20	170	2 DF	282341	-07	40	170	2 DF	062438	-11
20	160	2 DF	114878	-06	40	160	2 DF	253590	-11
20	150	2 DF	265204	-06	40	150	2 DF	058046	-10
20	140	2 DF	048596	-05	40	140	2 DF	103979	-10
20	130	2 DF	078170	-05	40	130	2 DF	159713	-10
20	120	2 DF	114848	-05	40	120	2 DF	216451	-10
20	110	2 DF	156442	-05	40	110	2 DF	259199	-10
20	100	2 DF	197778	-05	40	100	2 DF	269807	-10
20	090	2 DF	229719	-05	40	090	2 DF	235944	-10
20	080	2 DF	239588	-05	40	080	2 DF	163571	-10
20	070	2 DF	215200	-05	40	070	2 DF	081635	-10
20	060	2 DF	154470	-05	40	060	2 DF	248540	-11
20	050	2 DF	076992	-05	40	050	2 DF	034062	-11
20	040	2 DF	199422	-06	40	040	2 DF	113408	-13
20	030	2 DF	134076	-07	40	030	2 DF	213583	-16
20	020	2 DF	276700	-10	40	020	2 DF	272262	-22
20	010	2 DF	306302	-19	40	010	2 DF	043392	-40
2	20	F	156189	-04	2	40	F	156007	-09

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EXCITATION OF CHARACTERISTIC K X-RAYS BY THE IMPACT OF HEAVY CHARGED PARTICLES

BY

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København 1957
i kommission hos Ejnar Munksgaard

Synopsis.

The cross section for ejection of K-electrons by slow ions is evaluated in the Born approximation for the incident particles, using relativistic electron wave functions. Numerical results are given for lead (and silver) and compared with experimental cross sections for excitation of characteristic K x-rays. For silver, the relativistic corrections are small, but for lead they are appreciable and improve the agreement with experiment. Still, the theoretical cross sections for Pb as well as for Ag are not in quantitative agreement with the experimental values. The discrepancy is attributed mainly to a failure of the Born approximation.

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Bianco Lunos Bogtrykkeri A-S.

I. Introduction.

The characteristic x-rays following the ejection of inner atomic electrons by the impact of heavy charged particles have been investigated by several authors in the past*. Recently, more precise experimental data have become available[1) 2) 3) 4)]. The process has received increasing attention since it yields electrons and x-rays in the same energy range as nuclear transitions following Coulomb excitation of heavy nuclei. From the point of view of the nuclear physicist, the atomic process constitutes an undesirable background, and it is thus necessary to know its dependence on various parameters. On the other hand, it is, at least in principle, accessible to exact calculation and might therefore serve as a reference for calibration of nuclear cross sections.

Following the fundamental stopping power calculations by BETHE, HENNEBERG[5)] has presented a theory of the ionization of the K-shell by the impact of slow protons and α-particles. He neglected the Coulomb interaction between the incident particle and the nucleus. He justified the use of the Born approximation for the impinging particles by proving that the effective part of the product of initial and final wave functions of the heavy particle does not differ appreciably from its plane-wave substitute, though the wave functions themselves are heavily distorted**.

Assuming the Born approximation for the bombarding particles, the cross section for ejection of a K-electron is given by

$$\sigma = \frac{4\pi}{\hbar^2} Z_1^2 e^4 \frac{M}{E_1} \int_{q_{\min}}^{\infty} J \frac{dq}{q^3}. \tag{1}$$

---

* For historical details, see reference 1.

** One arrives at the same conclusion looking at the collision classically, which is permitted for slow bombarding particles. The main contribution to the cross section should arise from particles with impact parameters of the order of atomic dimensions. If their energy is not too low, these particles are but slightly deflected by the Coulomb field of the nucleus. Thus, the influence of the field is not very important for the calculations and the wave functions for the particles may be described throughout by plane waves.

Here Z_1, M, and E_1 are the charge, mass, and energy of the incoming particle, respectively. The momentum transfer in the collision is given by $\hbar\vec{q} = \hbar(\vec{K}_0 - \vec{K})$, where $\hbar\vec{K}_0$ and $\hbar\vec{K}$ are the momenta of the incident particle before and after the collision, respectively. $q_{\min}$ is defined as $q_{\min} = K_0 - K$ and, if the energy ΔE lost by the heavy particle is small compared to its initial energy E_1, we have approximately

$$q^2_{\min} \simeq \frac{(\Delta E)^2 M}{2\,\hbar^2 E_1}\left(1 + \frac{\Delta E}{2\,E_1}\right). \tag{2}$$

The quantity J is given by

$$J = \sum_f \left[\int e^{i\vec{q}\,\vec{r}}\,\psi_i(\vec{r})\,\psi_f(\vec{r})\,d\vec{r}\right]^2, \tag{3}$$

where $\psi_i(\vec{r})$ and $\psi_f(\vec{r})$ are the initial and final wave functions of the electron, respectively. The squares of the matrix elements for the different final states are summed, since we are not interested in the angular distribution of the ejected electrons.

Henneberg obtained his results by using non-relativistic Coulomb wave functions for $\psi_i(\vec{r})$ and $\psi_f(\vec{r})$. He roughly corrected for the screening by adding a constant term to the Coulomb potential and arrived at the following expression for the cross section for excitation of K x-rays*:

$$\sigma = \frac{3{,}51\,Z_1^2}{Z^4\,\Theta}\,\Phi_0(\eta') \times 10^{-16}\ \mathrm{cm}^2. \tag{4}$$

Z is the charge of the nucleus, Θ is the ratio of the observed K-shell ionization energy E_K to the "ideal ionization energy in the absence of outer screening", and $\Phi_0(\eta')$ is defined by

$$\Phi_0(\eta') = \frac{2}{5}\,e^{-\frac{4\eta'}{1+\eta'}}\left(\frac{4\eta'}{1+\eta'}\right)^4\left\{\frac{1}{4} + \frac{1}{12}\left(\frac{4\eta'}{1+\eta'}\right) + \ldots\right\}. \tag{5}$$

The quantity η' is given by

$$\eta' = \frac{4mE_1}{M\Theta E_K},$$

m being the mass of the electron. The above formulae are derived on the assumption that η' is small. Accordingly, the cross section depends mainly on the factor $Z_1^2\,\eta'^4 Z^{-4}$**.

The experiments confirm qualitatively Henneberg's theory, particularly the dependence of the cross section on the energy and mass of the incident

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* We quote this formula as given in reference 1.

** A simple derivation of essentially the same result has been given in reference 4.

particle and on the energy of the K-shell. However, there are serious quantitative discrepancies. Especially in heavy elements, the experimental cross sections are up to several times larger than those derived from formula (4).

This deviation is just in the direction expected, considering the neglect of the relativistic effects in the heavy atoms. As it can be seen from expression (2), the value of $1/q_{\min}$ is in cases of interest considerably smaller than the radius of the K-shell. The factor $e^{i\vec{q}\,\vec{r}}$ in the matrix element (3) is thus a fast oscillating function and any increase in the electron density at the origin, as caused by relativistic effects, will therefore raise the cross section appreciably.

Consequently, it seemed of interest to repeat the calculations, using relativistic wave functions for the electron. In the following chapter the derivation is outlined and the final formulae are given; mathematical details are, however, deferred to the Appendix. In Chapter III, the results are discussed and compared with experiments.

II. Framework of the Calculation.

We insert into the matrix element (3) the stationary6), 7) Coulomb solutions of the Dirac equation. They can be written8)

$$\psi(\vec{r}) = \begin{pmatrix} -if_{\varkappa}(r)\,\chi_{-\varkappa}^{\mu}(\vartheta,\varphi) \\ g_{\varkappa}(r)\,\chi_{\varkappa}^{\mu}(\vartheta,\varphi) \end{pmatrix} \qquad \varkappa = \mp 1, \mp 2, \ldots$$

with

$$\chi_{\varkappa}^{\mu} = \sum_{\tau} < l(\varkappa), 1/2, \mu-\tau, \tau \,\big|\, l(\varkappa), 1/2, j, \mu > \chi_{1/2}^{\tau}\, Y_{l(\varkappa)}^{\mu-\tau}(\vartheta,\varphi)$$

and

$$\left.\begin{array}{lll} j = |\varkappa| - 1/2 & l(\varkappa) = \varkappa \text{ if } \varkappa > 0 & \chi_{1/2}^{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ -j \leq \mu \leq j & l(\varkappa) = |\varkappa| - 1 \text{ if } \varkappa < 0 & \chi_{1/2}^{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{array}\right\} \tag{6}$$

We write the radial wave functions in the form

$$f_{\varkappa}(r) = Dr^{-1}u(r) \qquad g_{\varkappa}(r) = Dr^{-1}v(r).$$

For a discrete state, these quantities are given by9)

$$\left.\begin{array}{rl} u(r) = & -\sqrt{1-\vartheta}\; r^{\gamma_{\varkappa}} e^{-\varepsilon_N r}\left[n'\,\Phi(-n'+1, 2\gamma_{\varkappa}+1, 2\varepsilon_N r)\right. \\ & \left. +(N-\varkappa)\,\Phi(-n', 2\gamma_{\varkappa}+1, 2\varepsilon_N r)\right] \\ v(r) = & \sqrt{1+\vartheta}\; r^{\gamma_{\varkappa}} e^{-\varepsilon_N r}\left[-n'\,\Phi(-n'+1, 2\gamma_{\varkappa}+1, 2\varepsilon_N r)\right. \\ & \left. +(N-\varkappa)\,\Phi(-n', 2\gamma_{\varkappa}+1, 2\varepsilon_N r)\right] \end{array}\right\} \tag{7}$$

$$\left.\begin{aligned} &\vartheta = E/mc^2 = \left[1 + \frac{(\zeta Z)^2}{(n' + \gamma_\varkappa)^2}\right]^{-1/2} \qquad \gamma_\varkappa = \sqrt{|\varkappa|^2 - (\zeta Z)^2} \\ &\varepsilon_N = \frac{Z}{N a_0} \qquad N = \sqrt{n^2 - 2\,n'(|\varkappa| - \gamma_\varkappa)} \qquad n = n' + |\varkappa| \\ &D = \sqrt{\frac{\Gamma(2\gamma_\varkappa + n' + 1)}{4(n'!)\,N(N - \varkappa)}\,\frac{(2\varepsilon_N)^{\gamma_\varkappa + 1/2}}{\Gamma(2\gamma_\varkappa + 1)}}. \end{aligned}\right\} \tag{7}$$

Here, a_0 is the Bohr radius, ζ the fine structure constant, and E the total energy of the electron. We use the symbol Φ for the confluent hypergeometric function, regular at the origin. For the special case of a K-electron, we have $\varkappa = -1$, $n' = 0$, and

$$\left.\begin{aligned} &f(r) = -\sqrt{1 - \gamma_1}\, C r^{\gamma_1 - 1} e^{-\varepsilon_1 r} \qquad \varepsilon_1 = \frac{Z}{a_0} \\ &g(r) = \sqrt{1 + \gamma_1}\, C r^{\gamma_1 - 1} e^{-\varepsilon_1 r} \qquad C = \frac{(2\varepsilon_1)^{\gamma_1 + 1/2}}{\sqrt{2\Gamma(2\gamma_1 + 1)}}. \end{aligned}\right\} \tag{8}$$

In the continuum, we have10)

$$\left.\begin{aligned} &u(r) = -2\sqrt{W - 1}\, r^{\gamma_\varkappa} Im\left[e^{-ikr + i\eta}(\gamma_\varkappa + i\alpha)\,\Phi(\gamma_\varkappa + 1 + i\alpha, 2\gamma_\varkappa + 1, 2ikr)\right] \\ &v(r) = 2\sqrt{W + 1}\, r^{\gamma_\varkappa} Re\left[e^{-ikr + i\eta}(\gamma_\varkappa + i\alpha)\,\Phi(\gamma_\varkappa + 1 + i\alpha, 2\gamma_\varkappa + 1, 2ikr)\right] \\ &e^{2i\eta} = -\frac{\varkappa - i\beta}{\gamma_\varkappa + i\alpha} \qquad \beta = \frac{\varepsilon_1}{k} \qquad \alpha = \beta W \qquad W = E/mc^2 = \sqrt{1 + \left(\frac{\hbar k}{mc}\right)^2} \\ &D = \frac{2^{\gamma_\varkappa - 1}}{\Gamma(2\gamma_\varkappa + 1)\hbar}\sqrt{\frac{m}{\pi}}\, k^{\gamma_\varkappa - 1/2} e^{\pi\alpha/2} \left|\Gamma(\gamma_\varkappa + i\alpha)\right|, \end{aligned}\right\} \tag{9}$$

where *Im* and *Re* denote the imaginary and the real part of the expression in parentheses, respectively. These wave functions are normalized per unit energy interval.

In the matrix element (3) we integrate over the angles, sum over the final magnetic quantum numbers, and average over the initial magnetic quantum numbers, using standard techniques. We get

$$J = \sum_f |\varkappa_f| \left\{\int j_{l(\varkappa_f)}(qr)\,[f_i f_f^* + g_i g_f^*]\, r^2 dr\right\}^2, \tag{10}$$

$j_l(qr)$ being the spherical Bessel function.

The radial integration can be carried through, as outlined in the Appendix. The result is a power series in ε_1/q. We may write

$$I = \int j_l(qr)\,[f_i f_f^* + g_i g_f^*]\,r^2\,dr = A q^{-(\gamma_1+\gamma_f+1)}\,S(\varepsilon_1/q)$$

with

$$\left.\begin{aligned}
S(x) &= F\sum_m P_m(-1)^m x^{2m} + G\sum_m Q_m(-1)^m x^{2m+1}\\
F &= \frac{\Gamma(c)}{\Gamma(a+1/2)\Gamma(1-b)}, \quad G = \frac{\Gamma(c-1)}{\Gamma(a)\,\Gamma(1/2-b)}\\
A &= BD_f \qquad B = C\,\frac{\sqrt{\pi}\,\Gamma(a)}{2^{l+1}}\\
P_m &= \frac{(a)_m\,(b)_m}{(c)_m\,m!}\,p_m \qquad Q_m = \frac{(a+1/2)_m\,(b+1/2)_m}{(c+1)_m\,m!}\,q_m\\
a &= \frac{\gamma_1+\gamma_f+l+1}{2} \qquad b = \frac{\gamma_1+\gamma_f-l}{2} \qquad c = 1/2\\
a_m &= a\,(a+1)\dots(a+m-1).
\end{aligned}\right\}\quad (11)$$

The quantities p_m and q_m are different according to whether the final state is in the discrete or in the continuous spectrum. In the discrete spectrum, we have

$$\left.\begin{aligned}
p_m &= [s\,(N_f-\varkappa_f)\,\mathrm{F}(-2m,\,-n'_f,\,2\gamma_f+1,\,y)\\
&\qquad - tn'_f\,F(-2m,-n'_f+1,\,2\gamma_f+1,\,y)]\,v^{2m}\\
q_m &= [s\,(N_f-\varkappa_f)\,F(-2m-1,\,-n'_f,\,2\gamma_f+1,\,y)\\
&\qquad - tn'_f\,F(-2m-1,-n'_f+1,\,2\gamma_f+1,\,y)]\,v^{2m+1}\\
s &= \sqrt{1+\gamma_1}\sqrt{1+\vartheta_f}+\sqrt{1-\gamma_1}\sqrt{1-\vartheta_f}\\
t &= \sqrt{1+\gamma_1}\sqrt{1+\vartheta_f}-\sqrt{1-\gamma_1}\sqrt{1-\vartheta_f}\\
y &= \frac{2}{1+N_f} \qquad v = 1+\frac{1}{N_f},
\end{aligned}\right\}\quad (12)$$

where F is the usual symbol for the hypergeometric function.

For a final state in the continuum, we have

$$\left.\begin{aligned}
p_m &= 2\,Re\left\{F(-2m,\,\gamma_f+1+i\alpha,\,2\gamma_f+1,\,y)\,v^{2m}X\right\}\\
q_m &= 2\,Re\left\{F(-2m-1,\,\gamma_f+1+i\alpha,\,2\gamma_f+1,\,y)\,v^{2m+1}X\right\}\\
y &= \frac{2ik}{\varepsilon_1+ik} \qquad v = 1+i\frac{k}{\varepsilon_1}\\
X &= \left(\sqrt{W+1}\sqrt{1+\gamma_1}-i\sqrt{W-1}\sqrt{1-\gamma_1}\right)(\gamma_f+i\alpha)\,e^{i\eta}.
\end{aligned}\right\}\quad (13)$$

The limit $k = 0$ is not entirely trivial. We get

$$\left.\begin{aligned} p_m &= \sqrt{2\,(1+\gamma_1)}\,\Big[(\gamma_f+1-\gamma_1-\varkappa_f)\,\Phi\,(-2\,m,\,2\,\gamma_f+1,\,-2) \\ &\qquad + \frac{4\,m}{2\,\gamma_f+1}\,\Phi\,(-2\,m+1,\,2\,\gamma_f+2,\,-2)\Big] \\ q_m &= \sqrt{2\,(1+\gamma_1)}\,\Big[(\gamma_f+1-\gamma_1-\varkappa_f)\,\Phi(-2\,m-1,\,2\,\gamma_f+1,\,-2) \\ &\qquad + \frac{4\,m}{2\,\gamma_f+1}\,\Phi\,(-2\,m,\,2\,\gamma_f+2,\,-2)\Big]. \end{aligned}\right\} \qquad (14)$$

The radii of convergence of the series S are in the three cases

$$q^2 > \varepsilon_1^2\left(1+\frac{1}{N_f}\right)^2, \quad q^2 > \varepsilon_1^2 + k^2, \quad q^2 > \varepsilon_1^2,$$

respectively.

The arguments of all complex quantities have to be taken between $-\pi$ and $+\pi$.

The screening is taken into account by assuming an effective nuclear charge $Z_{eff} = Z - 0.3$ and by adding to the corresponding Coulomb potential a constant term $e^{-1}V$, representing the effect of the outer electrons. The energy V is the difference between the observed binding energy of the K-electron and the value which this binding energy would have in the absence of outer screening.

The electron wave functions are thus as given above with Z_{eff} instead of Z and the effective energy equal to $E_t - V$, where E_t is the true total energy of the electron. Therefore, the wave functions of the electrons with $E_t < \mathrm{mc}^2 + V$ are of the form given for the discrete spectrum, only that n' is in general non-integer.

In order to obtain the total cross section for ionization of the K-shell, we have to square I, given by (11), integrate over q (cf. (1)), sum over different $\varkappa_f$ (cf. (10)) and, finally, integrate over the energies of the outgoing electrons. The last two steps can only be done numerically.

III. Results and Discussion.

The cross section for K x-ray production by protons has been evaluated for two elements, lead and silver, and for the impact energy range in which the experiments were performed, i. e. 1—3 MeV. The numerical work of evaluating the series S was considerable, since the series is alternating with increasing coefficients. We calculated it for three different energies of the ejected electrons and all contributing final $\varkappa$-values, taking into account up to 15 terms. This was sufficient for $0 < x < 0.3$. In Table I, we give the quantity

$$T = (q/\varepsilon_1)^{4\gamma_1+4} \int_0^{\varepsilon_1/q} x^{2\gamma_1+2\gamma_f+3} S^2(x)\, dx$$

as a function of ε_1/q for lead. Also the normalization factors as calculated from formulae (7) to (9) are listed.

TABLE I.

ΔE $W_t(W_f)$	88,0 keV 1,0000 (0,9749)			101 keV 1,0251 (1,0000)			123 keV 1,0686 (1,0435)		
ε_1/q \ $\varkappa_f$	-1	$+1$	-2	-1	$+1$	-2	-1	$+1$	-2
0.00	0.3542	0	0	0.3333	0	0	0.3414	0	0
0.05	0.5030	0.00023	0.00036	0.4749	0.00055	0.00035	0.4890	0.00071	0.00036
0.10	0.6341	0.00116	0.00236	0.6001	0.00280	0.00232	0.6205	0.00362	0.00240
0.15	0.7266	0.00299	0.00718	0.6889	0.00722	0.00708	0.7145	0.00935	0.00734
0.20	0.7694	0.00557	0.01521	0.7302	0.01354	0.01503	0.7589	0.01759	0.01565
0.25	0.7626	0.00861	0.02574	0.7239	0.02082	0.02549	0.7524	0.02707	0.02660
0.30	0.7150	0.01155	0.03728	0.6781	0.02788	0.03690	0.7028	0.03608	0.03850
$\lvert\varkappa_f\rvert A'^2$	2.309	8.596	2.804	2.521	4.284	4.304	2.576	4.377	5.758

The quantity T, defined in the text, is given for Pb as a function of ε_1/q and $\varkappa_f$ for three different energies of the ejected electrons. W_t and W_f are defined by $W_t = E_t/\mathrm{mc}^2$ and $W_f = (E_t - V)/\mathrm{mc}^2$. In the last row the corresponding normalization factor is listed in units of $\varepsilon_1^{2\gamma_1+2\gamma_f}\, m/\hbar^2$, i. e. $A^2 = A'^2 \varepsilon_1^{2\gamma_1+2\gamma_f}\, m/\hbar^2$. Only those final states which contribute more than 1 % to the total cross section are taken into account.

From Table I it is seen that the values of T for the important transitions are not sensitive to the energy of the ejected electron and that, consequently, nearly the whole dependence of the cross section on this energy is contained in $q_{\min}$. The interpolation and extrapolation of the data in Table I and the subsequent integration over the energy of the ejected electrons could therefore be performed with sufficient accuracy. The cross sections for production of lead K x-rays, as calculated from the data listed in Table I, are presented in Table II and Figure 1 and compared with experiments and previous theory. The computational accuracy of our results should be better than 5 %. For silver, we had to extrapolate our values for T towards higher values of ε_1/q in order to come into the region covered by the experiments. Hereby, errors of the order of 20 % could easily be introduced. The result-

Table II.

Element	E_1 (MeV)	σ_{exp} (cm^2)	$\sigma_{\text{th}\,1}$ (cm^2)	$\sigma_{\text{th}\,2}$ (cm^2)
Pb	1.00			1.04×10^{-27}
	1.50			3.54
	1.92	3.6×10^{-27}	1.56×10^{-27}	7.0*
	2.00			7.91
	2.17	5.9	2.48	9.9*
	2.40	10.5	3.43	13.1*
	2.50			14.8
	2.88	30.5	6.30	22.0*
	3.00			24.2
Ag	1.70	0.69×10^{-24}	0.76×10^{-24}	
	1.92	1.3	1.15	
	2.17	2.1	1.61	
	2.40	3.0	2.20	
	2.64	4.3	2.77	
	2.88	8.2	3.49	

Experimental(1) and theoretical cross sections as a function of the proton energy. The last column gives the relativistic cross sections. Those marked with an asterisk have been obtained by graphical interpolation. The last but one column includes cross sections as calculated by Lewis et al.(1) according to Henneberg's theory. They have been partially corrected for relativistic effects since a relativistic screening factor Θ is used. A consistent non-relativistic procedure would yield cross sections smaller by ten to fifty per cent. In the case of silver, our relativistic cross sections agree with the semi-relativistic ones within computational errors.

ant cross sections are, however, somewhat accidentally equal to those evaluated by Lewis et al.(1) from Henneberg's theory.

It is seen that, as expected, the use of relativistic electron wave functions increases considerably the cross section for heavy elements, and the agreement with the experimental data is thereby improved significantly. Still, there remains a discrepancy between theory and experiment, especially as regards the energy dependence of the cross sections.

Some uncertainty in the theoretical calculations arises from the manner in which the screening effect is taken into account. Work in related fields(11) indicates that the form of the electron wave functions which we have employed is adequate, since, in the central regions of the atom which contribute to the integral J, the assumed potential is rather accurate. An improvement of the treatment would, however, be obtained by adjusting the normalization factors for the final state wave functions to take into account the modification of the potential at large distances. The effect is found to be small,

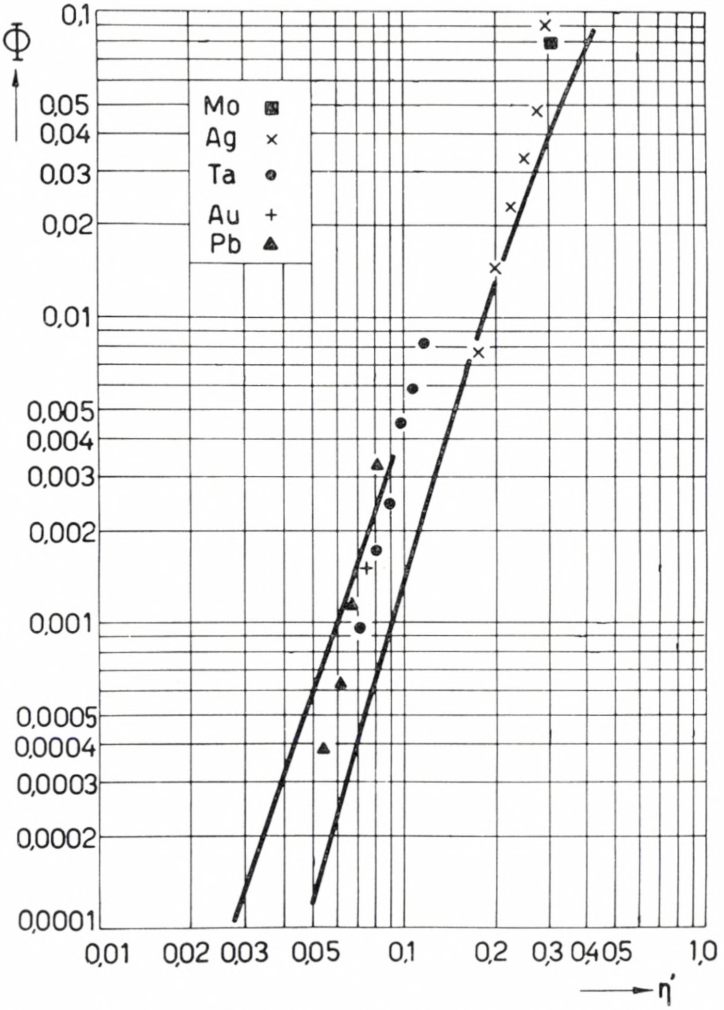

Fig. 1. The figure is taken from ref. 1 (Fig. 4) and includes our results. The points give the experimental quantity $\Phi = Z^4\Theta/3{,}51\,\sigma \times 10^{16}\ \mathrm{cm}^{-2}$ as a function of η'. The left-hand curve represents the function Φ obtained in the same way from the relativistic cross sections for lead. The right-hand curve represents the function Φ_0. In the case of silver, both curves coincide within computational errors. Relativistic screening factors Θ are used throughout.

except for very low electron energies, as is also indicated by the results obtained for the screening effect in other problems, such as internal conversion$^{12)}$. Still, since the low energy end of the spectrum of the ejected electrons contributes most of the total cross section, the correction might be significant. While no quantitative estimates have been made, it can be seen that the effect tends to decrease the cross section. In fact, the correct normalization factor is expected to be smaller than that in (7), which corresponds to bound states. Moreover, the effect on the energy dependence of the total cross section appears to be small. It thus seems unlikely that the discrepancies between theory and experiment can be removed by improving the electron wave functions and their normalization factors.

Another source of error arises from the use of the Born approximation for the bombarding particles, which neglects the deflections of the incident particle in the Coulomb field of the nucleus.

The deflection prevents particles with low energy from coming close enough to the nucleus and thus decreases the cross section for K-shell ionization. One is tempted to consider the quantity $r_0 q_{\mathrm{min}}$, where $r_0 = Z_1 Ze/E_1$ is the distance of closest approach, as a measure of the significance of this deflection* rather than the less stringent criteria of HENNEBERG. It would seem that, if $r_0 q_{\mathrm{min}} > 1$, the ionization cross section must be considerably less than predicted by the Born approximation and that, only if $r_0 q_{\mathrm{min}} \ll 1$, can the influence of the Coulomb field on the incident particle be neglected. Now, for electrons ejected with zero energy, we have $r_0 q_{\mathrm{min}} = 1$ at a proton energy of about 1.1 MeV in lead and about 0.3 MeV in silver. It should thus be understandable that, at proton energies of this order of magnitude or smaller, the cross sections fall below the predictions of the Born approximation.

While thus the failure of the Born approximation may account for the small cross sections observed at low energies and for the rapid energy dependence, it seems more difficult to explain the large experimental cross sections at higher bombarding energies. Additional measurements, especially of the absolute cross sections for silver, would therefore be of value as a further test of the theoretical calculations.

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* This has been suggested to us by A. BOHR.

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Appendix.

We have to evaluate the integral

$$I = \int j_l(qr)\,[f_i f_f^* + g_i g_f^*]\, r^2\, dr\,.$$

The functions f_i and g_i are defined in formula (8). We write the derivation for the case when the final wave functions f_f and g_f are as given in (9). The other case is analogous. We express $j_l(qr)$ as a confluent hypergeometric function

$$j_l(qr) = \frac{\sqrt{\pi}}{\Gamma(l+3/2)\,2^{l+1}}(qr)^l\, e^{-iqr}\, \Phi(l+1, 2l+2, 2iqr)\,.$$

Using integral representations for the occurring confluent hypergeometric functions we are able to carry out the radial integration and arrive at the following expression:

$$I = \frac{\sqrt{\pi}\,\Gamma(2a)}{\Gamma(l+3/2)}\, CD\left(\frac{q}{2}\right)^l Re\left\{X(\varepsilon_1 + ik + iq)^{-2a}\, F_2\left(2a, l+1, \gamma_f + 1 + i\alpha, 2l+2,\right.\right.$$
$$\left.\left. 2\gamma_f + 1;\, \frac{2iq}{\varepsilon_1 + ik + iq}, \frac{2ik}{\varepsilon_1 + ik + iq}\right)\right\}.$$

Here, the definition of the various quantities is the same as in the text. F_2 is the symbol for one of the Appell functions as defined in reference 13, page 230.

We may transform F_2 into H_4 using the equation$^{14)}$

$$F_2(\alpha, \beta, \beta', 2\beta, \gamma'; x, y) = \left(1 - \frac{x}{2}\right)^{-\alpha} H_4\left(\alpha, \beta', \beta + \frac{1}{2}, \gamma'; \frac{x^2}{4(2-x)^2}; \frac{2y}{2-x}\right)$$

and get

$$I = \frac{\sqrt{\pi}\,\Gamma(2a)}{\Gamma(l+3/2)}\, CD\left(\frac{q}{2}\right)^l Re\left\{X(\varepsilon_1 + ik)^{-2a}\, H_4\left(2a, \gamma_f + 1 + i\alpha, l + 3/2,\right.\right.$$
$$\left.\left. 2\gamma_f + 1; -\frac{q^2}{4(\varepsilon_1 + ik)^2}, \frac{2ik}{\varepsilon_1 + ik}\right)\right\}.$$

We require the analytical continuation for large values of q. It can be obtained in the following way. Using the notation of reference 13, we have

$$H_4(\alpha,\beta,\gamma,\delta;x,y)=\sum_{m,\,n}\frac{(\alpha)_{2m+n}(\beta)_n}{(\gamma)_m(\delta)_n\,m!\,n!}x^m y^n=\sum_{m,\,n}\frac{(\alpha/2)_m\left(\frac{\alpha+1}{2}\right)_m(\alpha+2m)_n(\beta)_n}{(\gamma)_m(\delta)_n\,m!\,n!}(4x)^m y^n$$

$$=\sum_{m}\frac{(\alpha/2)_m\left(\frac{\alpha+1}{2}\right)_m}{(\gamma)_m\,m!}\mathrm{F}(\alpha+2m,\beta,\delta,y)\,(4x)^m$$

$$=\frac{\Gamma(\delta)}{\Gamma(\beta)\,\Gamma(\delta-\beta)}\int_0^1 u^{\beta-1}(1-u)^{\delta-\beta-1}(1-yu)^{-\alpha}F\left(\frac{\alpha}{2},\frac{\alpha+1}{2},\gamma,\frac{4x}{(1-yu)^2}\right)du\,.$$

Applying here the equation for analytic continuation of the ordinary hypergeometric function and working the same way backward, we arrive at

$$H_4(\alpha,\beta,\gamma,\delta;x,y)$$

$$=\frac{\Gamma(1/2)\,\Gamma(\gamma)}{\Gamma\left(\frac{\alpha+1}{2}\right)\Gamma\left(\gamma-\frac{\alpha}{2}\right)}(-4x)^{-\frac{\alpha}{2}}\left[\sum_m\frac{(\alpha/2)_m\left(1-\gamma+\frac{\alpha}{2}\right)_m}{(1/2)_m\,m!}F(-2m,\beta,\delta,y)\,(4x)^{-m}\right]$$

$$+\frac{\Gamma(-1/2)\,\Gamma(\gamma)}{\Gamma(\alpha/2)\,\Gamma\left(\gamma-\frac{\alpha+1}{2}\right)}(-4x)^{-\frac{\alpha+1}{2}}\left[\sum_m\frac{\left(\frac{\alpha+1}{2}\right)_m\left(3/2-\gamma+\frac{\alpha}{2}\right)_m}{(3/2)_m\,m!}F(-2m-1,\beta,\delta,y)\,(4x)^{-m}\right].$$

Applying this result to the matrix element I, we get the final expression, given in formulae (11)—(14).

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ON THE PROBLEM OF THREE BODIES IN THE PLANE

BY

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1742

København 1957
i kommission hos Ejnar Munksgaard

Synopsis.

Three bodies with finite masses are assumed to move in a plane, subject to Newton's law of gravitation. By the introduction of suitable auxiliary variables the equations of motion are transformed into a system of differential equations of the second degree, permitting to expand the unknown quantities in powers of the time t, the coefficients of t^{ν} being calculated by means of a set of recurrence formulas. Sufficient conditions for the convergence of the resulting series are given, and the practical working of the method is illustrated by a numerical example.

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1. On a former occasion[1] I have shown how a particular case of the Problem of Three Bodies can be dealt with by transforming the equations of motion into a system of differential equations of the second degree in the unknown variables, permitting to expand these in powers of the time t, the coefficients of t^{ν} being calculated by a set of recurrence formulas. The same method can, in principle, be employed in other cases of the dynamical astronomy, and I propose in the present paper to extend it to the problem of three finite bodies moving in the same fixed plane and subject to Newton's law of gravitation. The number of recurrence formulas naturally increases, but without becoming unwieldy, as will be shown by a numerical example.

Let the three masses be m_1, m_2 and m_3, the coordinates of m_i being (x_i, y_i), and let us put

$$\left.\begin{aligned} r_1^2 &= (x_2-x_3)^2+(y_2-y_3)^2 \\ r_2^2 &= (x_3-x_1)^2+(y_3-y_1)^2 \\ r_3^2 &= (x_1-x_2)^2+(y_1-y_2)^2 \end{aligned}\right\} \quad (1)$$

so that r_1 is the distance between m_2 and m_3, etc.

Then the equations of motion are[2]

$$\left.\begin{aligned} \frac{d^2x_1}{dt^2} &= m_2\frac{x_2-x_1}{r_3^3}+m_3\frac{x_3-x_1}{r_2^3} \\ \frac{d^2x_2}{dt^2} &= m_3\frac{x_3-x_2}{r_1^3}+m_1\frac{x_1-x_2}{r_3^3} \\ \frac{d^2x_3}{dt^2} &= m_1\frac{x_1-x_3}{r_2^3}+m_2\frac{x_2-x_3}{r_1^3} \end{aligned}\right\} \quad (2)$$

and corresponding equations with y instead of x.

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[1] J. F. Steffensen: 'On the Restricted Problem of Three Bodies'. Mat. Fys. Medd. Dan. Vid. Selsk. **30**, no. 18 (1956).

[2] It is assumed throughout that none of the distances r_1, r_2, r_3 vanishes.

We now introduce for $i = 1, 2, 3$ the auxiliary variables

$$\varrho_i = r_i^2, \qquad \sigma_i = r_i^{-3}, \tag{3}$$

so that

$$2\varrho_i \frac{d\sigma_i}{dt} + 3\sigma_i \frac{d\varrho_i}{dt} = 0, \tag{4}$$

$$\left.\begin{aligned} \varrho_1 &= (x_2 - x_3)^2 + (y_2 - y_3)^2 \\ \varrho_2 &= (x_3 - x_1)^2 + (y_3 - y_1)^2 \\ \varrho_3 &= (x_1 - x_2)^2 + (y_1 - y_2)^2 \end{aligned}\right\} \tag{5}$$

while the equations of motion become

$$\left.\begin{aligned} \frac{d^2x_1}{dt^2} &= m_2\ (x_2 - x_1)\ \sigma_3 + m_3\ (x_3 - x_1)\ \sigma_2 \\ \frac{d^2x_2}{dt^2} &= m_3\ (x_3 - x_2)\ \sigma_1 + m_1\ (x_1 - x_2)\ \sigma_3 \\ \frac{d^2x_3}{dt^2} &= m_1\ (x_1 - x_3)\ \sigma_2 + m_2\ (x_2 - x_3)\ \sigma_1 \end{aligned}\right\} \tag{6}$$

and corresponding equations with y instead of x.

For the determination of the 12 unknowns x_i, y_i, σ_i, ϱ_i we now have the 12 equations (4), (5), (6) and the corresponding equations in y, which are all of the second degree in the unknowns and can be treated in the way indicated above.

2. If, however, only the distances of the masses from each other at any given time are required, the number of equations can be reduced to 10. In that case the absolute positions in the plane can be determined afterwards, if desired. This is the relativistic point of view, familiar from the treatment of the Restricted Problem of Three Bodies. In the present case we put

$$\left.\begin{aligned} \xi_1 &= x_2 - x_3, \qquad & \xi_2 &= x_3 - x_1 \\ \eta_1 &= y_2 - y_3, \qquad & \eta_2 &= y_3 - y_1 \end{aligned}\right\} \tag{7}$$

and for abbreviation

$$M_1 = m_2 + m_3, \qquad M_2 = m_1 + m_3. \tag{8}$$

We then obtain from (5)

$$\left.\begin{aligned} \varrho_1 &= \xi_1^2 + \eta_1^2, \qquad \varrho_2 = \xi_2^2 + \eta_2^2 \\ \varrho_3 &= \varrho_1 + \varrho_2 + 2\ \xi_1\ \xi_2 + 2\eta_1\ \eta_2 \end{aligned}\right\} \tag{9}$$

and from (6)

$$\left.\begin{aligned}\frac{d^2\xi_1}{dt^2} &= m_1\,(\xi_2\,\sigma_2 - \xi_1\,\sigma_3 - \xi_2\,\sigma_3) - M_1\,\xi_1\,\sigma_1\\ \frac{d^2\xi_2}{dt^2} &= m_2\,(\xi_1\,\sigma_1 - \xi_1\,\sigma_3 - \xi_2\,\sigma_3) - M_2\,\xi_2\,\sigma_2\end{aligned}\right\}\quad(10)$$

and, replacing ξ by η in this,

$$\left.\begin{aligned}\frac{d^2\eta_1}{dt^2} &= m_1\,(\eta_2\,\sigma_2 - \eta_1\,\sigma_3 - \eta_2\,\sigma_3) - M_1\,\eta_1\,\sigma_1\\ \frac{d^2\eta_2}{dt^2} &= m_2\,(\eta_1\,\sigma_1 - \eta_1\,\sigma_3 - \eta_2\,\sigma_3) - M_2\,\eta_2\,\sigma_2\,.\end{aligned}\right\}\quad(11)$$

(4) and (9)–(11) are 10 equations for determining the 10 unknowns $\xi_1, \xi_2, \eta_1, \eta_2, \varrho_i, \sigma_i$. We propose to satisfy them by power series in t, putting

$$\left.\begin{aligned}\xi_1 &= \Sigma\alpha_\nu\,t^\nu, & \xi_2 &= \Sigma\beta_\nu\,t^\nu\\ \eta_1 &= \Sigma\gamma_\nu\,t^\nu, & \eta_2 &= \Sigma\delta_\nu\,t^\nu\end{aligned}\right\}\quad(12)$$

$$\left.\begin{aligned}\varrho_1 &= \Sigma a_\nu\,t^\nu, & \varrho_2 &= \Sigma b_\nu\,t^\nu, & \varrho_3 &= \Sigma c_\nu\,t^\nu\\ \sigma_1 &= \Sigma d_\nu\,t^\nu, & \sigma_2 &= \Sigma e_\nu\,t^\nu, & \sigma_3 &= \Sigma f_\nu\,t^\nu\end{aligned}\right\}\quad(13)$$

the summation being everywhere from $\nu = 0$ to $\nu = \infty$.

Inserting these expansions in the aforesaid equations and demanding that the coefficients of t^n shall vanish, we obtain recurrence formulas for the determination of the coefficients.

We write for abbreviation

$$\varepsilon_\nu = \alpha_\nu + \beta_\nu, \qquad \zeta_\nu = \gamma_\nu + \delta_\nu \tag{14}$$

and for the product-sums

$$(\alpha d)_n = \sum_{\nu=0}^{n} \alpha_\nu\,d_{n-\nu}, \text{ etc.} \tag{15}$$

In this notation we obtain from (10) and (11)

$$\left.\begin{aligned}(n+2)^{(2)}\,\alpha_{n+2} &= m_1\,[(\beta e)_n - (\varepsilon f)_n] - M_1\,(\alpha d)_n\\ (n+2)^{(2)}\,\beta_{n+2} &= m_2\,[(\alpha d)_n - (\varepsilon f)_n] - M_2\,(\beta e)_n\\ (n+2)^{(2)}\,\gamma_{n+2} &= m_1\,[(\delta e)_n - (\zeta f)_n] - M_1\,(\gamma d)_n\\ (n+2)^{(2)}\,\delta_{n+2} &= m_2\,[(\gamma d)_n - (\zeta f)_n] - M_2\,(\delta e)_n\end{aligned}\right\}\quad(16)$$

where $(n+2)^{(2)}$ as usual is short for $(n+2)\,(n+1)$.

Further, we obtain from (9)

$$\left.\begin{aligned} a_n &= (\alpha\alpha)_n + (\gamma\gamma)_n \\ b_n &= (\beta\beta)_n + (\delta\delta)_n \\ c_n &= a_n + b_n + 2\,(\alpha\beta)_n + 2\,(\gamma\delta)_n \end{aligned}\right\} \quad (17)$$

and finally from (4)

$$\left.\begin{aligned} -2\,n\,a_0\,d_n &= \sum_{\nu=0}^{n-1} (3\,n-\nu)\,d_\nu\,a_{n-\nu} \\ -2\,n\,b_0\,e_n &= \sum_{\nu=0}^{n-1} (3\,n-\nu)\,e_\nu\,b_{n-\nu} \\ -2\,n\,c_0\,f_n &= \sum_{\nu=0}^{n-1} (3\,n-\nu)\,f_\nu\,c_{n-\nu}\,. \end{aligned}\right\} \quad (18)$$

3. The number of constants of integration in (10) and (11), where the σ_i are known functions of the ξ_i and η_i, is only 8 instead of 12 in the original statement of the problem. It is natural to choose as initial values the values of ξ_i, η_i, $\frac{d\xi_i}{dt}$ and $\frac{d\eta_i}{dt}$ for $t = 0$, that is

$$\alpha_0, \alpha_1, \beta_0, \beta_1, \gamma_0, \gamma_1, \delta_0, \delta_1. \quad (19)$$

We then obtain first from (17)

$$\left.\begin{aligned} a_0 &= \alpha_0^2 + \gamma_0^2 \\ b_0 &= \beta_0^2 + \delta_0^2 \\ c_0 &= a_0 + b_0 + 2\,\alpha_0\beta_0 + 2\,\gamma_0\delta_0 \end{aligned}\right\} \quad (20)$$

while the relation $\sigma_i^2\,\varrho_i^3 = 1$, resulting from (3), yields, σ_i and ϱ_i being positive,

$$d_0 = \frac{1}{a_0\sqrt{a_0}},\; e_0 = \frac{1}{b_0\sqrt{b_0}},\; f_0 = \frac{1}{c_0\sqrt{c_0}}. \quad (21)$$

After this we find by (17) and (18)

$$\left.\begin{aligned} a_1 &= 2\,(\alpha_0\,\alpha_1 + \gamma_0\,\gamma_1) \\ b_1 &= 2\,(\beta_0\,\beta_1 + \delta_0\,\delta_1) \\ c_1 &= a_1 + b_1 + 2\,(\alpha\beta)_1 + 2\,(\gamma\delta)_1\,. \end{aligned}\right\} \quad (22)$$

$$-2\,a_0\,d_1 = 3\,d_0\,a_1, \quad -2\,b_0\,e_1 = 3\,e_0 b_1, \quad -2\,c_0\,f_1 = 3\,f_0\,c_1\,. \quad (23)$$

The following coefficients are calculated in succession by (16) – (18). The first few of them are

$$\left.\begin{aligned} 2\,\alpha_2 &= m_1\,(\beta_0\,e_0-\varepsilon_0\,f_0)-M_1\,\alpha_0\,d_0\\ 2\,\beta_2 &= m_2\,(\alpha_0\,d_0-\varepsilon_0\,f_0)-M_2\,\beta_0\,e_0\\ 2\,\gamma_2 &= m_1\,(\delta_0\,e_0-\zeta_0\,f_0)-M_1\,\gamma_0 d_0\\ 2\,\delta_2 &= m_2\,(\gamma_0\,d_0-\zeta_0\,f_0)-M_2\,\delta_0\,e_0\,. \end{aligned}\right\} \tag{24}$$

$$\left.\begin{aligned} a_2 &= \alpha_1^2+\gamma_1^2+2\,(\alpha_0\,\alpha_2+\gamma_0\,\gamma_2)\\ b_2 &= \beta_1^2+\delta_1^2+2\,(\beta_0\,\beta_2+\delta_0\,\delta_2)\\ c_2 &= a_2+b_2+2\,(\alpha\beta)_2+2\,(\gamma\delta)_2\,. \end{aligned}\right\} \tag{25}$$

$$\left.\begin{aligned} -4\,a_0\,d_2 &= 6\,d_0\,a_2+5\,d_1\,a_1\\ -4\,b_0\,e_2 &= 6\,e_0\,b_2+5\,e_1\,b_1\\ -4\,c_0\,f_2 &= 6\,f_0\,c_2+5\,f_1\,c_1\,. \end{aligned}\right\} \tag{26}$$

$$\left.\begin{aligned} 6\,\alpha_3 &= m_1\,[(\beta\,e)_1-(\varepsilon\,f)_1]-M_1\,(\alpha\,d)_1\\ 6\,\beta_3 &= m_2\,[(\alpha\,d)_1-(\varepsilon\,f)_1]-M_2\,(\beta\,e)_1\\ 6\,\gamma_3 &= m_1\,[(\delta\,e)_1-(\zeta\,f)_1]-M_1\,(\gamma\,d)_1\\ 6\,\delta_3 &= m_2\,[(\gamma\,d)_1-(\zeta\,f)_1]-M_2\,(\delta\,e)_1\,. \end{aligned}\right\} \tag{27}$$

$$\left.\begin{aligned} a_3 &= 2\,(\alpha_0\,\alpha_3+\alpha_1\,\alpha_2+\gamma_0\,\gamma_3+\gamma_1\,\gamma_2)\\ b_3 &= 2\,(\beta_0\,\beta_3+\beta_1\,\beta_2+\delta_0\,\delta_3+\delta_1\,\delta_2)\\ c_3 &= a_3+b_3+2\,(\alpha\beta)_3+2\,(\gamma\delta)_3\,. \end{aligned}\right\} \tag{28}$$

$$\left.\begin{aligned} -6\,a_0\,d_3 &= 9\,d_0\,a_3+8\,d_1\,a_2+7\,d_2\,a_1\\ -6\,b_0\,e_3 &= 9\,e_0\,b_3+8\,e_1\,b_2+7\,e_2\,b_1\\ -6\,c_0\,f_3 &= 9\,f_0\,c_3+8\,f_1\,c_2+7\,f_2\,c_1\,. \end{aligned}\right\} \tag{29}$$

4. For the purpose of examining the convergence we put

$$H_\nu = \frac{\lambda^\nu}{(\nu+2)^{(2)}} \qquad (\lambda > 0) \tag{30}$$

and

$$s_n = \sum_{\nu=1}^{n} \frac{1}{\nu}. \tag{31}$$

We have then identically

$$\lambda^{-n} H_\nu H_{n-\nu} = \left(\frac{1}{\nu+1} + \frac{1}{n-\nu+1}\right)\frac{1}{(n+3)^{(2)}} - \left(\frac{1}{\nu+2} + \frac{1}{n-\nu+2}\right)\frac{1}{(n+4)^{(2)}} \tag{32}$$

whence

$$\sum_{\nu=0}^{n} H_\nu H_{n-\nu} = 2\,\lambda^n \frac{2 s_{n+1} + n + 1}{(n+4)^{(3)}}. \tag{33}$$

$$\sum_{\nu=0}^{n-1} H_\nu H_{n-\nu} = \lambda^n \frac{4 s_{n+1} + \frac{3}{2} n - 1 - \frac{3}{n+1}}{(n+4)^{(3)}} \qquad (n \geqslant 1). \tag{34}$$

$$\sum_{\nu=2}^{n-2} H_\nu H_{n-\nu} = \frac{2}{3}\lambda^n \frac{6 s_n + n - 10 - \frac{12}{n}}{(n+4)^{(3)}} \qquad (n \geqslant 4). \tag{35}$$

Furthermore we have the identity

$$\lambda^{-n} \nu H_\nu H_{n-\nu} = \left(\frac{n+1}{n-\nu+1} - \frac{1}{\nu+1}\right)\frac{1}{(n+3)^{(2)}} - \left(\frac{n+2}{n-\nu+2} - \frac{2}{\nu+2}\right)\frac{1}{(n+4)^{(2)}} \tag{36}$$

whence

$$\sum_{\nu=1}^{n-1} \nu H_\nu H_{n-\nu} = \frac{n\lambda^n}{(n+4)^{(3)}}\left(2 s_{n+1} + \frac{n}{2} - 2 - \frac{3}{n+1}\right) \qquad (n \geqslant 2). \tag{37}$$

5. After these preliminaries we begin with the first of the equations (17) which, keeping the constants of integration apart and assuming $n \geqslant 3$, we write in the form

$$a_n = 2\,(\alpha_0 \alpha_n + \alpha_1 \alpha_{n-1} + \gamma_0 \gamma_n + \gamma_1 \gamma_{n-1}) + \sum_{\nu=2}^{n-2} (\alpha_\nu \alpha_{n-\nu} + \gamma_\nu \gamma_{n-\nu}) \tag{38}$$

where the sum is interpreted as zero, if $n = 3$.

We now assume that for a certain $n \geqslant 3$ and for $2 \leq \nu \leq n$ is

$$|\,\alpha_\nu\,| \leq \alpha H_\nu, \; |\,\beta_\nu\,| \leq \beta H_\nu, \; |\,\gamma_\nu\,| \leq \gamma H_\nu, \; |\,\delta_\nu\,| \leq \delta H_\nu. \tag{39}$$

In that case we get from (38)

$$|\,a_n\,| \leq 2\,(\alpha\,|\,\alpha_0\,| + \gamma\,|\,\gamma_0\,|)\,H_n + 2\,(\alpha\,|\,\alpha_1\,| + \gamma\,|\,\gamma_1\,|)\,H_{n-1} + (\alpha^2 + \gamma^2)\sum_{\nu=2}^{n-2} H_\nu H_{n-\nu}. \tag{40}$$

By (35) we obtain from this

$$\left.\begin{aligned} |a_n| \leq 2\,(\alpha\,|\alpha_0| + \gamma\,|\gamma_0|)\,\frac{\lambda^n}{(n+2)^{(2)}} + 2\,(\alpha\,|\alpha_1| + \gamma\,|\gamma_1|)\,\frac{\lambda^{n-1}}{(n+1)^{(2)}} \\ + \frac{2}{3}\,(\alpha^2+\gamma^2)\left(6\,s_n + n - 10 - \frac{12}{n}\right)\frac{\lambda^n}{(n+4)^{(3)}}. \end{aligned}\right\} \quad (41)$$

In this, the last term is left out for $n < 4$, but since it vanishes for $n = 3$, (41) is valid for $n \geqslant 3$.

A sufficient condition for $|a_n| \leq AH_n$ for $n \geqslant 3$ is therefore that the right-hand side of (41) is $\leq A\,\frac{\lambda^n}{(n+2)^{(2)}}$ which, after multiplication by $\frac{1}{2}\,(n+2)^{(2)}\,\lambda^{-n}$ may be written

$$\alpha\,|\alpha_0| + \gamma\,|\gamma_0| + (\alpha\,|\alpha_1| + \gamma\,|\gamma_1|)\,\frac{n+2}{n\,\lambda} + \frac{\alpha^2+\gamma^2}{3}\left(6\,s_n + n - 10 - \frac{12}{n}\right)\frac{n+1}{(n+4)^{(2)}} \leq \frac{A}{2}. \quad (42)$$

From (42) we derive a sufficient condition which is independent of n, replacing the factors depending on n by absolute numbers which are at least as large. We first have

$$\frac{n+2}{n} = 1 + \frac{2}{n} \leq \frac{5}{3} \qquad (n \geqslant 3) \quad (43)$$

and proceed to prove that

$$\left(6\,s_n + n - 10 - \frac{12}{n}\right)\frac{n+1}{(n+4)^{(2)}} < 2 \qquad (n \geqslant 3). \quad (44)$$

Now it is verified directly that (44) is valid for $n = 3$ and $n = 4$, so that in the remainder of the proof we may assume $n \geqslant 5$. But we have obviously

$$s_n \leq s_k + \frac{n-k}{k+1} \qquad (n \geqslant k) \quad (45)$$

whence, in particular,

$$s_n \leq s_5 + \frac{n-5}{6} = \frac{n}{6} + \frac{29}{20} \qquad (n \geqslant 5) \quad (46)$$

and inserting this in (44) we get the more rigid inequality

$$\frac{2n - 1\cdot 3 - \frac{12}{n}}{n+4} \cdot \frac{n+1}{n+3} < 2$$

which is obvious, the first factor on the left being less than 2, and the second less than 1.

By (43) and (44) we finally obtain from (42) the following sufficient condition, which does not depend on n, for $|a_n| \leq AH_n$

$$\alpha\,|\alpha_0| + \gamma\,|\gamma_0| + \frac{5}{3\lambda}(\alpha\,|\alpha_1| + \gamma\,|\gamma_1|) + \frac{2}{3}(\alpha^2 + \gamma^2) \leq \frac{A}{2}, \tag{47}$$

always provided that $n \geqslant 3$.

After this, a comparison of the two first equations (17) shows that we obtain from (47), by a simple exchange of letters, as a sufficient condition for $|b_n| \leq BH_n$ for $n \geqslant 3$

$$\beta\,|\beta_0| + \delta\,|\delta_0| + \frac{5}{3\lambda}(\beta\,|\beta_1| + \delta\,|\delta_1|) + \frac{2}{3}(\beta^2 + \delta^2) \leq \frac{B}{2}. \tag{48}$$

As regards the third equation (17) we begin by writing it in the form, valid for $n \geqslant 3$,

$$\left.\begin{aligned} c_n = a_n + b_n &+ 2\,(\alpha_0\beta_n + \alpha_1\beta_{n-1} + \beta_0\alpha_n + \beta_1\alpha_{n-1} + \gamma_0\delta_n + \gamma_1\delta_{n-1} + \delta_0\gamma_n + \delta_1\gamma_{n-1}) \\ &+ 2\sum_{\nu=2}^{n-2}(\alpha_\nu\beta_{n-\nu} + \gamma_\nu\delta_{n-\nu}). \end{aligned}\right\} \tag{49}$$

From this we obtain in the same way as above

$$\left.\begin{aligned} |c_n| \leq 2\,H_n &\left(\frac{A+B}{2} + \alpha\,|\beta_0| + \beta\,|\alpha_0| + \gamma\,|\delta_0| + \delta\,|\gamma_0|\right) \\ &+ 2\,H_{n-1}(\alpha\,|\beta_1| + \beta\,|\alpha_1| + \gamma\,|\delta_1| + \delta\,|\gamma_1|) + 2\,(\alpha\beta + \gamma\delta)\sum_{\nu=2}^{n-2} H_\nu H_{n-\nu} \end{aligned}\right\} \tag{50}$$

A sufficient condition for $|c_n| \leq CH_n$ is therefore that the right-hand side of (50) is $\leq C\dfrac{\lambda^n}{(n+2)^{(2)}}$, and this may, by (30) and (35) and after multiplication by $\frac{1}{2}\,(n+2)^{(2)}\,\lambda^{-n}$, be written

$$\left.\begin{aligned} \frac{A+B}{2} &+ \alpha\,|\beta_0| + \beta\,|\alpha_0| + \gamma\,|\delta_0| + \delta\,|\gamma_0| + (\alpha\,|\beta_1| + \beta\,|\alpha_1| + \gamma\,|\delta_1| + \delta\,|\gamma_1|)\,\frac{n+2}{n\,\lambda} \\ &+ \frac{2}{3}(\alpha\beta + \gamma\delta)\left(6\,s_n + n - 10 - \frac{12}{n}\right)\frac{n+1}{(n+4)^{(2)}} \leq \frac{C}{2}. \end{aligned}\right\} \tag{51}$$

By (43) and (44) we obtain finally the more severe, but of n independent, condition, valid for $n \geqslant 3$, for $|c_n| \leq CH_n$

$$\left.\begin{aligned}\alpha\,|\,\beta_0\,|+\beta\,|\,\alpha_0\,|+\gamma\,|\,\delta_0\,|+\delta\,|\,\gamma_0\,|+\frac{5}{3\lambda}(\alpha\,|\,\beta_1\,|+\beta\,|\,\alpha_1\,|+\gamma\,|\,\delta_1\,|+\delta\,|\,\gamma_1\,|)\\ +\frac{4}{3}(\alpha\beta+\gamma\delta)\leq\frac{1}{2}(C-A-B).\end{aligned}\right\}\qquad(52)$$

6. We now consider (18), assuming that for a certain $n \geqslant 2$ we have proved that for $1 \leq \nu \leq n$

$$|\,a_\nu\,| \leq A H_\nu, \qquad |\,b_\nu\,| \leq B H_\nu, \qquad |\,c_\nu\,| \leq C H_\nu \qquad (53)$$

and for $0 \leq \nu \leq n-1$ that

$$|\,d_\nu\,| \leq D H_\nu, \qquad |\,e_\nu\,| \leq E H_\nu, \qquad |\,f_\nu\,| \leq F H_\nu. \qquad (54)$$

We then obtain from the first of the equations (18)

$$2\,n a_0\,|\,d_n\,| \leq D A\left(3\,n\sum_{\nu=0}^{n-1} H_\nu H_{n-\nu}+\sum_{\nu=1}^{n-1}\nu H_\nu H_{n-\nu}\right) \qquad (55)$$

whence by (34) and (37), after reduction

$$2\,a_0\,|\,d_n\,| \leq D A\left(14\,s_{n+1}+5\,n-5-\frac{12}{n+1}\right)\frac{\lambda^n}{(n+4)^{(3)}}. \qquad (56)$$

A sufficient condition for $|\,d_n\,| \leq D H_n$ is therefore that the right-hand side of (56) is $\leq 2\,a_0 D\dfrac{\lambda^n}{(n+2)^{(2)}}$, which may be written

$$\left(14\,s_{n+1}+5\,n-5-\frac{12}{n+1}\right)\frac{n+1}{(n+4)^{(2)}} \leq \frac{2\,a_0}{A}. \qquad (57)$$

We will now show that this condition may be replaced by the more restricted sufficient condition

$$3\,A \leq a_0 \qquad (58)$$

which is independent of n. This comes to proving that

$$\left(14\,s_{n+1}+5\,n-5-\frac{12}{n+1}\right)\frac{n+1}{(n+4)^{(2)}} \leq 6 \qquad (59)$$

or

$$s_{n+1} \leq \frac{n-1}{14}+3+\frac{24}{7\,(n+1)}. \qquad (60)$$

Now it is seen by a table of s_n[1] that (60) is satisfied for $n < 12$, while for $n \geqslant 12$ we may employ

$$s_{n+1} \leq s_{13} + \frac{n-12}{14}$$

which inserted in (60) gives, after reduction, the more rigid condition

$$s_{13} < \frac{53}{14} + \frac{24}{7(n+1)}$$

which is also satisfied. Hence, (60) and therefore (58) are proved.

Since the second and third of the equations (18) are obtained from the first by a simple exchange of letters, we may now write down as a sufficient condition for the validity of (54) for $0 \leq \nu \leq n$

$$3A \leq a_0, \qquad 3B \leq b_0, \qquad 3C \leq c_0. \tag{61}$$

7. As regards finally (16), we isolate the constants of integration, assume $n \geqslant 2$ and write the first of these equations in the form

$$\left.\begin{aligned}(n+2)^{(2)}\alpha_{n+2} &= m_1(\beta_0 e_n + \beta_1 e_{n-1} - \varepsilon_0 f_n - \varepsilon_1 f_{n-1}) - M_1(\alpha_0 d_n + \alpha_1 d_{n-1})\\ &\quad + m_1 \sum_{\nu=2}^{n} (\beta_\nu e_{n-\nu} - \varepsilon_\nu f_{n-\nu}) - M_1 \sum_{\nu=2}^{n} \alpha_\nu d_{n-\nu}.\end{aligned}\right\} \tag{62}$$

We write for abbreviation

$$P_1 = m_1(F+E), P_2 = m_2(F+D), Q_1 = m_1 F + M_1 D, Q_2 = m_2 F + M_2 E \tag{63}$$

and assume that (54) is satisfied for $0 \leq \nu \leq n$, (39) for $2 \leq \nu \leq n$. From (32) we obtain

$$\sum_{\nu=2}^{n} H_\nu H_{n-\nu} = \frac{\lambda^n}{(n+4)^{(3)}}\left(4 s_{n-1} + \frac{4n-7}{3} + \frac{2}{n+1}\right) \quad (n \geqslant 2) \tag{64}$$

and thereafter from (62) for $n \geqslant 2$

$$\left.\begin{aligned}(n+2)^{(2)} |\alpha_{n+2}| &\leq (|\alpha_0| Q_1 + |\beta_0| P_1)\frac{\lambda^n}{(n+2)^{(2)}} + (|\alpha_1| Q_1 + |\beta_1| P_1)\frac{\lambda^{n-1}}{(n+1)^{(2)}}\\ &\quad + (\alpha Q_1 + \beta P_1)\left(4 s_{n-1} + \frac{4n-7}{3} + \frac{2}{n+1}\right)\frac{\lambda^n}{(n+4)^{(3)}}.\end{aligned}\right\} \tag{65}$$

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[1] See, for instance, J. W. GLOVER: Tables of Applied Mathematics, Ann Arbor, Michigan, 1923, p. 456.

A sufficient condition for $|\alpha_{n+2}| \leq \alpha H_{n+2}$ is therefore that the right-hand side of (65) is $\leq (n+2)^{(2)} \alpha H_{n+2}$, which after multiplication by $\lambda^{-n} \dfrac{(n+4)^{(2)}}{(n+2)^{(2)}}$ may be written

$$\left.\begin{aligned} &(|\alpha_0| Q_1 + |\beta_0| P_1) \frac{(n+4)(n+3)}{(n+2)^2 (n+1)^2} + (|\alpha_1| Q_1 + |\beta_1| P_1) \frac{(n+4)(n+3)\lambda^{-1}}{(n+2)(n+1)^2 n} \\ &\qquad + \frac{\alpha Q_1 + \beta P_1}{(n+2)^2 (n+1)} \left(4 s_{n-1} + \frac{4n-7}{3} + \frac{2}{n+1} \right) \leq \alpha \lambda^2 . \end{aligned}\right\} \qquad (66)$$

In order to find a sufficient condition that does not depend on n we observe that, since we have assumed $n \geqq 2$,

$$\frac{(n+4)(n+3)}{(n+2)^2 (n+1)^2} = \left(1 + \frac{2}{n+2}\right)\left(1 + \frac{1}{n+2}\right) \frac{1}{(n+1)^2} \leq \frac{5}{24} \qquad (67)$$

and

$$\frac{(n+4)(n+3)}{(n+2)(n+1)^2 n} = \left(1 + \frac{2}{n+2}\right)\left(1 + \frac{3}{n}\right) \frac{1}{(n+1)^2} \leq \frac{5}{12} . \qquad (68)$$

We will finally show that for $n \geqq 2$

$$\frac{1}{(n+2)^2 (n+1)} \left(4 s_{n-1} + \frac{4n-7}{3} + \frac{2}{n+1} \right) \leq \frac{5}{48} . \qquad (69)$$

For $n = 2$ it is seen directly that this holds. For $n \geqq 3$ we insert the inequality

$$s_{n-1} \leq \frac{1}{2} + \frac{n}{3} \qquad (n \geqq 3) \qquad (70)$$

resulting from (45) for $k = 2$. The result may be written

$$128 \leq 5 (n+2)^2 + 48 \frac{3n+1}{(n+1)^2} \qquad (n \geqq 3)$$

which is easily verified. Hence (69) is proved for $n \geqq 2$.

If now we insert (67) – (69) in (66), we obtain the sufficient condition, valid for $n \geqq 2$, but otherwise independent of n,

$$2 (|\alpha_0| Q_1 + |\beta_0| P_1) + \frac{4}{\lambda} (|\alpha_1| Q_1 + |\beta_1| P_1) + \alpha Q_1 + \beta P_1 \leq \frac{48}{5} \alpha \lambda^2 . \qquad (71)$$

Since the three last equations (16) are obtained from the first by a simple exchange of letters, we may now by (71) write down the following sufficient conditions, valid for $n \geqq 2$

$$2\,(|\,\alpha_0\,|\,P_2+|\,\beta_0\,|\,Q_2)+\frac{4}{\lambda}\,(|\,\alpha_1\,|\,P_2+|\,\beta_1\,|\,Q_2)+\alpha P_2+\beta\,Q_2\leq\frac{48}{5}\,\beta\,\lambda^2. \qquad (72)$$

$$2\,(|\,\gamma_0\,|\,Q_1+|\,\delta_0\,|\,P_1)+\frac{4}{\lambda}\,(|\,\gamma_1\,|\,Q_1+|\,\delta_1\,|\,P_1)+\gamma\,Q_1+\delta\,P_1\leq\frac{48}{5}\,\gamma\,\lambda^2. \qquad (73)$$

$$2\,(|\,\gamma_0\,|\,P_2+|\,\delta_0\,|\,Q_2)+\frac{4}{\lambda}\,(|\,\gamma_1\,|P_2+|\,\delta_1\,|Q_2)+\gamma P_2+\delta\,Q_2\leq\frac{48}{5}\,\delta\,\lambda^2. \qquad (74)$$

8. We may summarize the result of the preceding investigation thus: If (39) is satisfied for $2\leq\nu\leq 3$, (53) for $1\leq\nu\leq 2$, (54) for $0\leq\nu\leq 2$, and if, besides, all the inequalities (47), (48), (52), (61), (71) – (74) are satisfied, then (12) and (13) are convergent provided that $\Sigma H_\nu t^\nu$ converges, that is, for $|\,t\,|\leq\frac{1}{\lambda}$.

It may be observed that the condition (52) implies that $A+B<C$.

The question arises whether it is always possible, when the initial values (19) are arbitrarily given, to find such values of λ, α, β, γ, δ, A, B, C, D, E, F that the aforesaid inequalities are all satisfied. This question must be answered in the affirmative. To begin with, λ can always be chosen so large that (71) – (74) are satisfied and that (47), (48) and (52) are reduced to

$$\alpha\,|\,\alpha_0\,|+\gamma\,|\,\gamma_0\,|+\frac{2}{3}\,(\alpha^2+\gamma^2)<\frac{A}{2}$$

$$\beta\,|\,\beta_0\,|+\delta\,|\,\delta_0\,|+\frac{2}{3}\,(\beta^2+\delta^2)<\frac{B}{2}$$

$$\alpha\,|\,\beta_0\,|+\beta\,|\,\alpha_0\,|+\gamma\,|\,\delta_0\,|+\delta\,|\,\gamma_0\,|+\frac{4}{3}\,(\alpha\beta+\gamma\delta)<\frac{1}{2}\,(C-A-B)$$

while (61) is unchanged. We now choose A, B and C so small that (61) is satisfied and, besides, $A+B<C$. After this α, β, γ, δ may be chosen so small that the three reduced inequalities are satisfied. Small values of A, B, C, α, β, γ, δ can always be compensated by an increase of λ.

9. As a simple numerical example to show the practical working of the recurrence formulas we choose

$$m_1=1\,,\,m_2=2\,,\,m_3=3 \qquad (75)$$

so that

$$M_1=5\,,\,M_2=4\,,\,M_3=3\,, \qquad (76)$$

and for the initial values

$$\left.\begin{array}{llll}\alpha_0 = \cdot 5, & \beta_0 = \cdot 9, & \gamma_0 = 1\cdot 2, & \delta_0 = -1\cdot 2 \\ \alpha_1 = \cdot 15, & \beta_1 = -\cdot 1, & \gamma_1 = -\cdot 2, & \delta_1 = -\cdot 3.\end{array}\right\} \quad (77)$$

From these I derive by (20) – (29) the coefficients in the table below[1] where the exact values of d_0, e_0, f_0 are

$$d_0 = \frac{1}{2\cdot 197}, \quad e_0 = \frac{1}{3\cdot 375}, \quad f_0 = \frac{1}{2\cdot 744} \quad (78)$$

and where at the time $t = 0$

$$r_1 = \sqrt{a_0} = 1\cdot 3, \quad r_2 = \sqrt{b_0} = 1\cdot 5, \quad r_3 = \sqrt{c_0} = 1\cdot 4. \quad (79)$$

As regards the convergence, the sufficient conditions established above are satisfied if we choose, for instance

$$\left.\begin{array}{l}\lambda = 20, \quad \alpha = \cdot 021, \quad \beta = \cdot 025, \quad \gamma = \cdot 047, \quad \delta = \cdot 038, \\ A = \cdot 14, \quad B = \cdot 17, \quad C = \cdot 60, \quad D = \cdot 92, \quad E = \cdot 60, \quad F = \cdot 73.\end{array}\right\} \quad (80)$$

The expansions (12) and (13) are therefore at least convergent for $|t| \leq \frac{1}{20}$.

I find for $t = \frac{1}{20}$

$$\left.\begin{array}{ll}\varrho_1 = 1\cdot 66270 & \sigma_1 = \cdot 466385 \\ \varrho_2 = 2\cdot 26598 & \sigma_2 = \cdot 293155 \\ \varrho_3 = 1\cdot 95711 & \sigma_3 = \cdot 365223\end{array}\right\} \quad (81)$$

and from $r_i = \sqrt{\varrho_i}$

$$r_1 = 1\cdot 28946, \quad r_2 = 1\cdot 50532, \quad r_3 = 1\cdot 39897. \quad (82)$$

10. A considerable simplification is obtained in the particular case where

$$\alpha_1 = \beta_1 = \gamma_1 = \delta_1 = 0. \quad (83)$$

Under these circumstances there are only the four arbitrary constants $\alpha_0, \beta_0, \gamma_0, \delta_0$ left. The significance of (83) is that at the outset we have

$$\frac{d\xi_1}{dt} = \frac{d\xi_2}{dt} = 0, \quad \frac{d\eta_1}{dt} = \frac{d\eta_2}{dt} = 0 \quad (t = 0) \quad (84)$$

---

[1] The number of decimals retained in the table has been cut down to seven.

TABLE.

ν	α_ν	β_ν	γ_ν	δ_ν	ε_ν	ζ_ν
0	·5	·9	1·2	—1·2	1·4	·0
1	·15	—·1	— ·2	— ·3	·05	— ·5
2	— ·6907264	— ·8159544	—1·5432762	1·2573105	—1·5066808	— ·2859657
3	— ·1273093	·1408788	— ·0205691	·0576473	·0135695	·0370782

ν	a_ν	b_ν	c_ν	d_ν	e_ν	f_ν
0	1·69	2·25	1·96	·4551661	·2962963	·3644315
1	— ·33	·54	·14	·1333179	— ·1066667	— ·0390462
2	—4·3320893	—4·3862630	—3·9662061	1·7826770	·8984223	1·1096677
3	·2334175	— ·4759671	·1732921	·7674704	— ·4347952	— ·2461544

or, expressed by the coordinates in the absolute movement,

$$\frac{dx_1}{dt} = \frac{dx_2}{dt} = \frac{dx_3}{dt}, \quad \frac{dy_1}{dt} = \frac{dy_2}{dt} = \frac{dy_3}{dt} \quad (t = 0). \tag{85}$$

From (83) follows at once by (22) and (23) that

$$a_1 = b_1 = c_1 = d_1 = e_1 = f_1 = 0, \tag{86}$$

whereafter the general recurrence formulas (16) – (18) show that all the coefficients of the odd order vanish.

11. We shall finally call attention to another particular case where considerable simplifications occur. Let h be an arbitrary constant, and let us for $\nu = 0$ and $\nu = 1$ choose

$$\gamma_\nu = h\alpha_\nu, \qquad \delta_\nu = h\beta_\nu, \qquad \text{whence } \zeta_\nu = h\varepsilon_\nu. \tag{87}$$

In that case comparison between the first and third, and between the second and fourth, of the equations (16) shows that (87) is valid for all ν. It follows that $(\alpha\delta)_n = (\beta\gamma)_n$, so that

$$\xi_1\eta_2 = \eta_1\xi_2 \tag{88}$$

or

$$\frac{y_3 - y_2}{x_3 - x_2} = \frac{y_3 - y_1}{x_3 - x_1}. \tag{89}$$

But a simple geometrical consideration shows that this means that the three bodies are always situated on a straight line.

Under these circumstances the calculation of the coefficients is simplified, because (87) shows that the two last equations (16) are identical with the two first and can be left out, while (17) is reduced to

$$\left.\begin{aligned} a_n &= (1+h^2)\,(\alpha\alpha)_n \\ b_n &= (1+h^2)\,(\beta\beta)_n \\ c_n &= a_n + b_n + 2\,(1+h^2)\,(\alpha\beta)_n . \end{aligned}\right\} \tag{90}$$

12. It was mentioned at the outset that if the absolute positions in the plane of the three bodies are required they can be determined afterwards. We will briefly indicate how this may be done.

Writing the third of the equations (6) in the form

$$\frac{d^2 x_3}{dt^2} = m_2 \xi_1 \sigma_1 - m_1 \xi_2 \sigma_2 \tag{91}$$

and putting

$$u_n = m_2\,(\alpha d)_n - m_1\,(\beta e)_n \tag{92}$$

we have

$$\frac{d^2 x_3}{dt^2} = \sum_{n=0}^{\infty} u_n t^n , \tag{93}$$

and integrating this twice, introducing thus two more arbitrary constants, we have the expansion of x_3, whereafter by (7)

$$x_2 = x_3 + \xi_1 , \qquad x_1 = x_3 - \xi_2 . \tag{94}$$

The equation for y_3

$$\frac{d^2 y_3}{dt^2} = m_2 \eta_1 \sigma_1 - m_1 \eta_2 \sigma_2 \tag{95}$$

may be treated in the same way. Putting

$$v_n = m_2\,(\gamma d)_n - m_1\,(\delta e)_n \tag{96}$$

we have

$$\frac{d^2 y_3}{dt^2} = \sum_{n=0}^{\infty} v_n t^n \tag{97}$$

whence, introducing two more arbitrary constants, we find y_3 and finally by (7)

$$y_2 = y_3 + \eta_1, \qquad y_1 = y_3 - \eta_2. \tag{98}$$

If the values at $t = 0$ of $x_i, \frac{dx_i}{dt}, y_i, \frac{dy_i}{dt}$ are chosen arbitrarily, the corresponding values of (19), or $\xi_i, \frac{d\xi_i}{dt}, \eta_i, \frac{d\eta_i}{dt}$ at $t = 0$, result immediately from (7).

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“SAROS” AND LUNAR VELOCITY IN BABYLONIAN ASTRONOMY

BY

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København 1957
i kommission hos Ejnar Munksgaard

Synopsis.

Babylonian ephemerides for the moon, written in the Hellenistic period, contain a column which is periodic with the period of the lunar anomaly. On the basis of a text recently discovered by A. Sachs in the British Museum, it is now possible to show that essential parameters for the determination of this periodic function are connected with the so-called Saros cycle of 223 mean synodic months.

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Introduction.

We have today a fair knowledge of the procedures by means of which the Babylonian astronomers of the last three centuries B.C. determined the moments of the syzygies.[1] Almost nothing, however, is known about the empirical or theoretical steps which led to the final theory. Only a few texts are preserved[2] which concern the earlier phases of mathematical astronomy, and their terminological and other difficulties are so great that we are still far from a real understanding of their contents. Nevertheless, this much is obvious: the 18-year eclipse cycle, commonly called "Saros",[3] plays an important role in this earlier development but is no longer apparent in the final form of the theory.

Our comparatively detailed insight into the latest phase of Babylonian lunar theory is marred by a particularly puzzling problem. The procedures of "System A"—considered to be the earlier of the two lunar systems (with how much justification, I do not know)—employ a column, which I denote by Φ, for the computation of the length of the synodic month. Until now we have been unable to explain the significance of its parameters except for the fact that its period is the same as the period of column F of the lunar velocity[4]. This is particularly disturbing since not only do we have a great number of texts dealing with the relations between Φ, F, and G[5]—the latter giving the excess of the synodic month over 29 days—but there exist additional tables of a closely related function Λ of equally unknown significance[6].

It is therefore of great interest that we now have a text which connects the elements of column Φ with the 18-year cycle. This fact was recognized

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[1] All material on Babylonian mathematical astronomy known to me so far is collected in my edition "Astronomical Cuneiform Texts" (3 vols., London, Lund Humphries, 1955), henceforth quoted as ACT.

[2] Example: TU 11 = AO 6455 (Thureau-Dangin, Tablettes d'Uruk, Paris 1922, Pl. 22 f.).

[3] This name is a modern invention; cf., e. g., my "Exact Sciences in Antiquity", Copenhagen 1951, p. 134 ff.

[4] For details cf. ACT I p. 44 and p. 58 ff.

[5] Cf. ACT II p. 508 s.v. column Φ.

[6] Cf. ACT I p. 264 ff.

by A. Sachs during his investigation of astronomical texts in the British Museum in 1954. He joined two fragments BM 36705 = 80-6-17,437 and BM 36725 = 80-6-17,458 which give us, except for broken edges and some surface damage, the major part of a text which contained in some 16 sections the theory of column Φ. Needless to say, the damage to the critical passages of the text is such that we have failed in repeated discussions to reach a consistent and thoroughgoing understanding. Nevertheless the mere fact that we now see a connection between the Saros and column Φ explains certain features in the lunar theory and opens a new approach which should be made accessible to others who might be more fortunate in finding the key to the final solution of the problem of column Φ.

The crucial passage which establishes the relation between Saros and lunar velocity is the following sentence in our text (rev. 13 and 16): 17,46,40 tab *u* lal *šá* 18 mu-meš "17,46,40 is the difference (lit.: addition and subtraction) for 18 years". It had been apparent from many texts that the constant

$$\varphi = 17,46,40,0 \tag{1a}$$[7]

plays an important role in the structure of column Φ; e.g., we knew[8] that the difference d_Φ of Φ was given by

$$d_\Phi = \frac{1}{\varepsilon}\varphi \tag{1b}$$

where

$$\varepsilon = \frac{1}{9;20} = \frac{3}{28} \tag{1c}$$

is a constant which repeatedly appears in related contexts. Similar connections exist between φ and the function Λ. But the sentence quoted above reveals a new relation which had been overlooked and which now can be formulated as follows: If the difference $y_n - y_o$ between the two values y_n and y_o of Φ is $\varphi = 17,46,40,0$, then we can determine the number n of mean synodic months which separate y_n from y_o and the corresponding number α of periods of length P_Φ of Φ. Indeed, using the standard Diophantine method,[9] we find

$$n \equiv -3,43 \text{ mod. } 1,44,7 \qquad \alpha \equiv -16 \text{ mod. } 7,28. \tag{2}$$

---

[7] The final zero is added in order to indicate that the digits of φ correspond to the last four digits of Φ, taken as integers. As we shall see presently $\varphi = 0;0,17,46,40^{\text{H}}$ where $1^{\text{H}} = 1,0^\circ$ of time (cf. ACT I p. 39).

[8] Cf. ACT I p. 59.

[9] Cf. ACT I p. 35 f.

This is identical with the statement of our text since

$$S = 3{,}43 \text{ mean synodic months} \tag{3}$$

is the length of the "Saros".

Utilizing this new insight into the significance of the constant φ we can derive several important relations. First of all we can show that (1b) and (1c) are the equivalent of the fundamental period relation between anomalistic and synodic months. Indeed, (1b) implies that the increase of Φ by the amount φ corresponds to the fraction $\varepsilon = \frac{3}{28}$ of one synodic month (cf. Fig. 1). Thus (1) and (2) combined indicate that

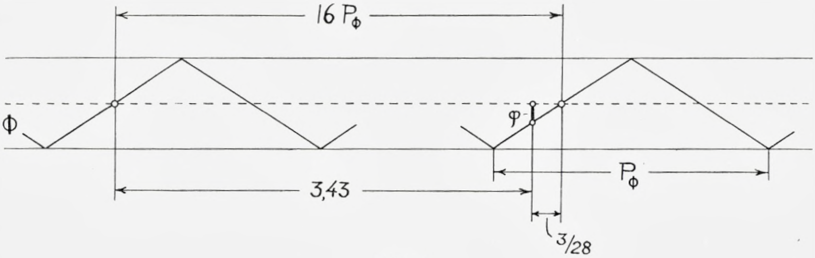

Fig. 1.

$$16\, P_{\Phi} = 3{,}43 + \frac{3}{28} \text{ syn. m.} \tag{4}$$

or

$$16 \cdot 28\, P_{\Phi} = 3{,}43 \cdot 28 + 3 = 1{,}44{,}7 \text{ syn. m.},$$

thus

$$P_{\Phi} = \frac{1{,}44{,}7}{7{,}28}. \tag{5}$$

This is indeed the value known from the ephemerides of System A. Since F and Φ agree in period and in phase[10] we obtain from (5) for the anomalistic months the well-known relation[11]

$$1{,}44{,}7 \text{ syn. m.} = 1{,}44{,}7 + 7{,}28 = 1{,}51{,}35 \text{ anom. m.} \tag{6}$$

Consequently the relation (6) is the exact equivalent of the statements (1b) and (1c).

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[10] Cf. ACT I p. 44 and p. 58.
[11] Cf. ACT I p. 58 (1c).

The relation

$$(7) \qquad 3,43 \text{ syn. m.} = 3,59 \text{ anom. m.}$$

which is usually caled "Saros" is only an approximation of (6) since division by 28 of (6) leads to

$$(8) \qquad 3,43 + \frac{3}{28} \text{ syn. m.} = 3,59 + \frac{3}{28} \text{ anom. m.}$$

and not to (7), which ignores the difference in length of the fractions of synodic and anomalistic months. In the following we shall use the word "Saros" exclusively as an abbreviation of (3), that is, for a time interval of 3,43 synodic months or about 18 years, as the texts usually say. We do not imply, however, any exact equivalence of this time interval with any other integer number of units.

Another important relation can be derived from the fact that Φ and F have identical periods and therefore so do also Φ and Ĝ since the identity of the periods of F (lunar velocity) and Ĝ (linearized length of the synodic months assuming mean solar motion) is astronomically necessary. From the identity of periods we can now explain the fact[12] that the texts assume

$$(9) \qquad d_{\hat{\mathrm{G}}} = \frac{1}{\varepsilon}\, d_{\Phi}\,.$$

Indeed, for the common period we have from (5):

$$P = \frac{2\,\Delta}{d} = \frac{\Pi}{Z} = \frac{1,44,7}{7,28}$$

and with (3)

$$S = 3,43$$

one finds

$$\Pi = 28\,S + 3 \qquad Z = 28 \cdot 16.$$

We now define the difference d_{Φ} of Φ by

$$(10) \qquad -\,d_{\Phi} = \hat{\mathrm{G}}_S - \hat{\mathrm{G}}_0\,.$$

Since for the linear zigzag function Ĝ

$$\hat{\mathrm{G}}_S - \hat{\mathrm{G}}_0 \equiv S \cdot d_{\hat{\mathrm{G}}} \qquad \operatorname{mod}\ 2\,\Delta_{\hat{\mathrm{G}}}$$

and since

$$S = \frac{\Pi - 3}{28} = \frac{16\,\Pi}{Z} - \frac{3}{28} = 16\,\frac{2\,\Delta}{d} - \varepsilon$$

---

[12] Cf. ACT I p. 59 (4) and the table ACT I p. 60. The steps of length ε are recognizable in this table by the corresponding change of Φ by the amount 17,46,40,0.

we have from (10)

$$-d_{\Phi} \equiv S\,d_{\hat{G}} = 16 \cdot 2\,\Delta_{\hat{G}} - \varepsilon\,d_{\hat{G}} \equiv -\varepsilon\,d_{\hat{G}} \quad \bmod\ 2\,\Delta_{\hat{G}}$$

or

$$d_{\Phi} = \varepsilon\,d_{\hat{G}}$$

q.e.d. Thus we have shown that the difference of Φ is the difference in the length of two synodic months one Saros apart.

A trivial consequence of the preceding derivation is the fact that not only is d_{Φ} derived from the variation of the length of the synodic months but Δ_{Φ} as well. Indeed, in every linear zigzag function,

$$\Delta = \frac{1}{2} P d$$

and since $P_{\Phi} = P_{\hat{G}}$ we know also Δ_{Φ} since d_{Φ} is now known.

In order to determine Φ completely, two more data would be required: its mean value and some initial value, or its equivalent, the phase difference between Φ and G. I have not succeeded in solving these problems. There are several sections in our new texts, particularly 12 and 13, which deal with the amplitudes of Ĝ and Φ and what seem to be maxima and minima which would determine the mean values. But none of these numbers agrees with the known parameters.

The problem of the phase difference is less intricate. The identity of period and phase of F and Φ leads easily to the conclusion that the maxima of Ĝ should follow at the distance of $\frac{1}{2}$ synodic month the minima of Φ[13]. In fact, however, this phase difference is not $\frac{1}{2}$ but $\frac{1}{2}(1-\varepsilon)$. As can easily be seen by considering the "true function", which represents the lunar velocity, this arrangement has the following consequence: there exists a certain Saros interval such that the moon is at its maximum velocity $\frac{1}{2}(1-\varepsilon)$ mean synodic months before the mean conjunction at the beginning of the Saros and $\frac{1}{2}(1+\varepsilon)$ mean synodic months before the last mean conjunction of the Saros. I cannot say, however, whether this kind of symmetrization is significant or not.

The problem of the function Φ will not be solved before we understand the numerical relations between the mean values of Φ, F, and Ĝ. It is now

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[13] Cf. ACT I p. 59 Fig. 25.

clear that the two previous attempts to explain the nature of column Φ can be discarded: Kugler's hypothesis that Φ represents the apparent lunar diameter and my own suggestion to connect Φ with the elongation.[13a] It is now certain that Φ measures time in comparing the length of lunations one Saros apart. It is on this basis that the solution of the remaining questions has to be sought.

Transcription.

Obv. Beginning destroyed.

Section 1.

1. [..............................]..........[........
2. [.........................] E-*ma* 14,48,53,20 mu-meš [......
3. *šá* 18 mu-meš *šá* E-ma 13,39,35,36 [....

Section 2.

4. 17,46,40 a-rá 9,20 DU-*ma* 2,45,55,[33,20 tab *u* lal]
5. ta *muḫ-ḫi* zi *sin* gal en *muḫ-ḫi* zi *sin* tur ..[...
6. 1,22,39,49,30 *si-man šu-ú ina* 18 mu-meš ..[....
7. *sin a-n*[*a*] *šamáš* kur *ù ina* 18 mu-meš ..[....
8. ta 3,13,21,4 danna nim-*ma re-ḫi* [............
9. 1,5,4,22,30 DU-*ma lu* 1,22,39,[49,30 1,16,]13,[10,11,24,36]
10. a-rá 1,5,4,22,30 DU-*ma* 1,22,39,49,30 ...13 [.....
11. ta *muḫ-ḫi* zi gal en *muḫ-ḫi* zi tur 1,16,13,10,11,2[4,36]
12. a-rá 9,20 DU-*ma* 11,51,22,55,6,29,36 a-rá 10 [DU-*ma*]
13. 1,58,{39,}33,49,11,4,56 27,33,16,30 blank [.......]
14. *ù* 1,58,33,49,11,4,56 *a-na muḫ-ḫi a-ḫa-meš* gar-gar[-*ma*]
15. 29,31,50,19,11,4,56 šit áb kur *ina* múrub áb *aná* áb [...]
16. *ina* 29 me *ina* 3,11,1,6,29,36 *si-man sin a-na šamáš* kur *si-man šá a-na tar-ṣi* [...]
17. 1,53,56,47,24,2,40 *si-man šá* ... *a-na tar-ṣi* 1,58,3[3,49,11,4,56]
18. 4,28,5,25,45,9,30 2,45,55,33,20 *šá* áb a-rá 9,20 DU-*m*[*a*]
19. 25,48,38,31,6,40 tab *u* lal *šá si-man-meš* 2,45,55,33,20 [...]
20. a-rá 7 DU-*ma* 19,21,28,53,20 19,16,51,6,40 ta *lìb* nim-*m*[*a*]
21. *re-ḫi* 4,37,46,40 $\frac{1}{2}$-*šú* GIŠ-*ma* 2,18,53,20 2,18,53,20
22. ta 2,45,55,33,20 ta *lìb* nim-*ma re-ḫi* 2,43,{42,43,}36,40

[13a] Kugler, Mondrechnung p. 125 ff. and ACT p. 44 f. respectively.

23. a-rá 9,20 DU-*ma* 25,27,2,13,20 blank 25,27,2,13,20
24. *ù* 51,37,17,2,13,20 gar-gar-*ma* 1,17,4,19,[1]5,33,20
25. ki . . . 3,11,1,6,29,26 blank *šá s*[*i-man*]

Section 3.

26. ta zi gal en zi tur 17,46,40 a-rá 12,38,45 DU-*ma* zi [gal]
27. 17,46,40 a-rá 50 DU-*ma* ta *muḫ-ḫi* zi *sin* gal en *muḫ-ḫi* z[i *sin* tur]
28. ta tur en gal 17,46,40 a-rá 2,25,37,30 DU-*ma* zi tur UL-LA-NI

Section 4.

29. [*ina* . . . . m]e 3,1,32 k[i D]U *ù*? zi-*šú* BE ta zi-*šú* gal
30. [. . . . .]4,55,46,40 me 1,.,46,1,30 DU
31. . . . .]30 DU *ina* 5,6,9,33,20 me
32. [. . . . .?4]8,45 me 3,1,32 ki DU
33. [. . . . .] . . . [. . . . m]e? zi *ina* DI zi gal? 1?-en? . . . [. . . .]
34. [. . . . .] . . . . . . [. . . . . .

Reverse. Probably little missing between obv. and rev., if anything.

Section 5.

1. [. . . . .]30? 1? 16,20 zi? 9,6,26 . . [. . . . .

Section 6.

2. [. . . . . 1,16,13,10,]11,24,36 zi *ina* ki zi [. . . .]
3. [. . . . . .z]i gal $\frac{1}{2}$? 3,30,?48,29,30,30 zi
4. [. . . . . .1]8 mu-meš *si-man šá* gal 2,13,20

Section 7.

5. [. . .] . . . [. . . . .]8 blank 1[0 . . . . . .]

Section 8.

6. 23,52,13,20 *šá* 18-mu-[meš . . . . 1]4,4,26,40 blank 7 áb

Section 9.

7. 34,24,51,21,28,53,2[0 . . . . . . *š*]*á si-man*-meš *šá* áb *aná* áb
8. 23,33,56,2,57,4[6,40 . . . . *š*]*á* ki *si-man* tab

Section 10.

9. 4,53,47,29,40,44,26,40 *s[i-man* . . . . .?]18,16,5,19,15,33,20 *si-man*

Section 11.

10. [1]3,46,38,15 me ta zi gal en z[i tur] a-rá 6 DU-*ma*
11. 1,22,39,49,30 danna me *a-na* 1,5,4,22,30 šeš-meš BAR-*ma*
12. 1,16,13,10,11,24,36 blank *šá*? u[š-m]eš

Section 12.

13. 17,46,40 tab *u* lal *šá* 18 mu-meš [a-rá] 1,5,4,22,3[0 DU-*ma* 19,]16,51,6,40
14. $\frac{1}{2}$-*šú* GIŠ-*ma* ki 1,16,13,10,1[1],2[4,]36 tab-*ma* [. . . . .]4,36
15. *aná tar-ṣi* 2,13,20 zi gal 1,4,5[4?, ...] zi tur

Section 13. Except for a few traces, only beginnings of lines are preserved.

16. 17,46,40 tab *u* lal *šá* 18 mu-[meš . . .
17. 2,45,55,33,20 [. . .
18. 25,48,38,31,6,[40 . . . .
19. [. u]š *sin ina* ki zi [. .]. . z[i . . . .
20. [. . .]1,30,3?6 [. . . . 21. [. . .]-*ú* . . [. . . .
22. ta .[. . . . 23. . . .[. . . . 24. *si-man* [. . . .

Section 14.

25. *ki-i* [. . . . .] zi tur
26. 1,6,41,30[. . . . . z]i gal
27. 1,25,42,4[0 . . .]44[. . . . .]. . [. .] blank
28. 1,6,42[. . . . . . .]48,4,30[. . . . . .z]i gal 1,5,4,22,30
29. $\frac{1}{2}$-*šú* GIŠ-*ma* a-rá 17,46,40 DU-*ma* 9,22,33,13,4[0] tab *u* [lal]
30. 1,25,58,17,38,40 *a-na tar-ṣi* blank zi [tur]
31. 1,6,41,26,32 *a-na tar-ṣi* zi gal 19,16,51,6,40 . .[. . . . . . .]

Section 15.

32. [*a*]-*na tar-ṣi* 2,17,4,48,53,20 2,15,31,6,35,3[3,20 . . . .
33. [*a-na t*]*ar-ṣi* 2,. .,59,15,33,20 4,46,42,57,46,[40 . . . . .
34. [*a-na tar-ṣi* 1,57,47,]57,46,40 5,15,2[8,23,37,46,40 . . . . .

Section 16.

35. [.....................] blank [..........
36. [.........................]... 57[......

Rest destroyed.

Critical Apparatus.

Obverse.

5. End of line: two vertical wedges visible, thus 2 or 3 possible.
6. End of line: 10 or *ù*.....?
7. End of line: traces of numbers which could be 11,4,3,6,2[0 ... or *ù* 3,6,2[0 ... .
8. 3,13,21,4: also 15 or 16 instead of 13 not excluded.
10. End of line: 13 or 23 seems certain. The preceding traces could be 30 or 20.
11. Last number: the 11 is badly written, perhaps a correction of a 9.
13. {39}: superfluous digit without influence on computation. The correct number appears in the next line.
16. *ina* 29 me: written on the left edge [Sachs].
17. *šá* ... : the *šá* is followed by an erasure, probably of a second *šá*.
18. ....,9,30 2,45,...: there is no space between 30 and 2, and one would read ...9,32,45,... were it not for the context. Furthermore, the last digit of the first number should be 20, not 30.
22. {42,43}: superfluous digits; scribal error without influence on subsequent numbers.
25. ki: followed by an erasure or a destroyed sign.
   ...,29,26: sic, instead of ...,29,36 (cf. line 16).
28. 2,25,37,30: also 38 or 36 would be possible instead of 37.
33. DI: probably error for KI.

Reverse:

1. Could be the last line of Section 4.
3. $\frac{1}{2}$: or *ina* 1 ?
   3,30,48,...: the 40 is very uncertain.
8. 23,33,...: reading of 20 very uncertain.
9. ..]18: or more tens before 8.
   ...19...: could also be read *ina* 9.
12. *šá*: or *aná*?

14. [. . . . .]4,36: the available space fits very well the expected length of 5 digits.
28. . .]48,4,30: or]58,4,30.
33. 2,.,59,15. . : reading very uncertain since the lower part of the numbers preceding 15 is broken away.
36.]. . .57[: or . .]22,58[. . .

Translation and Commentary.

Section 1. The beginning of the text is so badly damaged that only very little can be said about its contents. The number in line 2 can be explained as

$$14,48,53,20 = 50 \cdot 17,46,40 = 50 \cdot \varphi.$$

The same factors appear also in Section 3; the present passage seems to indicate that "years" are meant, though this seems very unlikely in view of the fact that 17,46,40 is only a little more than one hour (cf. note 7).

In line 3 the 18-year cycle is mentioned. The subsequent number occurs nowhere else; the element E in the term E-*ma* is probably a form of *qabū* "speak, declare".

Section 2. This section covers the major part of the obverse. At the beginning we read:

4. 17,46,40 multiply by 9,20 and 2,45,55,[33,20 add and subtract.]
5. From high lunar velocity to low lunar velocity . . [. . . . .]
6. 1,22,39,49,30 (is) its duration; in 18 years . . [. . . . .]
7. the moon reaches the sun and in 18 years . . [. . . . .]
8. subtract from 3,13,21,4 danna and the remainder [. . . . .]

Line 4 contains the statement that

$$0;0,17,46,40^{\mathrm{H}} \cdot 9;20 = 0;2,45,55,33,20^{\mathrm{H}}$$

or

$$\varphi \cdot \frac{1}{\varepsilon} = d_{\Phi}. \tag{1}$$

Lines 5 and 6 introduce a new constant, namely,

$$c = 1,22;39,49,30^{\mathrm{H}} \tag{11}$$

the duration of half the anomalistic month—"from high to low lunar velocity" as the text puts it. Since, according to Section 11, (11 a) $$1,22;39,49,30^{\mathrm{H}} = 6 \cdot 13;46,38,15$$

we see that the length of the anomalistic month corresponding to (10) is

(11 b) $$2 \cdot 13;46,38,15^{\mathrm{d}} = 27;33,16,30^{\mathrm{d}}$$

a value not attested in ACT-texts.[14]

I do not dare restore the numbers connected with the 18-year cycle (lines 6 and 7) nor do I know the meaning of 3,13,21,4 danna (= 6,26,42,8°?) in line 8.

There follows a derivation of the length of the synodic month from the anomalistic month:

9. [What] should be multiplied by 1,5,4,22,30 so that 1,22,39,[49,30 (is the result)? 1,16,]13,[10,11,24,36]
10. times 1,5,4,22,30 is 1,22,39,49,30 ....[..... (which is the time)]
11. from high lunar velocity to low lunar velocity. 1,16,13,10,11,2[4,36]
12. multiply by 9,20 and (the result) 11,51,22,55,6,29,36 multiply by 10 [and]
13. 1,58,{39,}33,49,11,4,56 (is the result). 27,33,16,30
14. and 1,58,33,49,11,4,56 add together and
15. 29,31,50,19,11,4,56 is the number (of days) of the month.

On the basis of Sections 11 and 12 we can explain the first number in line 9 as[15]

$$1,5;4,22,30 = \frac{19,16,51,6,40}{17,46,40,0} = \frac{\Delta\Phi}{\varepsilon \cdot d_{\Phi}} = \frac{1}{2\,\varepsilon} P_{\Phi}.$$

The division which follows means[16]

$$\frac{1,22;39,49,30^{\mathrm{H}}}{1,5\,;4,22,30} = 1;16,13,10,11,24,36^{\mathrm{H}} = \frac{\frac{1}{2} m_{\mathrm{a}}^{\mathrm{H}}}{\frac{1}{2\,\varepsilon} P_{\Phi}} = \varepsilon \frac{m_{\mathrm{a}}^{\mathrm{H}}}{P_{\Phi}}$$

where $m_{\mathrm{a}}^{\mathrm{H}}$ represents the length of the anomalistic month, measured in large-hours according to (11). If $m_{\mathrm{a}}^{\mathrm{d}}$ denotes the corresponding value expressed in days, as in (11 b), we have for the next step

---

[14] This is not very significant, however, since only approximate values for the anomalistic month are known from ACT (I p. 59: 27;33,1,... p. 76: 27,33,20). A very close value results from the data in the Surya Siddhanta I, 37–39: 27;33,16,32,...

[15] For $\Delta\Phi = 19,16,51,6,40$ cf. ACT I p. 44; for the denominator cf. the equations (1) and (3) above.

[16] The result is not quite accurate since the two last digits should be 25,46... instead of 24,36. The restoration in lines 9 and 11 is nevertheless certain on the basis of the product given in line 12 as well as from Section 11.

$$1;16,13,10,11,24,36 \cdot 9;20 \cdot 0;10 = 1;58,33,49,11,4,56^{\mathrm{d}}$$

$$= \varepsilon \frac{m_{\mathrm{a}}^{\mathrm{H}}}{P_{\Phi}} \cdot \frac{1}{\varepsilon} \cdot \frac{1}{6} = \frac{m_{\mathrm{a}}^{\mathrm{d}}}{P_{\Phi}}.$$

Since the periods of F and Φ are identical we can write for the last step

$$27;33,16,30 + 1;58,33,49,11,4,56 = 29;31,50,19,11,4,56^{\mathrm{d}}$$

$$= m_{\mathrm{a}}^{\mathrm{d}} + \frac{m_{\mathrm{a}}^{\mathrm{d}}}{P_{\mathrm{F}}} = m_{\mathrm{a}}^{\mathrm{d}}\left(1 + \frac{1}{P_{\mathrm{F}}}\right) = m_{\mathrm{a}}^{\mathrm{d}}\, p_{\mathrm{F}},$$

where

$$p_{\mathrm{F}} = \frac{P_{\mathrm{F}} + 1}{P_{\mathrm{F}}}$$

is the period, measured in terms of the mean synodic month, of the zigzag function which represents the lunar velocity. Thus

$$m_{\mathrm{a}}^{\mathrm{d}} \cdot p_{\mathrm{F}} = m_{\mathrm{s}}^{\mathrm{d}}$$

is the length of the mean synodic month expressed in days. As in the case of the anomalistic month the value $29;31,50,19,11,4,56^{\mathrm{d}}$ is slightly different from the values attested in ACT.[17]

Lines 15 to 18 swarm with difficulties of syntax as well as of contents, probably increased by scribal errors. What kur "reach" in line 15 refers to, I do not know. Then I consider as one sentence the second half of line 15 and the first half of the next line:

> For mean velocity month by month in 29 days (and) in the time of 3,11,1,6,29,36 the moon reaches the sun.

In the preceding passages we had reached the result that the mean synodic month had the length of $29;31,50,19,11,4,56^{\mathrm{d}}$. If we ignore, as is usual for column G, the 29 days and convert the remaining fractions into large-hours we obtain:

$$0;31,50,19,11,4,56 \cdot 6 = 3;11,1,55,6,29,36^{\mathrm{H}}$$

for the excess, that is, the number quoted in the text with the omission of the 55 in the fourth place. I can see no explanation other than the assumption of a scribal omission. Since all that follows is based on the incorrect figure, the remaining operations in this section cannot be taken as authoritative theory.

---

[17] The standard value is $29;31,50,8,20^{\mathrm{d}}$; cf. ACT I p. 70.

The next sentences (lines 17,18) seem to say

> the duration which is opposite 1,53,56,47,24,2,40
> the duration which is opposite 1,58,3[3,49,11,4,56]
> (is?) 4,28,5,25,45,9,20.[18]

The terminology "(*a*) is opposite (*b*)" is common in the procedure texts which associate values of G with given values of Φ.[19] In numerical respects, we find no agreement with the rules found in ACT. The value 1,53,56,47, 24,2,40 is smaller than the minimum 1,57,47,... of Φ, and with Φ = 1,58,33,49,11,4,56 would belong either the value G = 4,56,0,0,0,0,0 (for increasing Φ) or G = 4,21,26,7,40,37,20 (for decreasing Φ), neither showing any relation to the 4,28,5,... of the text. The latter number is the total of numbers in lines 24 and 25, though influenced by the error in line 16.

The final part of Section 2 is again in disagreement with the scheme familiar from ACT but it at least shows arithmetical consistency.

18. 2,45,55,33,20 of the month multiply by 9,20 and
19. 25,48,38,31,6,40 (is the) increase and decrease of the duration. 2,45,55,33,20
20. multiply by 7 and 19,21,28,53,20 (is the result). Subtract from it 19,16,51,6,40 and
21. the remainder is 4,37,46,40. Halve it and 2,18,53,20 (is the result). 2,18,53,20
22. subtract from 2,45,55,33,20 and the remainder is 2,43,36,40[20]
23. Multiply (it) by 9,20 and 25,27,2,13,20 (is the result). 25,27,2,13,20
24. and 51,37,17,2,13,20 add and 1,17,4,19,15,33,20 (is the result);
25. with 3,11,1,6,29,36[21] of the duration (it gives a total of 4,28,5,25,45,9,20).

The meaning of these operations can be described as follows. First we are reminded that

$$0;2,45,55,33,20^{H} \cdot 9;20 = 0;25,48,38,31,6,40^{H}$$

or:

$$d_{\Phi} \cdot 9;20 = d_{\hat{G}} .$$

---

[18] The text has 30 for the last digit but 20 is required by the subsequent computations.

[19] Cf., e. g., ACT I p. 204, p. 253, etc.

[20] The text gives here incorrectly 2,43,*42*,*43*,36,40 but all subsequent numbers are correct.

[21] The text gives for the last digit 26 instead of 36; the correct value is found in line 16.

Then we turn to the function Φ and form

$$\begin{aligned} 0;2,45,55,33,20^{\mathrm{H}} \cdot 7 = \quad & 0;19,21,28,53,20^{\mathrm{H}} && = 7 \cdot d_{\Phi} \\ - \; & 0;19,16,51,6,40^{\mathrm{H}} && = - \varDelta_{\Phi} \\ \text{thus:} \quad & 0;0,4,37,46,40^{\mathrm{H}} && = 7 \; d_{\Phi} - \varDelta_{\Phi} \end{aligned}$$

and

$$\frac{1}{2} \cdot 0;0,4,37,46,40^{\mathrm{H}} = 0;0,2,18,53,20^{\mathrm{H}} = \frac{1}{2}(7 \; d_{\Phi} - \varDelta_{\Phi})$$

and thus

$$0;2,45,55,33,20^{\mathrm{H}} - 0;0,2,18,53,20 = 0;2,43,36,40 = d_{\Phi} - \frac{1}{2}(7 \; d_{\Phi} - \varDelta_{\Phi}).$$

This result is now transformed into values of Ĝ by multiplying it by 9;20

$$0;2,43,36,40^{\mathrm{H}} \cdot 9;20 = 0;25,27,2,13,20^{\mathrm{H}} = d_{\hat{\mathrm{G}}} - \frac{1}{2}(7 \; d_{\hat{\mathrm{G}}} - \varDelta_{\hat{\mathrm{G}}})$$

to which is added

$$0;51,37,17,2,13,20^{\mathrm{H}} = 2 \, d_{\hat{\mathrm{G}}}$$

with the result

$$1;17,4,19,15,33,20^{\mathrm{H}} = \frac{1}{2}(\varDelta_{\hat{\mathrm{G}}} - d_{\hat{\mathrm{G}}}).$$

Finally mention is made of the number

$$\mu = 3;11,1,6,29,36^{\mathrm{H}}$$

which is known from line 16 as the length of a synodic month (beyond 29 days) which corresponds to a mean anomalistic month and can therefore be considered as the real value of the mean synodic month, though influenced by an omission of 55 in the fourth place.

Section 2 ends without giving the result of the addition which is indicated by the particle ki "with". If we add the two last mentioned figures we find

$$1;17,4,19,15,33,20^{\mathrm{H}} + 3;11,1,6,29,36^{\mathrm{H}} = 4;28,5,25,45,9,20^{\mathrm{H}}$$

$$\frac{1}{2}(\varDelta_{\hat{\mathrm{G}}} - d_{\hat{\mathrm{G}}}) + \mu = M - \frac{1}{2} d_{\hat{\mathrm{G}}}.$$

We have already encountered the same number at the end of the preceding section (line 18) as "the duration which is opposite 1;58,3[3,49,11,4,56]". Assuming the correctness of my restoration of the last number it represents the difference between the mean synodic and anomalistic month (cf. lines 13 and 14).

An explanation of these operations can, to a certain extent, be given as follows. Since the period of Φ is slightly less than 14 mean synodic months[22] $7\,d_\Phi$ slightly exceeds the amplitude Δ_Φ and $\frac{1}{2}(7\,d_\Phi - \Delta_\Phi)$ indicates by how much an interval of $7\,d_\Phi$ width exceeds in a symmetric position the extrema of Φ (cf. Fig. 2). Consequently $d_\Phi - \frac{1}{2}(7\,d_\Phi - \Delta_\Phi)$ indicates the distance of the first and last interior point of a branch from its nearest extremum. And since multiplication by 9;20 transforms all numbers into the corresponding quantities of $\hat{G}$, we see that $0;25,27,2,13,20^{H}$ is the amount which separates the extrema of $\hat{G}$ from the nearest values in an arrangement as represented in Fig. 2.

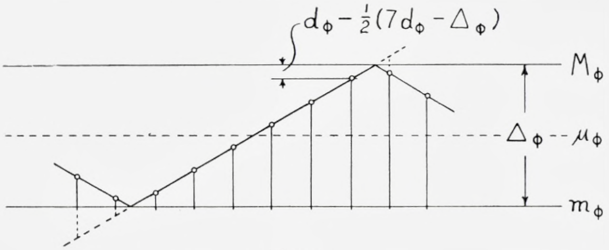

Fig. 2.

If we consider $\mu = 3;11,1,6,29,36^{H}$ as the mean value of $\hat{G}$ then

$$\mu + \frac{1}{2}(\Delta_{\hat{G}} - d_{\hat{G}}) = M - \frac{1}{2}\,d_{\hat{G}} = 4;28,5,25,45,9,20^{H}$$

is the value of $\hat{G}$ one half interval before its maximum. The motivation for this probably lies in the fact that it is this value which would, in general, be associated with the minimum of Φ or F.[23]

Section 3.

26. From high velocity to low velocity: 17,46,40 multiply by 12,38,45 and the [high] velocity (is the result).
27. 17,46,40 multiply by 50 and from the high lunar velocity to the [low lunar] velocity (is the result).

---

[22] $P\Phi = \frac{1,44,7}{4,28} = 13;56,39,\ldots$; cf. above p. 5 (5).

[23] Cf. ACT I p. 32 and p. 59.

28. From low to high: 17,46,40 multiply by 2,25,37,30 and the low (velocity ....(is the result).

I do not understand the meaning of these operations. In all three cases $1/\varepsilon$ is multiplied by a facto rwithout, however, giving the result. One would find

3,44,50,53,20 14,48,53,20 48,8,53,20

respectively. The second number occurs also in the damaged second line of Section 1.

Section 4 is badly damaged. So far as I can make out, certain intervals of days are listed together with the corresponding lunar motion. Unfortunately not a single pair is completely preserved and only one number is denoted as ki "degrees", thus presumably integer degrees. The remaining numbers in all probability contain fractional parts. I interpret the contents as follows:

[in ......] days 3,1,32° travel
and (?) its velocity; if (?) from its high velocity [........]
[in ....]4,55,46,40 days 1,0,46,1,30 travel
[in ..... days ....] 30 travel
in 5,6,9,33,20 days [......travel]
[in .....4]8,45 days 3,1,32° travel.

Since we are dealing with relatively large numbers of days, the results should not be much different from a motion with mean velocity. This would lead in the first line and in the last to an interval of about 13,46 days. Neither this nor any of the other numbers quoted is otherwise known.

Sections 5 to 10. Not much more can be done with the beginning of the reverse than to identify some of the numbers or words.

Line 1 concerns a velocity.

Line 2 I have tentatively restored from obv. 11 and rev. 12 and 14[24] though the association with velocities might make it suspect. Line 4 refers to the 18-year period and quotes the number 2;13,20 which, for decreasing Φ, marks the beginning of increasing G above its minimum value[25] of $2;40^{H}$. In certain passages of procedure texts the same number 2,13,20 is used as

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[24] Cf. p. 13.

[25] Cf. ACT I p. 60 Fig. 26 and table.

if it were a technical term.[26] In our text it occurs again in Section 12 (line 15).

None of the large numbers in lines 6 to 9 is otherwise known. The repeated references to *si-man* "duration" points to a connection with column G but even an interpretation as fractions of days does not lead to familiar numbers.

Section 11.

10. 13;46,38,15 days from high velocity to [low] velocity.
    Multiply (it) by 6 and
11. 1,22;39,49,30 .... (is the result). Divide (it) into 1,5;4,22,30 parts and 1;16,13,10,11,24,36 (is the result) . . .

The use of the units danna (= 30°) in line 11 must be a mistake for uš-meš (degrees) which are mentioned at the end of line 12. What me in line 11 means is not clear.

The purpose of this operation has already been explained in Section 2. The first two large numbers give the half of the length of an anomalistic month, counted in days and large-hours respectively. For the subsequent division see above p. 13 and the next section.

Section 12.

13. 17,46,40, the difference for 18 years, [multiply by] 1,5;4,22,30 [and (the result is) 19,]16,51,6,40.
14. Halve it and add to 1;16,13,10,11,24,36 and [. . . . .]4,36 (is the result).
15. Opposite 2,13,20, the high velocity, 1,4,5[4(?) . . . .] low velocity.

Again using the notation of Section 2 we see that line 13 computes

$$\varepsilon \cdot d_{\Phi} \cdot 1{,}5;4{,}22{,}30 = \Delta_{\Phi} = 0;19{,}16{,}51{,}6{,}40^{\mathrm{H}}.$$

The operation in the next line is most naturally interpreted as

$$\begin{aligned}\frac{1}{2}\Delta_{\Phi} + 1;16{,}13{,}10{,}11{,}24{,}36 &= \frac{1}{2}\Delta_{\Phi} + \varepsilon\frac{m_a}{P_{\Phi}}\\ &= [1;25{,}51{,}35{,}44{,}4]4{,}36^{\mathrm{H}}.\end{aligned}$$

It would be less plausible to refer the "it" to 17,46,40 and thus restore

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[26] Cf. ACT I p. 212.

$$\frac{1}{2}\varepsilon d_{\Phi} + \varepsilon \frac{m_a}{P_{\Phi}} = 0;0,8,53,20 + 1;16,13,10,11,24,36$$
$$= [1;16,22,3,31,2]4,36^{\mathrm{H}}.$$

Unfortunately neither of these combinations seems to make sense nor to explain its relation to the value 2,13,20 of Φ which is associated with the minimum of G (and thus with "high velocity" of the moon, as seems to be indicated by the text).[27]

Section 13 begins with the same sentence as Section 12. The number at the beginning of line 17 is d_{Φ}. Line 18 begins with $d_{\hat{G}}$, which can be obtained from d_{Φ} by multiplication by 9;20 (cf. obv. 18 and 19).

Sections 14 to 16. Nothing can be connected before line 28/29, which seems to indicate that

$$\frac{1}{2} \cdot 1,5;4,22,30 \cdot 17,46,40 = 9,22,33,13,40.$$

This result, however, is incorrect since we know from Section 12 that its value should be

$$\frac{1}{2}\Delta_{\Phi} = 9,38,25,33,20.$$

The result of the text is furthermore described as "add and [subtract]", which is the standard terminology for the difference of a zigzag function (e.g., obv. 19) but would not apply to $\frac{1}{2}\Delta_{\Phi}$.

The next two lines, 30 and 31, are numerically correct in so far as

$$1;25,58,17,38,40^{\mathrm{H}} = 1;6,41,26,32^{\mathrm{H}} + 0;19,16,51,6,40^{\mathrm{H}}$$

where the last-mentioned number is the value of Δ_{Φ}. The first number is associated with low velocity, the second with high velocity. Since their difference is Δ_{Φ} one would expect to find here the maximum and minimum of Φ respectively. In fact, however, these values are

$$M_{\Phi} = 2;17,4,48,53,20 \quad \text{and} \quad m_{\Phi} = 1;57,47,57,46,40$$

and are in no obvious relation to the above numbers.

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[27] Cf. also the end of Section 6 and our commentary to it (p. 9 and 19).

The numbers M_Φ and m_Φ do occur, however, in the next section (lines 32 and 34 respectively) where they are associated with two numbers whose difference is $\Delta_{\hat{G}}$ but in the opposite order of numerical value in accordance with the general rule for the phases of Φ and $\hat{G}$; but the numbers themselves

$$2,15,31,6,35,3[3,20] \quad \text{and} \quad 5,15,2[8,23,37,46,40]$$

are again different from the extrema of $\hat{G}$

$$m_{\hat{G}} = 2;4,59,45,11,6,40^{H} \quad \text{and} \quad M_{\hat{G}} = 5;4,57,2,13,20^{H}$$

though the discrepancy is no longer so great as with Φ in the preceding section.

In line 33 we find a pair of numbers which agrees with the scheme known from ACT (p. 60):

$$\Phi = 2;0,59,15,33,20^{H}(\uparrow) \text{ corresponds to } G = 4;46,42,57,46,40^{H}.$$

This pair is of particular importance since the value of G is the greatest value for which G and $\hat{G}$ are identical. Since this pair agrees with the known scheme it seems tempting to consider the values which are associated with M_Φ (line 32) and with m_Φ (line 34) as errors:

$$2;15,31,6,35,3[3,20 \quad \text{should be} \quad 2;16,31,6,40$$

and

$$5;15,2[8,23,37,46,40 \quad \text{should be} \quad 5;16,28,23,42,13,20$$

respectively. In this case Section 15 would have listed three values of $\hat{G}$ namely the values which correspond to the extrema of Φ and the maximum value for which $G = \hat{G}$.

Indleveret til selskabet den 15. januar 1957.
Færdig fra trykkeriet den 8. maj 1957.

PLATE I

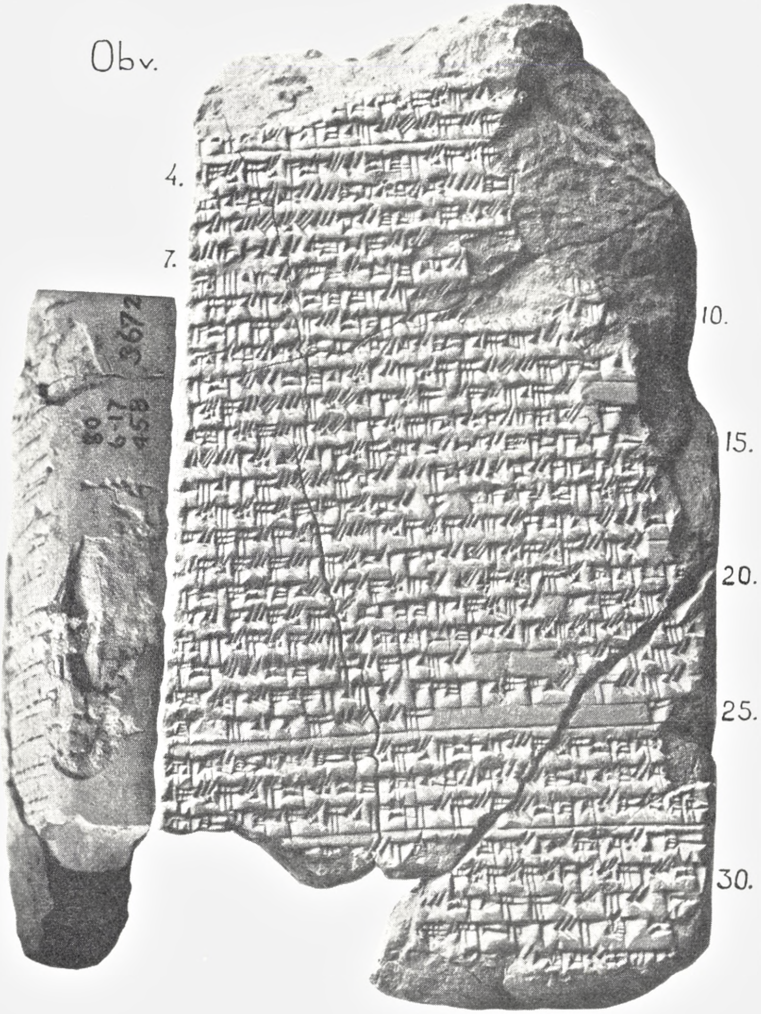
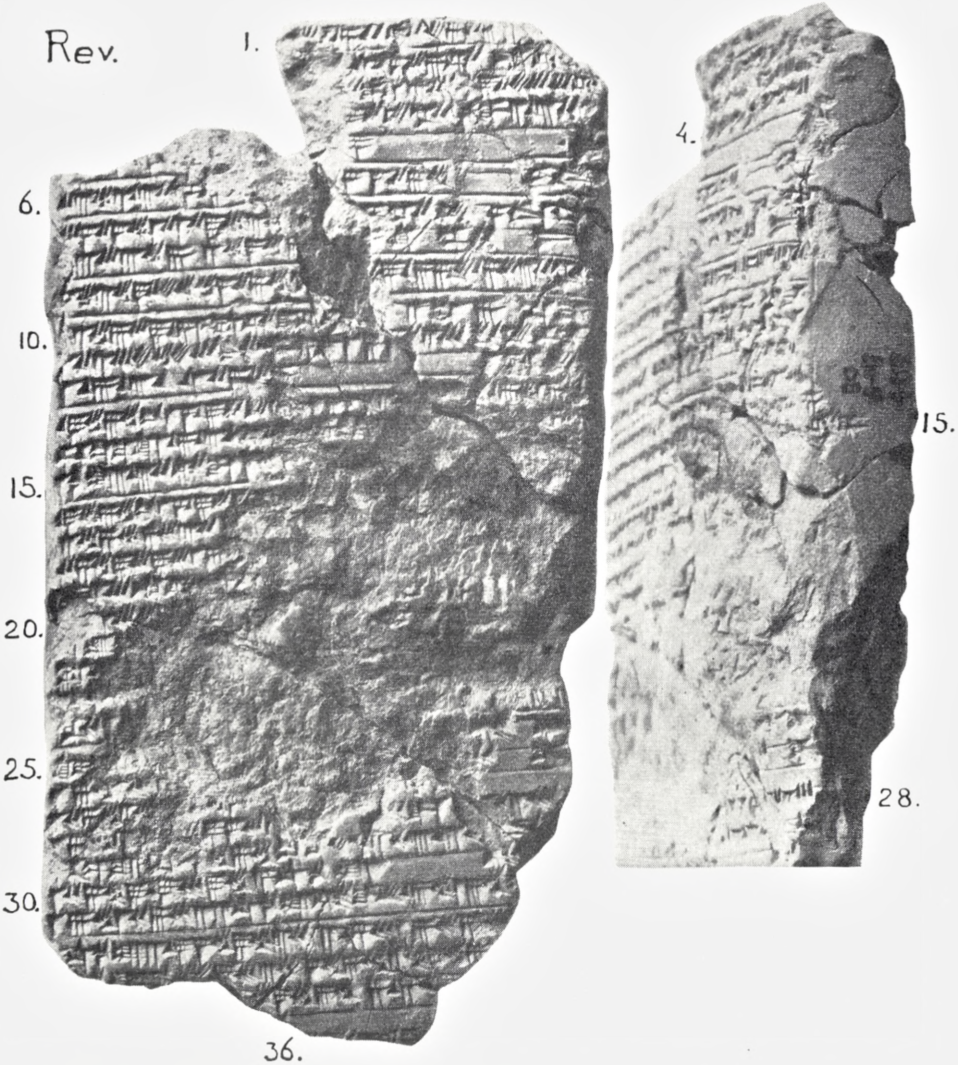


Plate II



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A THEOREM ON INVARIANT ANALYTIC FUNCTIONS WITH APPLICATIONS TO RELATIVISTIC QUANTUM FIELD THEORY

BY

D. HALL and A. S. WIGHTMAN

København 1957
i kommission hos Ejnar Munksgaard

Synopsis.

The paper is in three parts of which the first two are mathematical. In the first part, a detailed proof is given of a previously announced theorem: an analytic function of n four vector variables invariant under the orthochronous Lorentz group is an analytic function of their scalar products. The second part is devoted to a preliminary study of the domain of analyticity of such invariant analytic functions. The third part applies the preceding results to quantum field theory. It is shown that the vacuum expectation value $(\Psi_0, \varphi(x_1) \ldots \varphi(x_n) \Psi_0) = F^{(n)}(x_1, \ldots x_n)$ where $\varphi(x)$ is neutral scalar field, is an analytic function of the real variables $x_j - x_{j+1}$, $j = 1, \ldots n-1$ in a region where all these vectors are space-like. It is shown that the values of $F^{(n)}$ for all values of its arguments are uniquely determined in terms of its values for space-like separations, and that, for $n = 2, 3, 4$, $F^{(n)}$ is determined from its values at points where all times are equal. These results are applied to prove generalizations of two theorems of R. HAAG. In effect, these theorems show that, to give different physical predictions, two theories of an interacting field which satisfies the canonical commutation relations must use inequivalent representations of the commutation relations.

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Introduction.

In a preceding paper[1], the second-named author showed that the main content of a relativistic quantum theory of a scalar field, $\varphi(x)$, is contained in the vacuum expectation values, $F^{(n)}$, defined by

$$F^{(n)}(x_1, \ldots x_n) = (\Psi_0, \varphi(x_1) \ldots \varphi(x_n) \Psi_0),\ n = 1, 2, \ldots,$$

where Ψ_0 is the vacuum state. It was shown there that, as a consequence of the transformation law of the field under space-time translations and the absence of negative energy states, the distributions $F^{(n)}$ are boundary values of analytic functions. The analysis of the structure of the $F^{(n)}$ was carried further, using a theorem, quoted there without proof, which may be stated roughly as follows: an analytic function of n four-vector variables invariant under the orthrochronous Lorentz group is an analytic function of their scalar products.

The first part of the present paper is devoted to a proof of this theorem. Because the techniques introduced in the proof have further useful applications in quantum field theory, we have given a detailed exposition.

The second part of the paper contains a preliminary study of the set, $\mathfrak{M}_n$, of symmetric $n \times n$ complex matrices, Z, defined by $Z_{jk} = z_j \cdot z_k$, $j, k = 1, \ldots n$, where $z_1, \ldots z_n$ are complex four vectors of the form $z_j = \xi_j - i\eta_j$, with ξ_j and η_j real and η_j in the interior of the future light cone (this set of $z_1, \ldots z_n$ is called the tube). According to the theorem proved in the first part of the paper, the set $\mathfrak{M}_n$ is a domain of analyticity of the invariant analytic function which has the physical $F^{(n)}$ as its boundary value when all $\eta_j \rightarrow 0$. It is shown that there are points, $z_1, \ldots z_n$, on the boundary of the tube which yield matrices, $z_i \cdot z_j$, of scalar products lying in the interior of $\mathfrak{M}_n$. From this simple geometrical fact, it follows that an invariant function analytic in the tube cannot have an arbitrary invariant distribution as boundary value. In fact, it turns out that the boundary value has to be an analytic function of the real variables $\xi_j \cdot \xi_k$, $j, k = 1, \ldots n$ in a certain domain and that the analytic function is uniquely determined once its values are known in certain subdomains of the boundary of the tube.

In the third part of the paper, the results of the preceding sections are applied to the vacuum expectation values of a scalar field. It is shown that $F^{(n)}(x_1, \ldots x_n)$ is an analytic function of the real variables $(x_j - x_{j+1}) \cdot (x_k - x_{k+1})$, $j, k = 1, \ldots n-1$ when all $x_j - x_{j+1}$ are space-like and lie in a certain region. It is further shown that the values of $F^{(n)}$ for all values of its arguments are uniquely determined in terms of its values for space-like separation. For the cases $n = 2, 3, 4$, an even stronger result is obtained: $F^{(n)}$ is determined everywhere from its values at points where all the times (x_{j0}), $j = 1 \ldots . n$ are equal. These results are applied to prove generalizations of two theorems of R. HAAG, which can be stated roughly as follows: First, let there be given two theories of a field which transforms as a scalar under the rotations and translations of three space at a fixed time. Suppose that the canonical variables of the theories are unitary equivalent at that time via a unitary transformation V. Then, the representations of the Euclidean group of the two theories are unitary equivalent via V. Second, if the two theories just described are, in addition, invariant under the inhomogeneous Lorentz group and have no negative energy states and unique vacuum states, then the vacuum expectation values $(\Psi_0, \varphi(x_1) \ldots \varphi(x_n) \Psi_0)$ are identical in the two theories for $n = 1, 2, 3, 4$. The paper closes with a discussion of the physical significance of this generalized Haag's theorem.

We want to emphasize that the main results of the paper, as far as the structure of the $F^{(n)}$ are concerned (its determination everywhere in terms of its values for space-like separated arguments), are valid in both local and non-local field theory.

1. An Invariant Analytic Function of Vectors is an Analytic Function of Scalar Products.

The following theorem was stated without proof in I.

Theorem 1.

Let f be a complex valued function of n four-vector variables, $z_j = \xi_j - i\eta_j$, $j = 1, \ldots n$, where ξ_j and η_j are real. Suppose f is analytic in the tube defined by

$$\infty < \xi_{j\mu} < \infty,\ j = 1, \ldots\ n,\ \mu = 0, 1, 2, 3;$$

$$\eta_j \text{ in the future cone, i. e. } \eta_j^2 > 0,\ \eta_{j0} > 0,\ j = 1, \ldots n$$

and invariant under the orthochronous homogeneous Lorentz group, $L^{\uparrow}$:

$$f(z_1, \ldots z_n) = f(\Lambda z_1, \ldots \Lambda z_n) \text{ for } \Lambda \varepsilon L^{\uparrow}. \tag{1}$$

Then, f is a function of the scalar products $z_j \cdot z_k$, $j, k = 1, \ldots n$. It is analytic on the complex variety, $\mathfrak{M}_n$, over which the scalar products vary when the vectors $z_1, \ldots z_n$ vary over the tube.

Outline of the Proof.

If a function is analytic in the tube and satisfies (1) for $\Lambda \varepsilon L^{\uparrow}$, then (Lemma 1) it also satisfies (1) when Λ is an arbitrary complex Lorentz transformation, i. e., a matrix $\Lambda^{\mu}{}_{\nu}$ $\mu, \nu = 0, 1, 2, 3$, whose elements are complex numbers satisfying $\Lambda^{\mathsf{T}}\Lambda = 1$, which means

$$\sum_{\mu=0}^{3} \Lambda_{\mu}{}^{\varkappa} \Lambda^{\mu}{}_{\nu'} = g^{\varkappa}{}_{\nu}. \tag{2}$$

We call the set of such matrices the *complex Lorentz group*, $\mathfrak{L}$. Furthermore, if $\Lambda z_1, \ldots \Lambda z_n$ lies outside the future tube, (1) defines a single valued analytic continuation of the function f originally given. We shall refer to the set of points $\Lambda z_1, \ldots \Lambda z_n$, for $\Lambda \varepsilon \mathfrak{L}$ and $z_1, \ldots z_n$ in the tube, as the *extended tube*.

Next, (Lemma 2), we examine the sets of n vectors $z_1, \dots z_n$ and $\zeta_1, \dots \zeta_n$ which satisfy

$$z_j \cdot z_k = \zeta_j \cdot \zeta_k \quad j, k = 1 \dots n. \tag{3}$$

If the $n \times n$ matrix of the scalar products has rank three or four, there exists a complex Lorentz transformation Λ such that

$$\Lambda z_i = \zeta_i \quad i = 1, \dots n.$$

If the rank is two or one, the connection between z_i and ζ_i is more complicated:

$$\Lambda z_i = \zeta_i + \alpha_i \omega,$$

where the α_i, $i = 1, \dots n$ are complex numbers and ω is a vector of zero length orthogonal to Λz_i and ζ_i, $i = 1, \dots n$. For points at which the rank is three or four, the invariance of an analytic function, f, of n vectors $z_1, \dots z_n$, clearly implies the single valuedness of f regarded as a function of the scalar products (3). For points where the rank is two or one, a further argument is necessary and is supplied. Thus, f is a single valued function everywhere on the variety, $\mathfrak{M}_n$ defined by the scalar products $z_j \cdot z_k$, $j, k = 1, \dots n$. The points of $\mathfrak{M}_n$ are labeled by the $1/2\ n(n+1)$ scalar products. $\mathfrak{M}_n$ can be regarded as an algebraic variety in the space of all complex $n \times n$ symmetric matrices. In fact, it turns out to be an open subset of the set of all complex symmetric matrices of rank ≤ 4 and, as such, has dimension $1\ (n=1)$, $3\ (n=2)$, $4\,n-6\ (n \geq 3)$.

In order to be able to connect the continuity properties of invariant functions of vectors with their corresponding properties regarded as functions of scalar products, it is necessary to investigate the connection between neighbourhoods of sets of vectors and neighbourhoods of their sets of scalar products (Lemma 3). This connection is quite a simple one at points of $\mathfrak{M}_n$ where the rank is three or four, but where it is two or one the situation is quite delicate, because the structure of the set of points in the space of the vectors which map into a given point of $\mathfrak{M}_n$ is essentially more complicated. Nevertheless, the proof of the continuity of f as a function on $\mathfrak{M}_n$ can be, and is, carried out.

To complete the proof of the theorem, it remains to show that f is analytic on $\mathfrak{M}_n$. For $n \leq 4$, analyticity is a perfectly straightforward notion because $\mathfrak{M}_n$ is an open set in complex Euclidean $1/2\ n\,(n+1)$ space. However, for $n \geq 5$, $\mathfrak{M}_n$ is an open set on a $4\,n-6$ dimensional algebraic variety and the notion of analyticity requires some explanation. For a point P of $\mathfrak{M}_n$ ($\geqslant 5$) for which the rank is four, the tangent space to $\mathfrak{M}_n$ at P has dimension $4n-6$. (Recall that the tangent space to $\mathfrak{M}_n$ at P is the linear manifold of the space of all complex symmetric matrices spanned by the tangent vectors to $\mathfrak{M}_n$ at P.) Sufficiently small neighbourhoods of P on $\mathfrak{M}_n$ can be put in analytic one to one correspondence with sufficiently small neighbourhoods in the tangent space. Near such points, f can be regarded as defined in a neighbourhood of the origin in a complex $(4n-6)$-dimensional Euclidean space and its analyticity defined in the well-known way. The points of $\mathfrak{M}_n$, $n \geqslant 5$, where the rank is less than four are *singular* in the terminology of algebraic geometry 2*. For them, the tangent vector space has dimension $1/2\, n(n+1)$ and neighbourhoods are not locally Euclidean. (The reader may find it helpful to think of the example of the light cone. In that case, the point where the tips of the past and future cones touch is singular and its neighbourhoods are not locally Euclidean. However, it should be borne in mind that the actual situation is much more complicated since singular points only appear on $\mathfrak{M}_n$ for $n \geqslant 5$ and in the simplest case, $n=5$, already form a variety of 24 (real) dimensions.) Evidently, the above definition of analyticity does not apply at such a point. It is not impossible to extend the notion of analyticity to apply there. In fact, one can do it in a number of different ways. However, it can happen that physically important consequences of ordinary analyticity do not hold for "generalized analyticity". In the following, we prove analyticity at all points of $\mathfrak{M}_n$ for $n \leqslant 4$, analyticity at non-singular points for $n \geqslant 5$, and boundedness and continuity at singular points for $n \geqslant 5$, and that is what is to be understood by "analytic on $\mathfrak{M}_n$" in the statement of the theorem. It actually is sufficient to guarantee analyticity in the sense of BOCHNER and MARTIN[3].

The proof of the analyticity is completed in four steps. First, differential equations are derived which f satisfies by virtue of its invariance under $L^{\uparrow}$ or $\mathfrak{L}$ (Lemma 4). The scalar products $z_i \cdot z_j$, $j=1, \ldots n$, considered as functions of the vectors $z_1, \ldots z_n$, satisfy these differential equations. Next, it is shown that, in a neighbourhood of a point of $\mathfrak{M}_n$ at which the scalar products span all solutions of the differential equations, f is expandable in a power series of appropriately chosen scalar products (Lemma 5). Lemmas 6 and 7 then show that at every non-exceptional point the scalar products satisfy the conditions of Lemma 5. Finally, to complete the proof, a theorem

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* For $n \leqslant 4$, we shall refer to the points P of $\mathfrak{M}_n$ at which the rank is less than maximum as exceptional although, for $n \leqslant 4$, they are not singular in the sense of algebraic geometry.

on removable singularities is used to show that f is analytic even at the exceptional points for $n \leqslant 4$.

Lemma 1.

Let $f(z_1, \dots z_n)$ be analytic in the tube and invariant under the orthochronous real Lorentz group, $L^{\uparrow}$. Then, f is also invariant under the complex Lorentz group $\mathfrak{L}$, as long as $\Lambda z_1, \dots \Lambda z_n$ is in the tube. When $\Lambda z_1, \dots \Lambda z_n$ lies out of the tube, the relation $f(\Lambda z_1, \dots \Lambda z_n) = f(z_1 \dots z_n)$ defines a single valued analytic continuation of f to the extended tube.

Proof.

Let $z_1, \dots z_n$ be a fixed point of the tube. Then, for all Λ in a suitable neighbourhood of the identity in $\mathfrak{L}$, $\Lambda z_1, \dots \Lambda z_n$ again lies in the tube. In some sub-neighbourhood, N, we can introduce canonical coordinates $\lambda_1, \dots \lambda_6$ such that[4]

1. As Λ runs over N, $\lambda_1, \dots \lambda_6$ vary over a neighbourhood N' of the origin in the complex six-dimensional Euclidean space with (complex) coordinates $\lambda_1, \dots \lambda_6$.

2. The subset of N, for which $\Lambda \varepsilon L^{\uparrow}$, is the subset of N' for which the $\lambda_1, \dots \lambda_6$ are real.

3. The matrix elements $\Lambda^{\mu}{}_{\nu}$ (and therefore the vector components $\sum_{\nu=0} \Lambda^{\mu}{}_{\nu} z^{\nu}$) are analytic functions of $\lambda_1, \dots \lambda_6$.

Since an analytic function of analytic functions is again analytic, $f(\Lambda z_1, \dots \Lambda z_n)$ is an analytic function of $\lambda_1, \dots \lambda_6$ in N'. Furthermore it has the property that for *real* $\lambda_1, \dots \lambda_6$ it is constant. Therefore it is also constant for complex $\lambda_1, \dots \lambda_6$ in N'[5].

Thus, for $\Lambda \varepsilon N \subset \mathfrak{L}$, equation (1) is satisfied.

This result can be extended immediately in two ways. First, the argument applies when Λ runs over the neighbourhood $I_s N$ of the space inversion, $\Lambda = I_s$. Second, (1) also holds if $\Lambda z_1, \dots \Lambda z_n$ can be connected to $z_1, \dots z_n$ by a curve

$$\Lambda(t) z_1, \dots \Lambda(t) z_n;\ 0 \leqslant t \leqslant 1;\ \Lambda(0) = 1;\ \Lambda(1) = \Lambda,$$

lying entirely within the tube and such that it can be covered by a finite number of overlapping neighbourhoods: $\Lambda(t_j) N z_1, \dots \Lambda(t_j) N z_n$, *lying within the tube.*

However, this last argument by no means completes the proof of (1), because it is not clear that all pairs of points $z_1, \dots z_n$ and $\Lambda z_1, \dots \Lambda z_n$, each of which is in the tube, can be connected by a curve of the sort described above. (If Λ is improper, it is $I_s z_1, \ldots I_s z_n$ and $\Lambda z_1, \ldots \Lambda z_n$, which have to be connected by the curve. For simplicity of statement, we consider only proper Λ in the rest of this proof. The extension to improper Λ is trivial). We shall give an explicit construction of such a curve at the end of the proof of this Lemma. Assuming the construction for the present, we have completed the proof of the first statement of the Lemma.

The existence of curves of the above described type is closely connected with the possibility of making a single valued analytic continuation of $f(z_1, \ldots z_n)$ to the extended tube. For, starting from a fixed point $z_1, \ldots . z_n$ of the tube, we can extend the analytic function $f(\Lambda z_1, \ldots \Lambda z_n)$ of Λ over the whole complex Lorentz group, $\mathfrak{L}$. (It is the simplest possible analytic function on $\mathfrak{L}$, a constant.) f is then defined for points $\Lambda z_1, \ldots \Lambda z_n$ of the extended tube. Starting from a different point $z'_1 \ldots . z'_n$ of the tube, f can be defined for the points $Mz'_1, \ldots Mz'_n$, $M \varepsilon \mathfrak{L}$. If it happens that for some Λ and M, $\Lambda z_j = M z'_j$, $j = 1, \ldots n$, the single valuedness of the extension of f would be insured by: $f(z_1, \ldots z_n) = f(z'_1, \ldots z'_n) = f(M^{-1}\Lambda z_1, \ldots M^{-1}\Lambda z_n)$. It is just this identity which is guaranteed by our postponed construction of curves, and therefore f as extended is single valued.

The analyticity of f in the extended tube at $\Lambda z_1, \ldots \Lambda z_n$ follows from its analyticity at $z_1, \ldots z_n$ in the tube, because the partial derivatives at $\Lambda z_1, \ldots \Lambda z_n$ are expressible in terms of partial derivatives at $z_1, \ldots . z_n$, e.g.,

$$\frac{\partial f}{\partial (\Lambda z_1)_\mu}(\Lambda z_1, \ldots \Lambda z_n) = \sum_{\nu=0}^{3} \frac{\partial f(z_1, \ldots z_n)}{\partial (z_1)^\nu} \frac{\partial (z_1)^\nu}{\partial (\Lambda z_1)_\mu}.$$

This completes the proof of the second statement of the Lemma.

It remains to construct a curve $\Lambda(t) z_1, \ldots \Lambda(t) z_n$; $0 \leqslant t \leqslant 1$, $\Lambda(t) \varepsilon \mathfrak{L}$, beginning at an arbitrary point of the tube $z_1, \ldots z_n$, ending at the point $\Lambda z_1, \ldots \Lambda z_n$ of the tube, and lying entirely within the tube. The existence of such a curve is obvious if Λ is a *real* (orthochronous, proper) Lorentz transformation, because every such transformation leaves the tube invariant and their set is connected.

For Λ complex, the required calculations are simpler in a two dimensional matrix formalism in which the four vector z^μ is represented by the matrix

$$Z = \begin{pmatrix} z^0 + z^3 & z^1 - i z^2 \\ z^1 + i z^2 & z^0 - z^3 \end{pmatrix} = \begin{pmatrix} Z_{11} & Z_{12} \\ Z_{21} & Z_{22} \end{pmatrix}. \tag{4}$$

Then the most general proper complex Lorentz transformation is of the form $z^\mu \to z'^\mu$, where the four vector z'^μ belongs to a matrix, Z', given by

$$Z' = AZB^*. \tag{5}$$

Here A and B are 2×2 matrices of determinant one. In particular, the most general (orthochronous, proper) real Lorentz transformation is of this form with $A = B$. This last fact permits us to simplify our problem. Note that (5) can be written

$$Z' = (AB^{-1}) BZB^*, \tag{6}$$

so that the most general complex Lorentz transformation is of the form of a real Lorentz transformation followed by a complex Lorentz transformation of the special form

$$Z' = CZ. \tag{7}$$

It therefore suffices to consider complex Lorentz transformations of this special form. The problem can be simplified further by making a suitable real Lorentz transformation of the final vectors

$$Z' \to DZ'D^* = (DCD^{-1})\, DZD^*.$$

By suitable choice of D, we can bring C into triangular form. In fact, unless the proper values of C are equal, C can be diagonalized. Thus, we can restrict our attention to C of the form

$$\begin{pmatrix} \zeta & 0 \\ 0 & \zeta^{-1} \end{pmatrix}, \tag{8}$$

and

$$\begin{pmatrix} \pm 1 & \tau \\ 0 & \pm 1 \end{pmatrix}. \tag{9}$$

We shall prove that, if Z is in the tube and $Z' = CZ$ is in the tube where C is of the form (8) or (9), then $C(t)Z$ is in the tube where

$$C(t) = \begin{pmatrix} \exp\,[t(\varrho + i\theta)] & 0 \\ 0 & \exp\,[-t(\varrho + i\theta)] \end{pmatrix}, \quad \left.\begin{array}{l} 0 \leqslant t \leqslant 1, \\ \zeta = \exp\,(\varrho + i\theta), \end{array}\right\} \tag{10}$$

$$C\,(t) = \begin{pmatrix} \pm 1 & t\tau \\ 0 & \pm 1 \end{pmatrix}, \quad 0 \leqslant t \leqslant 1, \tag{11}$$

respectively. Thus, it will be possible to choose the same curve independent of the point Z. (Actually, it will be seen that the case of the minus sign in (11) can be excluded.)

The conditions which express in terms of the matrix Z' the fact that the vector $z'_\mu = \xi'_\mu - i\eta'_\mu$ lies in the tube are

$$-4(\eta')^2 = \det(Z' - Z'^*) < 0, \tag{12}$$

$$\eta'_0 = -\frac{1}{2} \operatorname{Im} tr(Z') > 0, \tag{13}$$

as can be derived by a simple computation. Our procedure will be to determine all ζ and τ in (8) and (9) consistent with (12) and (13) for fixed z^μ in the tube. We shall see that, if ζ and τ are consistent, so are ζ^t and $t\tau$ for $0 \leqslant t \leqslant 1$.

Consider first the case (9). Then, the condition (12) reads

$$0 > -4(\eta')^2 = \det\begin{pmatrix} \pm(Z_{11} - \overline{Z}_{11}) + \tau Z_{21} - \overline{\tau} Z_{21}, & \pm(Z_{12} - \overline{Z}_{21}) + \tau Z_{22} \\ \pm(Z_{21} - \overline{Z}_{12}) - \overline{\tau}\,\overline{Z}_{22}, & \pm(Z_{22} - \overline{Z}_{22}) \end{pmatrix}$$

$$= |\tau|^2 |Z_{22}|^2 \mp (s\overline{\tau} + \overline{s}\tau) + \det(Z - Z^*),$$

$$\text{where} \quad s = \overline{Z}_{21} Z_{22} - \overline{Z}_{22} Z_{12}.$$

This inequality can be rewritten in the form

$$|\tau \mp |Z_{22}|^{-2} s|^2 - [|Z_{22}|^{-4} |s|^2 + |Z_{22}|^{-2}(-\det(Z - Z^*))] < 0$$

which describes the interior of a circle in the τ plane about the point

$$\pm |Z_{22}|^{-2} s.$$

As far as the condition (13) is concerned, we note that it is satisfied by all points in the interior of the circle if it is satisfied by any one, because the vector η' must pass through a vector of zero length in order to change the sign of η'_0. With the plus sign in (9), the condition (13) is always satisfied and never for the minus sign, as one sees by considering the case $\tau = 0$.

Evidently, if the point τ is in the interior of the allowed circle, the points $t\tau$, $0 \leqslant t \leqslant 1$ will also be because the origin is in the circle and the circle is convex.

Now we turn to the case (8) in which C is diagonal. Here, there are also two two-dimensional domains of C's consistent with condition (12), one of which is excluded by (13), as we shall see by a detailed consideration. The boundary of the allowed domain is convex in terms of the parameters ϱ and θ defined in (10). This will have to be proved by a detailed computation since the boundary is not an elementary curve.

Condition (12) for the case (8) is

$$0 > -4(\eta')^2 = |Z_{12}|^2 |\zeta|^2 + |Z_{21}|^2 |\zeta|^{-2}$$
$$-(Z_{11}\,\overline{Z}_{22}\,\zeta\overline{\zeta}^{-1} + \overline{Z}_{11}\,Z_{22}\,\overline{\zeta}\zeta^{-1}) + 2\,Re\,(\det Z). \tag{14}$$

This condition is satisfied for $-\zeta$ if it is satisfied for ζ and, in particular, since by assumption it is satisfied for $\zeta = +1$, it is also satisfied for $\zeta = -1$. For $\zeta = -1$, the vector z' is not in the tube. Consequently, by the same type of continuity argument which we used in connection with equation (9), there must be at least two disconnected sets of ζ satisfying (14), one of which does not satisfy (13). Another consequence of (13), which we shall use in the following, is $Z_{11}\bar{Z}_{22} \neq 0$.

We divide the remainder of the argument into three parts.

Case 1.

$$Z_{12} \neq 0,\ Z_{21} \neq 0.$$

In this case, we can divide (14) by $2|Z_{12}|\,|Z_{21}|$, and introduce the new variables

$$\left.\begin{aligned} &\sigma_0 = \arg(\bar{Z}_{11} Z_{22}),\ \zeta = \exp(\varrho + i\theta),\\ &\chi = 2\varrho - ln\,(|Z_{21}||\,Z_{12}|^{-1}),\ \psi = 2\theta - \sigma_0,\\ &\nu = -|Z_{21}|^{-1}|Z_{12}|^{-1}\,Re\,(\det Z),\ \mu = |Z_{11}||Z_{22}||Z_{12}|^{-1}|Z_{21}|^{-1} > 0. \end{aligned}\right| \quad (15)$$

Equation (14) then reads

$$0 > P = \cosh\chi - (\mu\cos\psi + \nu). \quad (16)$$

Since P is periodic in ψ, it suffices to consider (16) in the strip $|\psi| \leq \pi$, $-\infty < \chi < \infty$, and show that it defines a convex region there.

There are two conditions on the coefficients μ and ν:

$$|\nu| \leqslant 1 + \mu, \quad (17)$$

and

$$\nu + \mu > 1. \quad (18)$$

The first of these merely says the real part of the determinant of a matrix is less in absolute value than the sum of the absolute values of the terms which comprise the determinant. The second is a consequence of the fact that for $\zeta = 1$, $P < 0$ by assumption, and therefore $\nu + \mu\cos\sigma_0 > 1$.

From (17) and (18) it follows that there exists an angle ψ_0, $0 < \psi_0 \leqslant \pi$, such that

$$\nu + \mu\ \cos\psi_0 = 1.$$

For

$$|\psi| \leqslant |\psi_0|,\ \nu + \mu\ \cos\ \psi \geqslant 1. \quad (19)$$

The expression (16) for P makes it clear that its behaviour in χ for fixed ψ is: if $\mu\cos\psi + \nu < 1$, $P > 0$ for all χ; if $\mu\cos\psi + \nu = 1$, $P = 0$ for $\chi = 0$ and $P > 0$

for $\chi \neq 0$; if $\mu \cos \psi + \nu > 1$, $P = 0$ for some $\chi_1 = \chi_1(\psi) > 0$ (and also for $\chi = -\chi_1$), $P < 0$ for $|\chi| < \chi_1$, and $P > 0$ for $|\chi| > \chi_1$.

The discussion of the preceding two paragraphs shows that the set of χ and ψ satisfying $P < 0$ in the strip $|\psi| \leqslant \pi$, $-\infty < \chi < \infty$, is connected and invariant under reflections in the $\chi = 0$ and $\psi = 0$ axes, being the domain: $-\chi_1(\psi) < \chi < \chi_1(\psi)$, $-\psi_0 < \psi < \psi_0$, where χ_1 is given by

$$\cosh \chi_1 = \mu \cos \psi + \nu, \; \chi_1 > 0. \tag{20}$$

To complete the argument we will show the convexity of the function χ_1 as a function of ψ.

Differentiating (20) twice and eliminating the first derivative, χ_1', of χ with respect to ψ, we find, for $|\psi| < \psi_0$, $(\sinh \chi_1)^3 \chi_1'' = -\mu Q$, where

$$Q = \cos \psi (\sinh \chi_1)^2 + \mu (\sin \psi)^2 \cosh \chi_1 \tag{21}$$

$$= (\mu \cos \psi + \nu)(\mu + \nu \cos \psi) - \cos \psi, \tag{22}$$

or

$$Q = \mu\nu (\cos \psi + 1)^2 - [1 - (\mu - \nu)^2] \cos \psi. \tag{23}$$

We assert that $Q > 0$ for $|\psi| < \psi_0$. For $0 \leqslant \psi \leqslant \frac{\pi}{2}$, this is an immediate consequence of (21), since both terms on the right hand side of (21) are positive there. For $1/2\, \pi < \psi < \psi_0$, we have $\cos \psi_0 < 0$, and from (19), $\nu = 1 + \mu |\cos \psi_0|$. Using this last fact, we see that, when $\mu > \nu$, $\mu \cos \psi + \nu > 0$, $\mu + \nu \cos \psi > 0$ and $-\cos \psi > 0$ so that (22) immediately implies $Q > 0$. Again, when $\mu \leqslant \nu$, we use the form (23), and note that $1 - (\mu - \nu)^2 = (1 - \mu + \nu)(1 + \mu - \nu)$, and $1 + \nu - \mu > 0$, and $1 + \mu - \nu = \mu (1 - |\cos \psi_0|) \geqslant 0$, so $Q > 0$ in this case too.

Case II.

$$Z_{12} = 0, \; Z_{21} \neq 0 \; (\text{or } Z_{12} \neq 0, \; Z_{21} = 0).$$

Here we define σ_0, ϱ, θ, and ψ as in (15), but μ, ν, χ as follows

$$\chi = -2\varrho + ln \left(\frac{1}{2} |Z_{21}|^2 \right), \; \mu = |Z_{11}||Z_{22}| > 0, \; \nu = -Re(\det Z). \tag{24}$$

Then, the basic inequality (14) takes the form

$$0 > P = e^{\chi} - (\mu \cos \psi + \nu), \tag{25}$$

and the analogues of the inequalities (17) and (18) are

$$|\nu| \leqslant \mu \tag{26}$$

and

$$\nu + \mu > 0\,. \tag{27}$$

(If $Z_{12} \neq 0$, $Z_{21} = 0$, then, in equation (24), replace the definition of χ by $\chi = 2\,\varrho + ln \left(\frac{|Z_{12}|^2}{2} \right)$. This case is essentially the same as that for $Z_{12} = 0$ and $Z_{21} \neq 0$ and will not be discussed further.)

A discussion analogous to that in Case I shows that the region of the strip $|\psi| \leqslant \pi$, $-\infty < \chi < \infty$, as determined by $P < 0$, is given by

$$-\infty < \chi < \chi_1(\psi), \ |\psi| < \psi_0 \leqslant \pi,$$

$$\mu \cos \psi_0 + \nu = 0, \text{ and } e^{\chi_1} = \mu \cos \psi + \nu.$$

Here, $\exp(2\,\chi_1)\,\chi_1'' = -\mu Q$, where $Q = \mu + \nu \cos \psi > 0$, so that the region is convex.

Case III.

$$Z_{12} = Z_{21} = 0\,.$$

Here the basic inequality is

$$0 > P = -(\mu \cos \psi + \nu),$$

with μ, ψ and ν defined as in Case II. μ and ν satisfy the same inequalities as in Case II, namely (26) and (27), so that there again exists a ψ_0 satisfying $\mu \cos \psi_0 + \nu = 0$, $0 < \psi_0 \leqslant \pi$, and the region permitted by $P < 0$ is the strip $|\psi| < \psi_0$, $-\infty < \chi < \infty$ which is obviously convex.

In each of these three cases we have proved that the region of χ, ψ space (or what is essentially the same thing since it is obtained by a translation and change of scale, ϱ, θ space) permitted by conditions (12) and (13) is convex. Since these regions contain the point $\varrho = 0$, $\theta = 0$, they also contain the points $t\varrho$, $t\theta$, $0 \leqslant t \leqslant 1$, corresponding to the transformations (10) and (11); so the proof of Lemma 1 is complete.

Lemma 2.

Let $z_1, \ldots z_n$ and $\zeta_1, \ldots \zeta_n$ be any two sets of n vectors such that

$$Z_{ij} = z_i \cdot z_j = \zeta_i \cdot \zeta_j,\ i, j = 1, \ldots n. \tag{28}$$

If the rank of the $n \times n$ matrix Z is three or four (or, for $n \leqslant 2$ if Z is non-singular), then there exists a complex Lorentz transformation, Λ, such that

$$\Lambda z_i = \zeta_i,\ i = 1, \dots n. \tag{29}$$

If the rank of Z is two or one (and $n > 2$ or $n > 1$, respectively), a $\Lambda \varepsilon \mathfrak{L}$ satisfying (29) will not exist, in general, but there always exists a Λ satisfying

$$\Lambda z_i = \zeta_i + \alpha_i \omega, \tag{30}$$

where α_i are complex numbers and ω is a vector of zero length orthogonal to ζ_i and Λz_i, $i = 1, \dots n$.

Proof.

We note the known fact that, for a symmetric matrix, the rank determined from principal minors is the same as the rank determined from all minors[6]. Thus, if the rank of Z is r, there exist r vectors, say $z_1, \dots z_r$, which have non-vanishing Gram determinant

$$0 \neq G(z_1, \dots z_r) = \det (z_i \cdot z_j),\ i, j = 1, \dots r.$$

This result will be used tacitly many times in the following.

The first step in the proof is to establish the connection between the condition, $G(z_1 \dots z_r) \neq 0$, and the linear independence of the set of vectors $z_1 \dots z_r$. If $G(z_1 \dots z_r) \neq 0$, then the set $z_1 \dots z_r$ is linearly independent. For a relation

$$\sum_{j=1}^{r} \alpha_j z_j = 0 \tag{31}$$

would imply

$$\sum_{j=1}^{r} \alpha_j (z_k \cdot z_j) = 0 \qquad k = 1 \dots r \tag{32}$$

and these last equations have a non-trivial solution $\alpha_1 \dots \alpha_r$ if and only if $\det (z_j \cdot z_k) = 0$, $j, k = 1 \dots r$. The converse, that the linear independence of the set $z_1 \dots z_r$ implies $G(z_1 \dots z_r) \neq 0$, is not true in general. For example,

$$z_1 = (0, 1, 0, 0), \qquad z_2 = (1, 1, 1, 0)$$

is a pair of linearly independent vectors having zero Gram determinant. However, for $r = 4$, the converse holds, for $G(z_1 \dots z_4) = 0$ implies that the equations (32) have a non-trivial solution α_1, a_2, α_3, α_4. This, in turn, implies that there is a vector of the form $\sum_{j=1}^{4} \alpha_i z_j$, with at least one $\alpha_j \neq 0$, which is orthogonal to all z_j. If the z_j were linearly independent, this last would be impossible, since $\sum_{j=1}^{4} \alpha_j z_j$ would then be orthogonal to every vector. Thus, $G(z_1 \dots z_4) = 0$ implies that the set $z_1 \dots z_4$ is linearly dependent.

Next, we show that, under certain circumstances, we can confine our attention to the case $n \leqslant 4$. Let $z_1, \dots z_n$ and $\zeta_1, \dots \zeta_n$ be two sets of vectors such that any $r+1$ element subset of either is linearly dependent, and the matrices $z_j \cdot z_k$ and $\zeta_j \cdot \zeta_k$, $j, k = 1, 2, \dots n$, are equal and of rank r. For convenience, we may suppose that $G(z_1, \dots z_r) \neq 0$. Expand the z_j, $j = r+1, \dots n$ in terms of the z_j, $j = 1, \dots r$.

$$z_j = \sum_{l=1}^{r} \alpha_{jl} z_l, \quad j = r+1, \dots n. \tag{33}$$

The α_{jl} are expressible in terms of scalar products since they are the solutions of the linear equations

$$z_k \cdot z_j = \sum_{l=1}^{r} \alpha_{jl} z_k \cdot z_l, \quad \begin{matrix} j = r+1, \dots n \\ k = 1, \dots r. \end{matrix} \tag{34}$$

The equations (34) have a unique solution because $G(z_1, \dots z_r) \neq 0$. Thus, we see that, if a Lorentz transformation Λ can be found satisfying (29) or (30) for $j = 1, \dots r$, it will also satisfy them for $j = r+1, \dots n$, provided that the rank of $z_i \cdot z_j = \zeta_i \cdot \zeta_j$ is r and there are at most r linearly independent z_i and ζ_i. These last provisos are *always* satisfied if $r = 4$ or 3. For $r = 4$, we have just established the equivalence of $G(z_1 \dots z_4) \neq 0$ and linear independence of the vectors z_1, z_2, z_3, z_4. By the very same argument, it cannot happen that the rank of $z_i \cdot z_j$ is three and the number of linearly independent z_j is four. The fact that there can be "extra" linearly independent vectors when the rank of $z_i \cdot z_j$ is one or two is the source of the possibility that (30), but not (29), may hold.

Now we will construct a Λ satisfying (29) under the assumption of the preceding paragraph, i. e., that there is at most a linearly independent set of r z's and at most a linearly independent set of r ζ's and the matrix $z_i \cdot z_j = \zeta_i \cdot \zeta_j$ has rank r. Our preceding considerations assure us that it suffices to consider the case $n \leqslant 4$. The z_i, $i = 1, \dots n$ span an r-dimensional linear manifold, M. For convenience, we let the $z_1, \dots z_r$ be a linearly independent set. Let the corresponding r-dimensional manifold spanned by the ζ_i, $i = 1, \dots n$ be devoted by N. The orthogonal manifolds $M^{\perp}$ and $N^{\perp}$ respectively, are $4-r$ dimensional and the intersections $M \cap M^{\perp}$ and $N \cap N^{\perp}$ contain only the vector zero. A proof of these last statements is obtained as follows. Supplement the vectors $z_1, \dots z_r$ by $z'_1, \dots z'_{4-r}$ and the vectors $\zeta_1, \dots \zeta_r$ by $\zeta'_1, \dots \zeta'_{4-r}$ so that the resulting sets are bases for the whole four-dimensional space. Then the r equations

$$\sum_{l=1}^{r} \alpha_l (z_l \cdot z_j) + \sum_{l=1}^{4-r} \alpha_{r+l} (z_l' \cdot z_j) = 0 \quad j = 1, \ldots r,$$

have rank r, so they have $4-r$ linearly independent solutions

$$(\alpha_1, \alpha_2, \alpha_3, \alpha_4).$$

Because the basis vectors are linearly independent, the vectors

$$\sum_{l=1}^{r} \alpha_l z_l + \sum_{l=1}^{4-r} \alpha_{l+r} z_l'$$

constitute a linearly independent $4-r$ element set. Consequently, $M^\perp$ has dimension $4-r$. That $M \cap M^\perp$ contains no non-zero vector is equivalent to the statement that the equations

$$\sum_{l=1}^{r} \alpha_l (z_l \cdot z_j) = 0 \quad j = 1, \ldots r \tag{35}$$

have no non-trivial solution. The analogous statements for $N^\perp$ and $N \cap N^\perp$ are obtained by replacing z_i by ζ_i in the above proof.

Notice that the Gram determinant of the entire basis

$$z_1, \ldots z_r, z_1', \ldots z_{4-r}'$$

is the product of the Gram determinants of the sets $z_1, \ldots z_r$ and $z_1', \ldots z_{4-r}'$ so that the Gram determinant of $z_1', \ldots z_{4-r}'$ is non-zero. A similar statement holds for the $\zeta_1', \ldots \zeta_{4-r}'$, and we want to use these facts to show that new bases $z_1'', \ldots z_{4-r}''$ and $\zeta''_1, \ldots \zeta_{4-r}''$ for $M^\perp$ and $N^\perp$, respectively, can be chosen so that

$$z_i'' \cdot z_j'' = \delta_{ij} = \zeta_i'' \cdot \zeta_j'' \quad i, j = 1, \ldots 4-r. \tag{36}$$

Consider $M^\perp$. Since the Gram determinant of the $z_1', \ldots z_{4-r}'$ does not vanish, some scalar product of these vectors does not vanish, and, consequently, there is at least one vector of non-zero length in $M^\perp$. Adjust its length to 1 and call it z_1''. By induction, using the arguments of this and the immediately preceding paragraph, we can construct $z_1'', z_2'', \ldots z_{4-r}''$ orthogonal to each other and of length one. An analogous construction holds for the $\zeta_1'', \zeta_2'', \ldots \zeta_{4-r}''$. It is evidently crucial for the success of the construction that at each stage the relevant Gram determinants are non-zero[7].

Now we are in a position to define the Λ required by (29) as the complex linear transformation determined by the equations

$$\begin{aligned} \Lambda z_j &= \zeta_j \qquad & j &= 1, \ldots r, \\ \Lambda z_j'' &= \zeta_j'' \qquad & j &= 1, \ldots 4-r. \end{aligned}$$

Λ so defined preserves scalar products by virtue of (35) and (36):

$$\left.\begin{aligned} &\left[\Lambda\left(\sum_{j=1}^{r}\alpha_j z_j + \sum_{j=1}^{4-r}\alpha_{j+r} z_j''\right)\right]\cdot\left[\Lambda\left(\sum_{j=1}^{r}\beta_j z_j + \sum_{j=1}^{4-r}\beta_{j+r} z_j''\right)\right] \\ &= \sum_{j,k=1}^{r}\alpha_j\beta_k(\Lambda z_j)\cdot(\Lambda z_k) + \sum_{j,k=1}^{4-r}\alpha_{j+r}\beta_{k+r}(\Lambda z_j'')\cdot(\Lambda z_k'') \\ &= \sum_{j,k=1}^{r}\alpha_j\,\beta_k\,\zeta_j\cdot\zeta_k + \sum_{j,k=1}^{4-r}\alpha_{j+r}\,\beta_{k+r}\,\zeta_j''\cdot\zeta_k'' \\ &= \sum_{j,k=1}^{r}\alpha_j\,\beta_k\,z_j\cdot z_k + \sum_{j,k=1}^{4-r}\alpha_{j+r}\,\beta_{j+r}\,z_j''\cdot z_k'' \\ &= \left(\sum_{j=1}^{r}\alpha_j z_j + \sum_{j=1}^{4-r}\alpha_{j+r} z_j''\right)\cdot\left(\sum_{j=1}^{r}\beta_j z_j + \sum_{r=1}^{4-r}\beta_{j+r} z_j''\right). \end{aligned}\right\} \qquad (37)$$

It is therefore the required Lorentz transformation, and the proof of Lemma 2 is complete for the rank three and four cases.

For rank two and one we must deal with the cases in which the number of linearly independent z_j (or ζ_j) is larger than the rank of the matrix $z_j \cdot z_k$. That we cannot expect to find a Λ satisfying (29) in this case is clear from the example $z_1 = (1, 0, 0, 0)$, $z_2 = (1, 1, i, 0)$; $\zeta_1 = (1, 0, 0, 0)$, $\zeta_2 = (1, 0, 0, 0)$ of vectors satisfying (28) with a matrix of rank one; a Λ certainly cannot carry linearly independent vectors (the z's) into linearly dependent vectors (the ζ's).

Let Z be of rank $r = 1$, or 2, and let $n > r$. There is a subset of r vectors z_i with non-vanishing Gram determinant. They span a subspace which we call M_1. It is a subspace of M, the subspace spanned by all z_i', $i = 1, \ldots n$, whose dimension we denote by m. The corresponding subspaces for the vectors ζ_i, we denote by N_1 (of dimension r) and N (of dimension m'). Because M_1 and N_1 have non-vanishing Gram determinants there is a unique decomposition of the vectors z_i and ζ_i:

$$\begin{aligned} z_i &= z_i' + z_i'' \quad & i &= 1, \ldots n,\ z_i' \,\varepsilon\, M_1,\ z_i'' \,\varepsilon\, M_1^{\perp} \cap M \\ \zeta_i &= \zeta_i' + \zeta_i'' \quad & i &= 1, \ldots n,\ \zeta_i' \,\varepsilon\, N_1,\ \zeta_i'' \,\varepsilon\, N_1^{\perp} \cap N. \end{aligned}$$

Now the rank of the matrices $z_i'' \cdot z_j''$, $\zeta_i'' \cdot \zeta_j''$, $i, j = 1, \ldots n$ must be zero, since the rank of $z_i' \cdot z_j'$ and $\zeta_i' \cdot \zeta_j'$ is already r. Furthermore, the subspaces $M_1^\perp \cap M$ and $N_1^\perp \cap N$ of the $4-r$ dimensional spaces $M_1^\perp$, and $N_1^\perp$ can at most be one-dimensional since they are isotropic and $M_1^\perp$ and $N_1^\perp$ have non-vanishing Grammian[7]. Thus, $z_i'' = \gamma_i \omega'$, $i = 1, \ldots n$, $\gamma_1, \ldots \gamma_n$ complex numbers and $(\omega')^2 = 0$, $\omega' \cdot z_i' = 0$, $i = 1, \ldots n$, and similarly $\zeta_i'' = \delta_i \omega$, $\omega^2 = 0 = \omega \cdot \zeta_i'$, $i = 1, \ldots n$. Incidentally, we see that the dimensions m and m' of M and N are $r+1$ at most.

Now we choose an orthonormal basis ω_i, $i = 1, \ldots 4-r$ for $M_1^\perp$ and η_i, $i = 1, \ldots 4-r$ for $N_1^\perp$ so that ω' and ω lie in the subspaces spanned by ω_1, ω_2 and η_1, η_2 respectively. For $r = 2$, no construction is required to obtain this property of ω's and η's. For $r = 1$, we know the construction is possible because there has to be at least one vector of non-zero length orthogonal to ω' (or ω) and we can take it suitably normalized to be ω_3 (or η_3). Since ω' is a linear combination of ω_1 and ω_2 and of zero length, it must be of the form $a(\omega_1 \pm i\omega_2)$ and by changing the sign of ω_2, if necessary, we can arrange it so that $\omega' = a(\omega_1 + i\omega_2)$. Similarly, $\omega = b(\eta_1 + i\eta_2)$.

Finally, the Lorentz transformation Λ required by (30) is the linear transformation defined by

$$\begin{aligned} \Lambda z_i' &= \zeta_i' \quad \text{for the } r \text{ vectors } z_i' \text{ and } \zeta_i' \text{ which span } M_1 \text{ and } N_1 \\ \Lambda \omega_i &= \eta_i \quad i = 1, 2, \ldots, 4-r. \end{aligned}$$

That this is indeed a Lorentz transformation follows by an argument like that used for the higher ranks. That Λ satisfies (30) follows from the computation

$$\begin{aligned} \Lambda z_k &= \Lambda z_k' + \gamma_k a(\Lambda\omega_1 + i\Lambda\omega_2) \\ &= (\zeta_k - \delta_k \omega) + \gamma_k a(\eta_1 + i\eta_2) \\ &= \zeta_k + (\gamma_k a - \delta_k b)(\eta_1 + i\eta_2) \qquad k = 1, \ldots n. \end{aligned}$$

Therefore, when the rank r of $z_i \cdot z_j$ is one or two, there exists a Lorentz transformation, Λ, such that the Λz_i and ζ_i differ by multiples of a fixed vector orthogonal to all Λz_i and ζ_i, i $= 1, \ldots n$, and of length zero. This completes the proof.

To round out the information provided by Lemma 2, we make three additional remarks. First of all, if Z is an arbitrary complex symmetric $n \times n$ matrix of rank $r \leqslant 4$, it can be written in the form

$$Z_{ij} = \zeta_i \cdot \zeta_j, \; i, j = 1, \ldots n, \tag{38}$$

where $\zeta_1, \ldots \zeta_n$ are four vectors which span a linear manifold M of dimension r. This follows immediately from the standard theorem of algebra which says that, if Z is a complex symmetric $n \times n$ matrix of rank r, there exists a non-singular $n \times n$ matrix S such that

$$Z = S \left\{ \begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array} \right\} S^{\mathsf{T}}, \qquad (39)$$

where the one in the upper left hand corner of the matrix indicated in curly brackets stands for the $r \times r$ unit matrix[8]. One can then take the components ζ_j^{μ} as S_{j1}, iS_{j2}, $\ldots$ iS_{jr} followed by $4-r$ zeros. Equation (39) then reduces to (38). At most r of these vectors can be linearly independent and, in fact, exactly r are because otherwise Z would have rank less than r.

Our second remark is that, if the point $\zeta_1+\alpha_1\omega, \ldots \zeta_n+\alpha_n\omega$ is in the tube and $\omega^2 = 0 = \omega\cdot\zeta_j$, $j=1, \ldots n$, then ω and ζ_j are of the form

$$\omega = a(\omega_1+i\omega_2), \text{ where } \omega_1 \text{ and } \omega_2 \text{ are real and}$$

$$\omega_1^2 = \omega_2^2 = -1,\ \omega_1\cdot\omega_2 = 0,$$

$$\zeta_j = \zeta_j'+\beta_j\,\omega, \text{ where } \zeta_j'\cdot\omega_1 = 0 = \zeta_j'\cdot\omega_2, j = 1, \ldots n,$$

$$\text{and } \zeta_1' \ldots \zeta_n' \text{ is a point of the tube.}$$

To prove these statements, we split ω into its real and imaginary parts: $\omega = q+ir$. Then, $\omega^2 = 0$ implies $q^2 = r^2$ and $q\cdot r = 0$ so that q and r are either light-like and collinear or space-like and orthogonal. The first alternative cannot occur, because the requirement $\omega\cdot\zeta_j = 0$ would then force q and r to be orthogonal to a time-like vector, and the first half of (40) follows if we choose ω_1 and ω_2 as q and r normalized to length minus one. The second half is easily seen if the real and imaginary parts of ζ_j are expanded in terms of ω_1 and ω_2 as follows:

$$\left.\begin{aligned} \xi_j &= \varrho_1^{(j)}\omega_1+\varrho_2^{(j)}\omega_2+\xi_j', \text{ where } \xi_j'\cdot\omega_1 = 0 = \xi_j'\cdot\omega_2,\ j = 1, \ldots n, \\ \eta_j &= \sigma_1^{(j)}\omega_1+\sigma_2^{(j)}\omega_2+\eta_j', \text{ where } \eta_j'\cdot\omega_1 = 0 = \eta_j'\cdot\omega_2,\ j = 1, \ldots n. \end{aligned}\right\} \qquad (40)$$

The orthogonality condition $(\xi_j - i\eta_j)\cdot\omega = 0$ then leads directly to $\sigma_1^{(j)} = \varrho_2^{(j)}$ and $\sigma_2^{(j)} = -\varrho_1^{(j)}$, and therefore

$$\zeta_j = \xi_j - i\eta_j = \xi_j' - i\eta_j' + (\varrho_1^{(j)} - i\sigma_1^{(j)})\,(\omega_1+i\omega_2).$$

If we write $\zeta_j' = \xi_j' - i\eta_j'$, it remains to verify that the point $\zeta_1', \ldots \zeta_n'$ is in the tube. Because $\zeta_1+\alpha_1, \omega, \ldots \zeta_n+\alpha_n\omega$ lies in the tube by assumption, the squares of the lengths of the imaginary parts of $\zeta_j+\alpha_j\omega$, $j = 1, \ldots n$ are positive:

$$[\eta_j' - (\beta_j''\omega_1+\beta_j'\omega_2)]^2 = \eta'^2 - (\beta_j'')^2 - (\beta_j')^2 > 0, \qquad (41)$$

where $(\beta_j+\alpha_j)\ a = \beta_j'+i\beta_j''$ with β_j' and β_j'' real, and β_j and a defined in (40). Clearly, (41) implies $\eta_j'^2 > 0$. Furthermore, β_j'' and β_j' can be continuously decreased to zero without (41) losing its validity. Consequently, if the imaginary part of $\zeta_j + \alpha_j\,\omega$ points into the forward cone, so must that of ζ'_j, so that the point $\zeta'_1, \dots \zeta'_n$ is in the tube.

Our third remark is that, if ζ'_j, $j = 1, \dots n$ and ω have the properties $\omega = a\,(\omega_1 + i\omega_2)$, with ω_1 and ω_2 real and $\omega^2{}_1 = -1 = \omega_2{}^2$, $\omega_1 \cdot \omega_2 = 0$, $\zeta'_j \cdot \omega_1 = 0 = \zeta'_j \cdot \omega_2$ for $j = 1, \dots n$, then there exists a one-parameter family of Lorentz transformations $\Lambda(\theta)$, $0 \leqslant \theta \leqslant \infty$ with the properties $\Lambda(\theta)\zeta'_j = \zeta'_j$, $j = 1, \dots n$ and $\Lambda(\theta)\,\omega = e^{-\theta}\omega$. The transformation $\Lambda(\theta)$ is defined as the identity on vectors orthogonal to ω_1 and ω_2, but

$$\left.\begin{aligned} \Lambda(\theta)\,\omega_1 &= \omega_1 \cos i\theta - \omega_2 \sin i\theta \\ \Lambda(\theta)\,\omega_2 &= \omega_1 \sin i\theta + \omega_2 \cos i\theta\,. \end{aligned}\right\} \tag{42}$$

With its definition completed by linearity, $\Lambda(\theta)$ is a Lorentz transformation with the required properties.

Two important consequences follow immediately from these remarks. The first is that, if a point $\zeta_1 + \alpha_1\omega, \dots \zeta_n + \alpha_n\omega$ with $\omega^2 = 0$, $\omega \cdot \zeta_j = 0$, $j = 1, \dots n$ lies in the extended tube, then all points of the form $\zeta_1 + \alpha'_1\omega, \dots \zeta_n + \alpha'_n\omega$ do also, where $\alpha'_1, \dots \alpha'_n$ are arbitrary complex numbers. Since $\zeta_1 + \alpha_1\omega, \dots \zeta_n + \alpha_n\omega$ is in the extended tube, there exists a complex Lorentz transformation Λ such that $\Lambda\zeta_1 + \alpha_1\Lambda\omega, \dots \Lambda\zeta_n + \alpha_n\Lambda\omega$ is in the tube. Using the second remark, we may then write $\Lambda\zeta_j + \alpha'_j\Lambda\omega$ as $\Lambda\zeta'_j + (\beta_j + \alpha'_j)\Lambda\omega$, where $\Lambda\zeta'_1, \dots \Lambda\zeta'_n$ is a point of the tube, and $\Lambda\omega = a\,(\omega_1 + i\omega_2)$, $\omega_1^2 = -1 = \omega_2^2$ and $\omega_1 \cdot \omega_2 = \Lambda\zeta'_j \cdot \omega_1 = \Lambda\zeta'_j \cdot \omega_2 = 0$, $j = 1, \dots n$. Using the third remark, we obtain a family of transformations $\Lambda(\theta)$ such that

$$\Lambda(\theta)\,[\Lambda\zeta_j + \alpha'_j\Lambda\,\omega] = \Lambda\zeta'_j + e^{-\theta}(\beta_j + a'_j)\Lambda\omega,\ j = 1, \dots n.$$

These equations say that the point $\Lambda\zeta_1 + \alpha'_1\Lambda\omega, \dots \Lambda\zeta_n + \alpha'_n\Lambda\omega$ can be brought arbitrarily near to the point $\Lambda\zeta'_1, \dots \Lambda\zeta'_n$ (which lies in the tube) by a complex Lorentz transformation. Therefore, the point $\Lambda\zeta_1 + \alpha'_1\Lambda\omega, \dots \Lambda\zeta_1 + \alpha'_n\Lambda\omega$ and, consequently, the point $\zeta_1 + \alpha'_1\omega, \dots \zeta_n + \alpha'_n\omega$ lie in the extended tube.

The second consequence is that an invariant analytic function (satisfying the hypotheses of Lemma 1) is necessarily single-valued on $\mathfrak{M}_n$. For points of $\mathfrak{M}_n$ where the rank of $z_i \cdot z_j$ $i, j = 1, \dots n$ is three or min $(3, n)$ the statement follows immediately, because $f(z_1, \dots z_n) = f(\zeta_1, \dots \zeta_n)$ is a consequence of $z_i \cdot z_j = \zeta_i \cdot \zeta_j$, $i, j = 1, \dots n$, since, by Lemma 2 there exists a $\Lambda \varepsilon \mathfrak{L}$ such that $\Lambda z_j = \zeta_j$, $j = 1, \dots n$. For $z_i \cdot z_j$, $i, j = 1, \dots n$, of rank 2, $n > 2$, or 1, $n > 1$, we know by Lemma 2 that $z_i \cdot z_j = \zeta_i \cdot \zeta_j$ implies $\Lambda z_j = \zeta_j + \alpha_j\,\omega$, $j = 1, \dots n$, so to show the single valuedness of f at such points of $\mathfrak{M}_n$ it suffices to show that

$$f(\zeta_1, \ldots \zeta_n) = f(\zeta_1 + \alpha_1\omega, \ldots \zeta_n + \alpha_n\omega). \tag{43}$$

Furthermore, without loss of generality, we may restrict ourselves to the case in which ζ_j and ω have the properties $\omega = a(\omega_1 + i\omega_2)$ with ω_1 and ω_2 real and $\omega_1^2 = \omega_2^2 = -1$, $\omega_1 \cdot \omega_2 = 0$, and $\zeta_j \cdot \omega_1 = 0 = \zeta_j \cdot \omega_2$, $j = 1, \ldots n$. By introducing the $\Lambda(\theta)$ defined in our third remark above, we get

$$\begin{aligned} & f(\zeta_1, \ldots \zeta_n) - f(\zeta_1 + \alpha_1\omega, \ldots \zeta_n + \alpha_n\omega) \\ &= f(\Lambda(\theta)\zeta_1, \ldots \Lambda(\theta)\zeta_n) - f(\Lambda(\theta)\zeta_1 + \alpha_1\Lambda(\theta)\omega, \ldots \Lambda(\theta)\zeta_n + \alpha_n\Lambda(\theta)\omega) \\ &= f(\zeta_1, \ldots \zeta_n) - f(\zeta_1 + \alpha_1 e^{-\theta}\omega, \ldots \zeta_n + \alpha_n e^{-\theta}\omega). \end{aligned}$$

From the continuity of f at $\zeta_1, \ldots \zeta_n$, we see that the last expression vanishes in the limit as $\theta \to \infty$, which proves (43).

Now we turn to the connection between the topology of the vectors $z_1, \ldots z_n$ and the topology on $\mathfrak{M}_n$.

Lemma 3.

Let Z be an $n \times n$ complex symmetric matrix of rank r, $1 \leqslant r \leqslant 4$ and ω an arbitrary real positive number. Then there exists a set of n four vectors $z_1, \ldots z_n$ and a neighbourhood of them consisting of the four-vectors $z_1 + v_1, \ldots z_n + v_n$ with

$$|v_j^\mu| < \omega \quad j = 1, \ldots n;\ \mu = 0, 1, 2, 3 \tag{44}$$

such that $Z_{ij} = z_i \cdot z_j$, $i, j = 1, \ldots n$ and the matrices, Z'_{ij}, defined by

$$Z'_{ij} = (z_i + v_i) \cdot (z_j + v_j),\ i. j, = 1 \ldots n, \tag{45}$$

cover a neighbourhood of Z in the set of complex symmetric matrices of rank $\leqslant 4$, i.e., for suitably chosen $\eta > 0$, every complex symmetric matrix Z' of rank $\leqslant 4$ which satisfies

$$|Z_{ij} - Z'_{ij}| < \eta \qquad i, j = 1, \ldots n$$

is of the form (45) with v_j satisfying (44).

Proof.

The direct determination of the vectors v_i, $i = 1, \ldots n$ satisfying (45) would be somewhat involved, so we make a series of transformations to reduce the problem to a simpler one.

We know from the first remark following Lemma 2 that the matrix Z may be written as a matrix of scalar products: $Z_{ij} = z_i \cdot z_j$, $i, j = 1, \ldots n$, where, if Z has rank r, the vectors z_j, $j = 1, \ldots n$ span a linear manifold of dimension r. That being the case, there exists an r-element linearly independent subset of the n vectors which may as well, for convenience, be taken as $z_1, \ldots z_r$. A new set of z's, which we denote by z'_j, $j = 1, \ldots n$, is defined by

$$z'_j = z_j \quad j = 1, \ldots r$$

$$0 = z'_j = z_j - \sum_{k=1}^{r} \alpha_{jk} z_k, \quad j = r+1, \ldots n.$$

This linear transformation from z's to z''s has determinant 1 and is therefore non-singular. Subsequent to this transformation, we carry out a linear transformation on the subspace M which normalizes and orthogonalizes the z'_j, $j = 1, \ldots r$. The product of these two transformations is given by a matrix A which has the property

$$AZA^{\mathsf{T}} = \begin{array}{c} \\ r \end{array}\!\!\begin{array}{c} r \\ \left(\begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array}\right) \end{array}.$$

Now, since A is non-singular, it maps neighbourhoods of $z_1, \ldots z_n$ into neighbourhoods of $\sum_{j=1}^{n} A_{1j} z_j, \ldots \sum_{j=1}^{n} A_{nj} z_j$ and neighbourhoods of Z into neighbourhoods of AZA^{T} in an invertible manner. Thus, it suffices to prove Lemma 3, in the case that the first r of the vectors z_j are orthonormal and the rest are zero.

This first simplification of the problem uses a transformation, A, which depends only on the z_j, but not on which point in the neighbourhood of the z_j is under consideration. The second transformation we make will be different for each Z', and makes the first r of the vectors $z_j + v_j$ orthogonal to the rest.

Define a new set of v_j by the equations

$$v'_j = v_j \quad j = 1, \ldots r,$$

$$v'_j = v_j - \sum_{k=1}^{r} \beta_{jk} (z_k + v_k) \quad j = r+1, \ldots n,$$

where the numbers β_{jk}, $j = r+1, \ldots n$, $k = 1, \ldots r$, are determined from the condition

$$v'_j \cdot (z_k + v_k) = 0, \; j = r+1, \ldots n, \; k = 1, \ldots r. \tag{46}$$

An elementary calculation yields

$$\beta_{jl} = \sum_{k=1}^{r} Z'_{jk} (Z'^{-1})_{kl} \qquad j = r+1, \ldots n, \; l = 1, \ldots r,$$

where the indicated matrix inverse means the inverse of the $r \times r$ matrix Z'_{jk}, $j, k = 1, \ldots r$. The simplification of the problem achieved in the preceding paragraph enables us to write $Z' = Z + B$ where $Z_{jk} = \delta_{jk}, j, k = 1, \ldots r$, $Z_{jk} = 0$, $j, k > r$. When the matrix elements of B satisfy $|B_{jk}| < \eta, j, k = 1, \ldots n$ and η is sufficiently small, the estimates $|Z'_{jk}| < \eta; j = r+1, \ldots n, k = 1, \ldots r$, and $|(Z'^{-1})_{kl} - \delta_{kl}| < \eta\,(1 - r\eta)^{-1}, k, l = 1, \ldots r$, hold, so that the transformation from the v's to the v''s has an inverse and carries small neighbourhoods of the origin in v space into small neighborhoods in v' space, and vice versa. Thus the problem has been reduced to that of finding $v'_1, \ldots v'_n$ satisfying

$$\left(\begin{array}{c|c} (z_j + v'_j)\cdot(z_k + v'_k) & (z_j + v'_j)\cdot v'_k \\ \hline v'_j\cdot(z_k + v'_k) & v'_j \cdot v'_k \end{array}\right) = \left(\begin{array}{c|c} 1 & 0 \\ \hline 0 & 0 \end{array}\right) + \left(\begin{array}{c|c} B_1 & 0 \\ \hline 0 & B_2 \end{array}\right), \qquad (47)$$

where the dividing line in the matrix is at the r^{th} row and column and

$$(B_1)_{jk} = B_{jk}, \quad j, k = 1, \ldots r, \text{ while}$$

$$(B_2)_{jk} = B_{jk} - \sum_{l, m = 1}^{r} (Z')_{jl}(Z'^{-1})_{lm}(Z')_{mk} \quad j, k = r+1, \ldots n.$$

When $|B_{jk}| < \eta, j, k = r+1, \ldots n$ we have $|(B_2)_{jk}| \leqslant \eta\,(1 - r\eta)^{-1}$.

The simple expedient of requiring v'_k, $k = 1, \ldots r$ to have vanishing components beyond the r^{th} and v'_k, $k = r+1, \ldots n$, vanishing components before the $(r+1)$st in a basis in which the vectors z_k, $k = 1, 2, \ldots r$, are the first r coordinate axes guarantees the orthogonality relations (46). The problem of satisfying the upper left hand corner of the relation (47) then reads in $r \times r$ matrix form

$$(1 + v')\,(1 + v')^{\mathsf{T}} = 1 + B_1,$$

where $1 + v'$ is the $r \times r$ matrix whose k^{th} row is composed of the components of $z_k + v'_k$. By making the special choice of the components of v'_k, $k = 1, 2 \ldots r$, which makes $1 + v'$ symmetric, we are led to the solution

$$1 + v' = [1 + B_1]^{\frac{1}{2}},$$

the right hand side being defined by its power series about the matrix $B_1 = 0$. This series converges for sufficiently small η and leads to components of v' which satisfy $|(v')_j^{\mu}| \leqslant \eta\,(1 - r\eta)^{-1}, j = 1, \ldots r$.

To be sure that the lower right hand corner problem has a solution in terms of vectors with only $4 - r$ components, we have to be sure that the rank of B_2 is $\leqslant 4 - r$. This follows immediately by an argument which we used several times in the proof of Lemma 2. The right hand side of (47) is a matrix of rank $\leqslant 4$. The $r \times r$ matrix $1+B_1$ is of rank r, therefore B_2 is of rank $\leqslant 4-r$. (Compute the determinant of all principal minors of the right hand side of (47), which have $1+B_1$ in their upper left hand corner. They vanish if they have more than four rows and columns.) Then, by the theorem quoted in (39), we know v'_k, $k = r+1, \ldots n$, exist such that $v'_k \cdot v'_l = (B_2)_{kl}$, $k, l = r+1, \ldots n$. Of course, there is a variety of sets of vectors v'_k, $k = r+1, \ldots n$ satisfying this last relation. We have to be sure that sets can be chosen so that their components are uniformly small when the matrix elements of B_2 are small. It can be shown that the v'_k can always be chosen so that*

$$|v_k'^{\mu}| < 8^{\frac{1}{2}[(4-r)-1]} [\sup_{i,j} |(B_2)_{ij}|]^{\frac{1}{2}}. \tag{48}$$

Collecting the estimates of the v'_k and $|(B_2)_{ij}|$ we see that, when η is sufficiently small, components of the v_i satisfying (45) can always be chosen so as to satisfy (44).

Lemmas 1 and 2 enabled us to prove that an invariant analytic function, f, (satisfying the hypotheses of the theorem) is necessarily a single-valued function on $\mathfrak{M}_n$. The continuity of f on $\mathfrak{M}_n$ is an immediate consequence of Lemma 3, because it demonstrates that small neighbourhoods of any point, P, on $\mathfrak{M}_n$ can have pre-images in the space of vectors which are small neighbourhoods of a pre-image of P.

We now turn to the proof of the analyticity of f on $\mathfrak{M}_n$.

Lemma 4.

If $f(z_1, \ldots z_n)$ is a function of the vector variables $z_1, \ldots z_n$ analytic in the tube (extended tube) and invariant under transformations of $L^{\uparrow}$, then the following equations are satisfied at every point of the tube (extended tube).

$$\sum_{j=1}^{n} \left(z_{j\mu} \frac{\partial f}{\partial z_j^{\nu}} - z_{j\nu} \frac{\partial f}{\partial z_j^{\mu}} \right) = 0. \tag{49}$$

Proof.

Let $\Lambda(a)$, $-\infty < a < \infty$, be any one parameter subgroup of real Lorentz transformations, and $z_1, \ldots z_n$ a point of the tube (extended tube). Differentiating the identity

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* The inequality (48) can be proved by going through the classical induction proof of (39) estimating the size of each term. We are indebted to V. BARGMANN for pointing out (48), as well as showing us a version of the proof of this Lemma which we have followed rather closely.

$$f(\Lambda(a)z_1, \ldots \Lambda(a)z_n) = f(z_1, \ldots z_n)$$

with respect to a, we obtain

$$\frac{df}{da} = \sum_{j=1}^{n} \frac{\partial f}{\partial(\Lambda(a)z_j)^\mu} \frac{\partial(\Lambda(a)z_j)^\mu}{\partial a} = 0.$$

At $a = 0$, we have

$$\left.\frac{\partial(\Lambda(a)z_j)^\mu}{\partial a}\right|_{a=0} = \lambda^\mu{}_\nu\, z_j{}^\nu,$$

where $\lambda^\mu{}_\nu$ is a real 4×4 matrix satisfying

$$\lambda^\mu{}_\nu = -\lambda_\nu{}^\mu, \tag{50}$$

and defining the one parameter subgroup. Hence

$$\sum_{j=1}^{n} \lambda^\mu{}_\nu\, z_j{}^\nu \frac{\partial f}{\partial z_j{}^\mu} = 0. \tag{51}$$

Now, any real 4×4 matrix satisfying (50) generates a one parameter subgroup, so we may take λ to have zero matrix elements except for a fixed pair $\lambda_{\mu\nu}$ and $\lambda_{\nu\mu}$, then (51) reduces to (49) and the Lemma is proved.

Considered for fixed z_k, the equations (49) are a set of linear equations in the $4\,n$ unknowns $\frac{\partial f}{\partial z_j{}^\mu}$, $j = 1, \ldots n$, $\mu = 0, 1, 2, 3$. There are at most 6 independent equations. The derivatives of any invariant function must satisfy this set of equations at each point of the tube (extended tube). Of course, the coefficient matrix of the equations varies from point to point.

Lemma 5.

If at a point, $z_1, \ldots z_n$, of the extended tube, the number of linearly independent solutions of the equations (49) is ϱ and this ϱ dimensional linear manifold of solutions is spanned by the solutions which come from ϱ scalar products, then any invariant analytic function, f, may be represented in a neighbourhood of $z_1, \ldots z_n$ of the extended tube as a convergent power series in the ϱ scalar products, i.e., f is an analytic function of the ϱ scalar products at $z_1, \ldots z_n$.

Proof.

In the customary nomenclature, a set of analytic functions $f^{(i)}$ $i = 1, \ldots m \leqslant 4\,n$ of the four-vector variables $z_1, \ldots z_n$ is functionally independent at the point $z_1, \ldots z_n$ if the Jacobian matrix $\frac{\partial f^{(i)}}{\partial z_j{}^\mu}$ ($i = 1, \ldots m$ labels rows; $j = 1, \ldots n$, $\mu = 0, 1, 2, 3$ label columns) has rank m at $z_1, \ldots z_n$. In other words, the m rows of the Jacobian matrix regarded as $4\,n$ component vectors with components labeled by j and μ are linearly independent. Since functional independence at a point is equivalent to the requirement that the determinant of some $m \times m$ minor of the Jacobian matrix be different from zero, functional independence at a point implies functional independence in some neighbourhood of the point.

In this terminology, the hypothesis of the Lemma is that ϱ functionally independent scalar products exist. We shall denote these scalar products by $f^{(i)}$, $i = 1, \ldots \varrho$. Since the Jacobian matrix has rank ϱ, there exists a ϱ element subset, T, of the $4\,n$ variables $z_j{}^\mu$, $j = 1, \ldots n$, $\mu = 0, 1, 2, 3$, such that the determinant of the square matrix

$$\frac{\partial f^{(i)}}{\partial z_j{}^\mu} \quad i = 1, \ldots \varrho,\; z_j{}^\mu \,\varepsilon\, T$$

is non-zero.

Then, by the implicit function theorem for several complex variables,* the $z_j{}^\mu \,\varepsilon\, T$ are analytic functions of $f^{(i)}$ $i = 1, \ldots \varrho$ in a neighbourhood of $f^{(i)}(z_1, \ldots z_n)$ and

$$f(z_1, \ldots z_n) = g\,(f^{(1)}, \ldots f^{(\varrho)}, h^{(1)}, \ldots h^{(4n-\varrho)}),$$

where g is analytic in the variables $f^{(i)}$, $i = 1, \ldots \varrho$ and $h^{(j)}$, $j = 1, \ldots 4\,n - \varrho$ in a neighbourhood of

$$f^{(1)}(z_1, \ldots z_n), \ldots f^{(\varrho)}(z_1, \ldots z_n),\; h^{(1)}(z_1, \ldots z_n), \ldots h^{(4n-\varrho)}(z_1, \ldots z_n).$$

The variables $h^{(j)}$ are the $z_k{}^\mu$ which are not in T. The variables

$$f^{(i)},\; i = 1, \ldots \varrho \text{ and } h^{(j)},\; j = 1, \ldots 4\,n - \varrho$$

are obviously functionally independent in a neighbourhood of $z_1, \ldots z_n$.

The derivatives of f can now be expressed in terms of the derivatives of g as follows:

$$\frac{\partial f}{\partial z_j{}^\mu} = \sum_{i=1}^{\varrho} \frac{\partial g}{\partial f^{(i)}} \frac{\partial f^{(i)}}{\partial z_j{}^\mu} + \sum_{k=1}^{4n-\varrho} \frac{\partial g}{\partial h^{(k)}} \frac{\partial h^{(k)}}{\partial z_j{}^\mu}.$$

However, according to the hypothesis of the Lemma, at the point $z_1, \ldots z_n$

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* See B and M, p. 39, theorem 9.

$$\frac{\partial f}{\partial z_j^{\mu}} = \sum_{i=1}^{\varrho} \alpha_i \frac{\partial f^{(i)}}{\partial z_j^{\mu}}.$$

Hence,

$$\sum_{i=1}^{\varrho} \left(\frac{\partial g}{\partial f^{(i)}} - \alpha_i \right) \frac{\partial f^{(i)}}{\partial z_j^{\mu}} + \sum_{i=1}^{4n-\varrho} \frac{\partial g}{\partial h^{(i)}} \frac{\partial h^{(i)}}{\partial z_j^{\mu}} = 0.$$

But regarded as vectors with $4n$ components, $\frac{\partial f^{(i)}}{\partial z_j^{\mu}}$, $i = 1, \ldots \varrho$ and $\frac{\partial h^{(i)}}{\partial z_j^{\mu}}$, $i = 1, \ldots 4n - \varrho$ are linearly independent. (That is what the functional independence of the $f^{(i)}$ and $h^{(i)}$ means.) Therefore, their coefficients in this equation must vanish. In particular,

$$\frac{\partial g}{\partial h^{(i)}} = 0, \quad i = 1, \ldots 4n - \varrho,$$

so g is independent of the $h^{(i)}$ and the Lemma is proved.

Lemma 6.

Let N be the maximum number of linearly independent vectors contained in the set of 4-vectors $z_1, \ldots z_n$, then the set of six linear equations

$$\sum_{j=1}^{n} (z_{j\mu} X_{j\nu} - z_{j\nu} X_{j\mu}) = 0 \quad \mu, \nu = 0, 1, 2, \quad 3\ \mu < \nu \tag{52}$$

for the $4n$ quantities $X_{j\mu}$, $j = 1, \ldots n$, $\mu = 0, 1, 2, 3$ has the rank

N	1	2	$\geqslant 3$
rank	3	5	6

Proof.

If R is a non-singular linear transformation of four dimensional space, it is clear that the set of equations (52) has the same rank as the set

$$\sum_{j=1}^{n} [(Rz_j)_{\mu} (RX_j)_{\nu} - (Rz_j)_{\nu} (RX_j)_{\mu}] = 0, \quad \mu_1 v = 0, 1, 2, 3$$

for the $4n$ quantities $(RX_j)_{\mu}$. Then, with a suitable choice of R, the last $(4-N)$ components of vectors Rz_j, $j = 1, \ldots n$ can be made to vanish. Having reduced the problem to this simplified form, we drop the R and assume the last $4-N$ of the components of the Z_j vanish.

To find the number of linearly independent equations (52), consider a possible linear dependence among them

$$\sum_{\substack{\mu,j=0\\ \mu<\nu}}^{3} a^{\mu\nu} \sum_{j=1}^{n} (z_{j\mu}X_{j\nu} - z_{j\nu}X_{j\mu}) = 0$$

for all $X_{l,k}$, i.e.,

$$\sum_{\substack{\mu=0\\ \mu<k}}^{3} a^{\mu\varkappa} z_{l\mu} - \sum_{\substack{\nu=0\\ k<\nu}}^{3} a^{\varkappa\nu} z_{l\nu} = 0\,,\ l = 1, \ldots n,\ \varkappa = 0, 1, 2, 3$$

or

$$Az_l = 0\,,\ l = 1, \ldots n,$$

where we have written

$$-A^{\nu\mu} = A^{\mu\nu} = a^{\mu\nu},\ \mu<\nu,\ A^{\mu\mu} = 0\,,\ \mu, \nu = 0, 1, 2, 3.$$

Thus, the rank of the equations (52) is six minus the number of linearly independent skew symmetric matrices, A such that $Az_i = 0\,,\ i = 1, 2, \ldots n$. The most general A has the form $\begin{pmatrix} 0 & 0 \\ 0 & A' \end{pmatrix}$ where A' is an arbitrary antisymmetric $(4-N) \times (4-N)$ matrix. The numbers tabulated in the Lemma are just six minus the number of linearly independent A'.

Lemma 7.

Let $z_1, \ldots z_n$ be a set of n four-vectors of which some four-element subset (or n element subset if $n<4$) is linearly independent. Then, the number of linearly independent solutions of equations (52) which arise from scalar products $f^{(i)}$ of the four vectors according to

$$X_{j\nu}^{(i)} = \frac{\partial f^{(i)}}{\partial z_{j\nu}}$$

is $4\,n-6$ if $n \geqslant 3$, is 3 if $n = 2$, and 1 if $n = 1$.

Proof.

It is clear that, for $n>3$, *not more* than $4\,n-6$ linearly independent solutions of equations (52) can be obtained from scalar products because there are at most $4\,n-6$ functionally independent scalar products. This follows immediately from equation (34), which expresses $z_k \cdot z_l$, k, $l \geqslant 5$ in terms of $z_i \cdot z_j$, where $i = 1, 2, \ldots n, j = 1, 2, 3, 4$. Of these $4\,n$, 6, namely $z_i \cdot z_j$, $i>j$, i $= 1, 2, 3, 4$ are expressible in terms of the rest. For $n = 3, 2, 1$ it is obvious that there are respectively 6, 3 and 1 independent scalar products at most and therefore 6, 3, and 1 linearly independent solutions of (52) at most.

To show that these upper limits on the number of solutions are actually realized under the hypothesis of the Lemma, we proceed as follows.

Denote a vector in the space of solutions of (52) by $(\zeta_1, \dots \zeta_n)$ where the ζ_i are four-dimensional vectors. This notation is chosen so that an invariant analytic function F generates a solution $\left(\frac{\partial F}{\partial z_1} \dots \frac{\partial F}{\partial z_n}\right)$ where $\frac{\partial F}{\partial z_j}$ stands for the four-dimensional vector with components, $\frac{\partial F}{\partial z_j^\mu}$. In this notation, the solution of (52) which comes from the scalar product $z_j \cdot z_k$ is

$$(0, \dots 0, z_k, 0, \dots 0, z_j, 0, \dots 0), \tag{53}$$

$$\xrightarrow[j^{th}\ place]{}$$

$$\xrightarrow{k^{th}\ place}$$

and from z_j^2

$$(0, \dots 0, 2\, z_j, 0, \dots 0), \tag{54}$$

$$\xrightarrow[j^{th}\ place]{}$$

By convention, we will accept (54) as the value of (53) for $j = k$.

The most general solution of (52) arising from scalar products is of the form

$$(\zeta_1, \dots \zeta_n) = \sum_{j,k=1}^{n} a_{jk}\, (0, \dots 0, z_k, 0, \dots 0, z_j, 0, \dots 0).$$

Here, evidently

$$\zeta_j = \sum_{k=1}^{n} (a_{jk} + a_{kj})\, z_k,$$

so that the antisymmetric part of the matrix a_{ik} does not contribute and a_{jk} may as well be chosen symmetric.

Now, for convenience, let the first four z_j (or first n if $n < 4$) be the linearly independent set whose existence is assumed in the Lemma. Then we can write

$$z_k = \sum_{l=1}^{m} b_{kl} z_l, \quad k = 1, \dots n, \tag{55}$$

where $m = \min(4, n)$ and b is an $n \times m$ matrix of rank m. Substituting (55) into the expression for the solution vector we see that, in the basis for solution vectors provided by $(z_{l_1}, z_{l_2}, \dots z_{l_n})$, $l_j = 1, \dots m$, $j = 1, \dots n$, the most general solution arising from scalar products is of the form of an $n \times m$ matrix AB, where A is an arbitrary symmetric $n \times n$ matrix and B is a fixed $n \times m$ matrix of rank m.

To count the number of linearly independent AB simply, write B as the product of a non-singular $n \times n$ matrix B' and the $n \times m$ matrix whose first m rows form the unit matrix and whose last $n - m$ are zero:

$$B = B'\left(\frac{1}{0}\right).$$

This is always possible because B is of rank m. The number of linearly independent matrices AB is the same as the number of linearly independent matrices

$$(B')^{\mathsf{T}} AB'\left(\frac{1}{0}\right),$$

i.e., the same as the number of linearly independent matrices of the form

$$\begin{pmatrix} S_1 \\ S_2 \end{pmatrix},$$

where S_2 is an arbitrary $(n-m)\times m$ matrix and S_1 is an arbitrary symmetric $m\times m$ matrix. There are obviously $m(n-m)+\frac{1}{2}\,m(m+1)$ linearly independent of these, which immediately yields the statement of the Lemma.

Completion of the proof.

Lemmas 1 to 7 establish the single valuedness, boundedness, and continuity of f everywhere on $\mathfrak{M}_n$, and its analyticity on $\mathfrak{M}_n$ at every non-exceptional point, i.e., every point where the matrix $z_i\cdot z_j$, $i,j = 1, 2 \ldots n$, has the maximum possible rank, min $(4,n)$. To complete the proof of the theorem, we want to show that in those cases where the set of exceptional points is not singular in the sense of algebraic geometry, viz. $n = 1, 2, 3, 4$, f is also analytic there. For this purpose, we use a standard theorem on removable singularities which asserts*: Let f be a function which is analytic in a neighbourhood of a point, P, with the possible exception of a variety passing through P, the variety being defined as the set of zeros of a function analytic in the neighbourhood of P. Suppose that f is continuous or merely bounded throughout the neighbourhood of P. Then f is analytic throughout the neighbourhood of P. In our case, the variety is obtained by setting the analytic function det $(z_j\cdot z_k) = 0$. The required analyticity and continuity of f having been established by our Lemmas 1–7, the proof of the theorem is complete.

2. The varieties $\mathfrak{M}_n$.

As we have seen in Lemma 3, every rank $\leqslant 4$ complex symmetric matrix is a matrix of scalar products of four vectors, so that $\mathfrak{M}_n$ is a subset of the set of all complex symmetric $n\times n$ matrices of rank $\leqslant 4$. The same Lemma

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[*] B and M, p. 173, theorem 5.

shows that $\mathfrak{M}_n$ is an open subset. It is clearly connected because it is the continuous image of a connected set, the tube. It is also simply connected by virtue of Lemma 3, although we shall forgo a formal proof. (The idea is, given a closed curve on $\mathfrak{M}_n$ which has to be shrunk to a point, to construct a closed curve of vectors in the tube whose image in $\mathfrak{M}_n$ is the given curve. Then, because the tube is simply connected, the curve of vectors can be shrunk to a point which implies that their image can be shrunk to a point.) Not every rank < 4 complex symmetric $n \times n$ matrix, Z, is in $\mathfrak{M}_n$, for example if Z has real positive diagonal elements it is not in $\mathfrak{M}_n$. We shall not attempt a quantitative characterization of $\mathfrak{M}_n$ at this stage, but only remark that it need not be the natural domain of analyticity for the analytic functions which occur in field theory. For example, the first named author showed in his thesis[9] that the local commutativity conditions, I equation (11), always make it possible to extend the analytic function determined by the threefold vacuum expectation value $(\Psi_0\, \varphi(x_1)\, \varphi(x_2)\, \varphi(x_3)\, \Psi_0)$ beyond $\mathfrak{M}_2$. On the other hand, it is clear that such functions cannot in general be extended to all complex symmetric rank $\leqslant 4$, $n \times n$ matrices because they must have branch lines in order to conform with physical requirements. (See, for example, the discussion of $F^{(2)}(z_{12}^2)$ in I, Section 4.)

The restriction to $n \times n$ matrices of rank $\leqslant 4$ is of course no restriction at all for $n \leqslant 4$ so the $\mathfrak{M}_n$ for $n \leqslant 4$ are open sets in Euclidean $1/2\, n(n+1)$ space. For $n \leqslant 5$ the restriction to rank $\leqslant 4$ on an $n \times n$ matrix Z_{ij} can be stated

$$\det \begin{pmatrix} Z_{i_1 j_1} & \ldots & Z_{i_1 j_5} \\ & & \\ Z_{i_5 j_1} & \ldots & Z_{i_5 j_5} \end{pmatrix} = 0$$

for each pair of five element subsets $i_1, \ldots i_5$ and $j_1, \ldots j_5$ of $1, 2, \ldots n$. The tangent spaces of $\mathfrak{M}_n$ are determined by taking the differential of the left hand side of (56). The result is a set of linear equations for the dZ_{ij} whose coefficients are determinants of 4×4 minors of Z. At any point of $\mathfrak{M}_n$ where all determinants of 4×4 principal minors of Z vanish, these equations are satisfied for any choice of dZ_{ij}. Consequently, at such a singular point, the tangent space is $1/2\, n\, (n+1)$ dimensional. On the other hand, as we learned in Lemma 7, the dimension at a non-singular point is $4\,n-6$.

Now we want to study the relation of the points of $\mathfrak{M}_n$ to those of the form $Z_{ij} = \xi_i \cdot \xi_j$, ξ_i real, $i,j = 1, \ldots n$. We will refer to such Z as physical because the arguments of the physically given vacuum expectation values are real vectors. We remark that every physical point Z is either in the interior of $\mathfrak{M}_n$ or on its boundary, because $\xi_j \cdot \xi_k$ is the limit of $(\xi_j - i\eta_j)\cdot(\xi_k - i\eta_k)$ as the η's approach zero. No physical point Z can be in the interior of $\mathfrak{M}_n$ if any of the vectors $\xi_j, j = 1, 2, \ldots, n$ (of which Z is the set of scalar products) is light-like or time-like. To see this, consider a general point $\xi'_j - i\eta_j$, $j = 1, 2, \ldots n$ of the tube. The corresponding point of $\mathfrak{M}_n$ is given by

$$Z'_{jk} = \xi'_j \cdot \xi'_k - \eta_j \cdot \eta_k - i\,(\xi'_j \cdot \eta_k + \eta_j \cdot \xi'_k).$$

If Z' is to be real, it is necessary that each of the ξ'_j be space-like since it is orthogonal to a vector inside the light cone. But then the diagonal elements of Z', $\xi'^2_j - \eta^2_j, j = 1, \ldots n$, are negative so that Z' can be a physical point $Z, Z_{jk} = \xi_j \cdot \xi_k, j, \varkappa = 1, \ldots n$ only if the vectors ξ_j satisfy $\xi^2_j = \xi'^2_j - \eta^2_j$. On the other hand, as we now will show, some physical points with space-like ξ_j do lie in the interior of $\mathfrak{M}_n$. Since this is a fact of considerable physical significance, and the geometrical relationships are rather involved, it is worth introducing some notation to describe the situation. We denote by S_n the set of all physical points, Z, which arise from space like vectors, i.e. of the form $Z_{jk} = \xi_j \cdot \xi_k$, $j, k = 1, \ldots n$ with ξ_j real and space-like. The subset of S_n which arises from ξ_j, $j = 1, \ldots n$, lying in a space-like three dimensional linear manifold, we will denote by T_n. We will also call T_n the equal time-manifold since it is the set of matrices whose elements can be taken as scalar products of vectors arising from vectors $\xi_j = x_j - x_{j+1}$, $j = 1, \ldots n$, where the x_j have equal first components.

We first prove that a subset of T_n lies in the interior of $\mathfrak{M}_n$, and then pass to neighbourhoods of that subset. Consider the vectors $\xi'_j - i\eta_j$, $j = 1, \ldots n$, where $\eta_j = \alpha_j \eta$, α_j is a real positive number, η is a real unit vector in the direction of the time axis, and ξ'_j, $j = 1, \ldots n$ are real vectors with zero component in the time direction and in one space direction, say the direction of the third axis. Then,

$$Z' = (\xi'_j - i\eta_j) \cdot (\xi'_k - i\eta_k) = \xi'_j \cdot \xi'_k - \alpha_j \alpha_k = \xi_j \cdot \xi_k,$$

where ξ_j is defined as ξ'_j plus a vector along the third axis with component α_j. The vectors ξ_j evidently all have zero time components, so that Z' is in T_n. Although the point $\xi_1, \ldots \xi_n$ does not lie in the tube, it must, by Lemmas 2 and 3, lie in the extended tube. Furthermore, by suitable choice of the components of ξ'_j, $j = 1, \ldots n$, it can be arranged that Z' has rank three. By Lemma 3, it then follows that vectors lying in neighbourhoods of ξ_j have scalar products which cover full neighbourhoods of Z' in $\mathfrak{M}_n$. Thus, the fact that the particular points Z' chosen above lie in $\mathfrak{M}_n$ implies that the physical points which arise from all $\xi_1, \ldots \xi_n$ lying in a suitably small neighbourhood of the chosen $\xi_1, \dots \xi_n$ also lie in $\mathfrak{M}_n$. This shows that $T_n \cap \mathfrak{M}_n$ and $S_n \cap \mathfrak{M}_n$ have the same dimension as T_n and S_n, respectively.

Not all of S_n lies in $\mathfrak{M}_n$, but we will not attempt to prove this now nor to characterize those points of S_n which lie on the boundary of $\mathfrak{M}_n$. We content ourselves here with the simplest consequences of the preceding results on T_n and S_n. The set $S_n \cap \mathfrak{M}_n$ has been shown to be of the same dimension as S_n and to contain, for suitably chosen ε, all real symmetric matrices Z' of rank $\leqslant 4$ satisfying $|Z'_{jk} - \xi_j \cdot \xi_k| < \varepsilon$. This set is a real environment* for an analytic function defined on $\mathfrak{M}_n$; an analytic function f is uniquely determined all over $\mathfrak{M}_n$ if its values are given on this set. We shall see in the next section that this result has important physical consequences.

The points of T_n are always of rank $\leqslant 3$ so that for $n \geqslant 5$, $T_n \cap \mathfrak{M}_n$ lies in the singular subset of $\mathfrak{M}_n$ where the ordinary definition of analyticity fails. The set $T_4 \cap \mathfrak{M}_4$ is of (real) dimension nine while $S_4 \cap \mathfrak{M}_4$ is of dimension ten so that $T_4 \cap \mathfrak{M}_4$ is not a real environment. On the other hand, $T_1 \cap \mathfrak{M}_1$, $T_2 \cap \mathfrak{M}_2$ and $T_3 \cap \mathfrak{M}_3$ have the same dimension as $S_1 \cap \mathfrak{M}_1$, $S_2 \cap \mathfrak{M}_2$ and $S_3 \cap \mathfrak{M}_3$, so that they form real environments for analytic functions on $\mathfrak{M}_1$, $\mathfrak{M}_2$, and $\mathfrak{M}_3$, respectively.

3. Physical Applications.

Some physical applications of the theorem of Section 1 were already discussed in I (See, for example, the formulation of local commutativity given in I equation (11).) They arise, like those to be discussed below, when the theorem is applied to the invariant analytic function

$$F^{(n)}(z_1, z_2, \dots z_{n-1})$$

whose boundary value, as all $\eta_j \to 0$, $j = 1, 2, \dots n$, is the vacuum expectation value

$$F^{(n)}(\xi_1, \dots \xi_{n-1}) = (\Psi_0, \varphi(x_1) \dots \varphi(x_n)\, \Psi_0).$$

Here, in a notation somewhat different from I, we have written

$$z_j = \xi_j - i\eta_j \text{ and } \xi_j = x_j - x_{j+1} \quad j = 1, \dots n-1.$$

The first consequence of the theorem is that $F^{(n)}(\xi_1, \dots \xi_{n-1})$ *is an analytic function of the real variables* $Z_{ij} = \xi_i \cdot \xi_j$ $i, j = 1, \dots n-1$ *in an open subset of the set where all* ξ_j *are space-like,* i.e. *in the notation of the preceding section, as long as* Z *belongs to a certain open subset of* $S_{n-1} \cap \mathfrak{M}_{n-1}$. This con-

---

* See B and M, pp. 33–34, for the definition of a real environment in Euclidean space. The same definition works here because a neighbourhood of a non-singular point in $\mathfrak{M}_n$ is essentially a Euclidean neighbourhood.

clusion follows immediately from the analysis which showed that $S_{n-1} \cap \mathfrak{M}_{n-1}$ is a real environment in $\mathfrak{M}_{n-1}$. (Recall that $\mathfrak{M}_n$ is the set of all complex symmetric matrices of the form $z_i \cdot z_j$, $i,j = 1, 2, \ldots n$, with z_i in the tube. Of course, on $\mathfrak{M}_n$ for $n \geqslant 5$, the ordinary definition of analyticity has no meaning at the exceptional points where the rank of $z_i \cdot z_j$ is less than 4. See the discussion in the outline of the proof in Section 1.

Furthermore, *the vacuum expectation value*

$$(\Psi_0, \varphi(x_1) \ldots \varphi(x_n) \Psi_0)$$

is uniquely determined from its values for space-like separated $x_1, \ldots x_n$. It is possible to regard this result as a quantitative formulation of the intuitive feeling that in a Lorentz invariant theory the equivalence of descriptions in different Lorentz frames should somehow restrict the possible correlations between the values of physical quantities at different points in space time.

For $F^{(2)}(\xi_1)$, $F^{(3)}(\xi_1, \xi_2)$, and $F^{(4)}(\xi_1, \xi_2, \xi_3)$ an even more striking result holds:

$$(\Psi_0, \varphi(x_1)\varphi(x_2)\Psi_0), \quad (\Psi_0, \varphi(x_1)\varphi(x_2)\varphi(x_3)\Psi_0),$$

and

$$(\Psi_0, \varphi(x_1)\varphi(x_2)\varphi(x_3)\varphi(x_4)\Psi_0)$$

are uniquely determined from their values at equal times, i.e., in the notation of the preceding section from their values for $Z_{ij} = \xi_i \cdot \xi_j$ *with* $Z \varepsilon T_1, \ T_2, T_3$, *respectively.* We want to emphasize that all three of these results hold in both local and non-local field theory.

The most important application of the preceding remarks we know of is to the proof of the following theorems which are extensions of results stated by R. HAAG[10].

Theorem (Generalized HAAG's Theorem First Part).

Let two theories (distinguished by a subscript $j = 1, 2$) of a neutral scalar field be given whose canonical variables are related at time t by a unitary transformation, V:

$$U_j(\vec{a}, R)\,\varphi_j(\vec{x}, t)\,U_j(\vec{a}, R)^{-1} = \varphi_j(R\vec{x} + \vec{a}, t) \quad j = 1, 2 \tag{57}$$

$$U_j(\vec{a}, R)\,\pi_j(\vec{x}, t)\,U_j(\vec{a}, R)^{-1} = \pi_j(R\vec{x} + \vec{a}, t) \quad j = 1, 2. \tag{58}$$

(Transformation law of field variable and canonical conjugate under Euclidean transformation.)

$$\left.\begin{aligned} \left[\pi_j(\vec{x}, t), \ \varphi_j(\vec{y}, t)\right] &= i^{-1}\delta(\vec{x} - \vec{y}) \quad j = 1, 2 \\ \left[\pi_j(\vec{x}, t), \pi_j(\vec{y}, t)\right] = 0, &\ \left[\varphi_j(\vec{x}, \ t), \ \varphi_j(\vec{y}, t)\right] = 0 \end{aligned}\right\} \tag{59}$$

(Commutation Relations)

$$\varphi_2(\vec{x}, t) = V\varphi_1(\vec{x}, t) V^{-1}, \quad \pi_2(\vec{x}, t) = V\pi_1(\vec{x}, t) V^{-1}. \tag{60}$$

Here $(\vec{a}, R)$ represents the Euclidean transformation: rotate by R and translate by $\vec{a}$; the unitary transformations, $U_j(\vec{a}, R)$, give the corresponding transformations of the states in the two theories.

Then

$$U_2(\vec{a}, R) = VU_1(\vec{a}, R) V^{-1}. \tag{61}$$

If each of the theories contains a unique normalizable state Ψ_{0j}, $j = 1, 2$, invariant under Euclidean transformation:

$$U_j(\vec{a}, R) \Psi_{0j} = \Psi_{0j} \quad j = 1, 2,$$

then

$$c\,\Psi_{02} = V\Psi_{01},$$

where c is a constant of absolute value 1.

Proof.

From (57), (58), and (60) we can easily derive that the operators

$$U_1(\vec{a}, R)^{-1} V^{-1} U_2(\vec{a}, R) V \tag{62}$$

commute with $\varphi_1(\vec{x}, t)$ and $\pi_1(\vec{x}, t)$ for all $\vec{x}$. Because the φ_1 and π_1 form an irreducible set* of operators, (62) must be a constant multiple of the identity operator: $\omega(\vec{a}, R)\,1$ and

$$U_2(\vec{a}, R) = \omega(\vec{a}, R)\, VU_1(\vec{a}, R)V^{-1}. \tag{63}$$

From (63), it follows that $(\vec{a}, R) \to \omega(\vec{a}, R)$ is a continuous unitary one dimensional representation of the Euclidean group and therefore $\omega(\vec{a}, R) = 1$.[11] This completes the proof of the first half of the theorem. To prove the second half, note that

$$U_1(\vec{a}, R)\, \Psi_{01} = \Psi_{01}$$

and (63) imply

$$U_2(\vec{a}, R)\, V\, \Psi_{01} = V\, \Psi_{01}.$$

Thus, by the uniqueness of Ψ_{02}, $V\Psi_{01}$ is a multiple, c, of Ψ_{02}. Since V is unitary, $|c| = 1$.

---

* That $\varphi_1(\vec{x}, t)$ and $\pi_1(\vec{x}, t)$ form an irreducible set is what we mean by our assumption that the theory is a theory of the scalar field φ_1. This assumption is made for simplicity. In a theory in which the field φ_1 interacted with a spinor field, ψ, one would only have to introduce the hypothesis that $\varphi_1, \pi_1, \psi, \bar{\psi}$, form an irreducible set, together with the appropriate extension of (57) . . . (61), to obtain an analogous theorem.

It should be noticed that only the properties of the fields and states under Euclidean transformation at time t have been used in the proof of the theorem. To one accustomed to the formalism of non-relativistic quantum mechanics, the conclusion of the theorem is in no way surprising; V always exists in such theories. Of course, there, V is a function of time, and physically different theories will give a different time dependence for V. The surprise comes when, following HAAG, one combines the preceding assumptions with those of relativistic invariance.

Theorem (Generalized HAAG's Theorem Part II).

Let two theories of a neutral scalar field be given satisfying the hypotheses of the preceding theorem. Let the theories be invariant under inhomogeneous Lorentz transformations (a, Λ) and suppose the fields transform as follows:

$$U_j(a,\Lambda)\,\varphi_j(x)\,U_j(a,\Lambda)^{-1} = \varphi_j(\Lambda x + a) \qquad j = 1, 2. \tag{64}$$

Suppose further that the states Ψ_{0j} are invariant under inhomogeneous Lorentz transformation

$$U_j(a, \Lambda)\,\Psi_{0j} = \Psi_{0j} \qquad j = 1, 2, \tag{65}$$

and that no states of negative energy exist.

Then the first four vacuum expectation values are equal in the two theories.

$$(\Psi_{01}, \varphi_1(x_1) \ldots \varphi_1(x_n)\,\Psi_{01}) = (\Psi_{02}, \varphi_2(x_1) \ldots \varphi_2(x_n)\,\Psi_{02}) \tag{66}$$

Proof.

From the preceding theorem we have for equal times $x_1^0 = x_2^0 = \ldots = x_n^0$:

$$\begin{aligned}(\Psi_{01}, \varphi_1(x_1) \ldots \varphi_1(x_n)\,\Psi_{01}) &= (V\Psi_{01}, V\varphi_1(x_1)V \ldots\ldots V\varphi_1(x_n)V^{-1}V\Psi_{01})\\ &= (\Psi_{02}, \varphi_2(x_1) \ldots \varphi_2(x_n)\,\Psi_{02}).\end{aligned}$$

Thus, all vacuum expectation values are equal for equal times in the two theories. For $n = 1, 2, 3, 4$, equality for all times $x_1^0 + x_2^0 + \ldots + x_n^0$ follows from equality for equal times by the argument presented earlier in this section. This completes the proof. The hypotheses about the absence of negative energy states and the existence of the vacuum are necessary in order that the vacuum expectation values be boundary values of analytic functions to which our previous analysis applies.

It should be noticed that we have *not* made the assumption that the two theories transform according to equivalent representations of the inhomogeneous Lorentz group; our hypotheses do not exclude a priori the possibility that the two theories have different bound states, for example. Further, we have not assumed any particular transformation law for the operators π under Lorentz transformations and time translations. Only the behaviour of $\pi(\vec{x}, t)$ for one particular time under Euclidean transformations is needed.

The uniqueness of the vacuum state is crucial to the argument. If it were possible to form normalizable states of zero three-momentum from states of mass greater than zero, the hypothesis of a unique normalizable state of zero three-momentum would be unnatural and the second theorem physically trivial. V could then carry Ψ_{01} into a superposition of Ψ_{02} and those other states of zero three-momentum. However, Wigner's analysis of the unitary representations of the inhomogeneous Lorentz group[12] shows that states can never be normalizable which are superpositions of states of mass greater than zero and have zero three-momentum, and Haag's theorem is very far from physically trivial.

As a particular case one can take the field φ_1 to be a free field satisfying

$$(\Box + m^2)\,\varphi_1(x) = 0\,,\ [\varphi_1(x),\, \varphi_1(y)] = i^{-1}\Delta(x-y).$$

Then we conclude: *no theory of interaction exists in which the ordinary representation of the annihilation and creation operators is used and the first four vacuum expectation values differ from their free field values. If relativistic theories of interaction exist with vacuum expectation values, $F^{(n)}$, different from the free field values for $n = 1, 2, 3, 4$, either they must use other representations of the canonical commutation relations or they do not satisfy the canonical commutation relations at all.* (This is essentially HAAG's conclusion[10].) This result shows that the situation which was found by WIGHTMAN and SCHWEBER[13] in a special non-relativistic example is typical of relativistic theories of interaction which satisfy the canonical commutation relations (if such exist at all): For each different value of the coupling constant one must use an inequivalent representation of the commutation relations (assuming that different values of the coupling constant will give rise to some difference in the vacuum expectation values $F^{(n)}$ for $n = 1, 2, 3, 4$.) Of course, the converse is not true; inequivalent representations of the commutation relations need not always give rise to physically distinct theories.

From both the aesthetic and physical point of view, the version of the generalized Haag's theorem proved here is somewhat deficient because it only asserts the equality of the first four vacuum expectation values. It seems physically plausible that two theories in which the two-particle propagator, the vertex part, and the two-particle scattering for all energies are identical (as they must be if the first four vacuum expectation values are identical) should be completely identical. On this basis, one would conjecture the aesthetically more satisfying result that *all* vacuum expectation values coincide, which would (from the work of I Section 5) indeed imply the physical equivalence of the two theories. To prove this result along the lines of the present paper would require one to establish a unique analytic continuation out of the equal time-manifold T_n into $\mathfrak{M}_n$; it would require an analysis going essentially beyond what we have presented in Section 1. (In fact, it is not difficult to see that under the hypothesis of Section 1, the analytic continuation is *not* unique for $n \geqslant 4$.)

A second matter which the present paper leaves untouched is the question of the existence of theories which use representations of the commutation relations different from those of a free field. If it turns out that no such representation gives rise to a relativistically invariant theory which is physically interesting, that would be very strong evidence of the incompatibility of the canonical commutation relations, relativistic invariance and interaction. In fact, it would show that the fact that a field strength renormalization constant is infinite in quantum electrodynamics[14] is not a special consequence of the Hamiltonian of the theory, but a general result arising from relativistic invariance.

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1. A. S. Wightman, Phys. Rev. **101**, 860 (1956). This paper will be referred to as I. We adopt the notation of I, except when it is explicitly stated otherwise.
2. See, for example, S. Lefshetz, Algebraic Geometry, Princeton Press (1953), pp. 35–40.
3. S. Bochner and W. T. Martin, Annals of Math. **57**, 490 (1953).
4. For proof of these statements, see L. Pontrjagin, Topological Groups, Princeton Press (1939), Chapters VI and IX. See especially pp. 265–66.
5. For a proof of this basic property of analytic functions, see S. Bochner and W. T. Martin, Several Complex Variables, Princeton Press (1948), p. 34, theorem 4. We shall refer to this book as B and M.
6. See, for example, L. Kronecker, Journal für Reine u. Angew. Math. **72**, 152 (1870) or C. C. Mac Duffee, Ergebnisse der Math. **2**, 364 (1933).
7. The constructions of these paragraphs are given in detail, because they solve a problem in linear algebra not standard in the physical literature. They are well known in the mathematical literature. See, for example, E. Witt, Journal für Math. **176**, 31 (1936) or C. Chevalley, The Algebraic Theory of Spinors, Columbia University Press, New York (1954), pp. 8–15. The essential points are the following. Even for a complex valued scalar product such as $z\cdot w = z_\mu w^\mu$, provided it is non-degenerate (i. e. provided $z\cdot w = 0$ for all vectors w implies $z = 0$), it remains true that a linear manifold and its orthogonal manifold $M^\perp$ have dimensions satisfying

   $$\dim M + \dim M^\perp = 4.$$

   However, unlike the case with a positive scalar product, it can happen that M and $M^\perp$ have non-zero vectors in common; then M and $M^\perp$ do not together span the whole space. A necessary and sufficient condition that $M \cap M^\perp = (0)$ is that M have a basis whose Gram determinant is not zero. Then, all bases for M, and $M^\perp$ as well, have non-vanishing Gram determinant. In that case, a general vector has a unique decomposition into a sum of a vector in M and a vector in $M^\perp$. There is a simple formula for the projection of a vector v into a subspace with basis $v_1, \dots, v_m$

   $$-|G(v_1 \dots v_m)|^{-1} \det \left(\begin{array}{c|c} & v_1\cdot v \\ & \cdot \\ v_i\cdot v_j & \cdot \\ & \cdot \\ & v_m\cdot v \\ \hline v_1, \dots v_m & 0 \end{array} \right)$$

If a subspace has the property that every vector in it is of zero length, it is called isotropic. Isotropic subspaces can have dimensions no larger than half the dimension of the whole space. Most of these results follow directly from arguments of the type given in the preceding paragraphs of the proof. They will be used without comment in the remainder of the proof.

8. See, for example, C. C. MacDuffee, Ref. 6, p. 408, theorem 34.1.
9. D. Hall, thesis, Princeton (1956), Chapter III, unpublished.
10. R. Haag, Mat. Fys. Medd. Dan. Vid. Selsk. **29**, no. 12 (1955), especially pp. 30–32. In the opinion of the present authors, Haag's proof is, at least in part, inconclusive. We thank Dr. Haag for a correspondence on the matter. It will not escape the discerning reader of Haag's paper that, while we have generalized his results, eliminated one of his assumptions (the asymptotic condition), completed his proofs, and sharpened his conclusions, the essential physical points are Haag's.
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A COMMENT ON LANDAU'S METHOD OF INTEGRATION IN QUANTUM ELECTRODYNAMICS

BY

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Synopsis.

It is shown that the integration method of Landau et al. is inconsistent even in the energy region below the cut-off. This inconsistency is present also when no ghost states appear. This result implies that Landau's method is not self-consistent even for a finite cut-off.

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§ 1. Introduction and Summary.

Notwithstanding the brilliant success of the renormalization theory of quantum electrodynamics in explaining the experimental results with great accuracy, doubts have been raised from various sides whether or not the theory contains some logical inconsistencies. Thus, it was shown by Källén[1)] that at least one of the renormalization constants is infinite in magnitude. Even if one connives at this point, there still remain some questions concerning the finite part of the theory, e. g., the problem of the so-called ghost state. In connection with the Lee model[2)], Källén and Pauli were the first to point at this question, and along these lines many other authors have discussed the mathematical consistency of renormalized quantum electrodynamics[3)].

Independently of this approach, Landau and others[4)] have concluded that difficulties similar to those met with in Lee's model also appear in quantum electrodynamics as long as the concept of point interaction is used. The same conclusion has been reached by other workers in this field who started from somewhat different viewpoints[5)]. One very important point in Landau's approach to the consistency problem of quantum electrodynamics lies in the expansion of a certain quantity, the so-called "vertex part", in a power series in e^2. It turns out that every coefficient in this expansion has a very simple limiting form for high energies, and it is then argued that the limiting form of the vertex part itself is given as the sum of the limiting forms of the coefficients. Mathematically, such a conclusion is certainly not very well justified, and counterexamples can easily be given. It is the aim of the present paper to investigate whether or not Landau's method is selfconsistent in spite of these mathematical objections.

To this end, it is very helpful to follow the interesting argument as to the mathematical consistency of this theory, developed by Källén in his general consideration[6)] developed in a recent lecture in Geneva. By introducing some assumptions on the asymptotic form of the current operator, he has shown that the theory might contain internal inconsistencies of a kind different from the difficulty connected with the ghost state. In the case of Landau's approximation, however, no further assumptions of this kind need to be introduced, since we can take full advantage of his fundamental assumptions from which sufficient information can be derived about the asymptotic behaviour of the current operator as well as a very simple relation between the bare and the renormalized charges. It will appear that the functional equation for the current operator, which is required from the invariance property of the theory under the renormalization transformation, can easily be solved by virtue of Landau's condition, and it turns out that the result is essentially what was conjectured by Källén.

Thus, in accordance with Källén's argumentation, we are finally led to some results contradicting the premises on which our arguments are based. Consequently, we have to conclude that one of the following alternative statements, or both of them simultaneously, are valid.

(i) Landau's approximation is incorrect;

(ii) The theory in itself contains an inconsistency independent of that found in Landau's argumentation and, thus, the present quantum field theory has no mathematically consistent solution at all.

In order to remove from Landau's theory the difficulty connected with the appearance of a ghost state, we have first to introduce a cut-off factor into our formalism and then to consider the consistency of the resulting theory. However, the following question arises immediately. Since a cut-off has been introduced, we are no longer left with the canonical formalism as usual, because we have modified the canonical commutation relations. Does it therefore make any sense to discuss further points of the theory? From the viewpoint of correspondence principle, however, we should expect that those elements in the present theory, where intimate correspondence with reality is established and where the results are strongly supported by experimental evidence, might still survive in a future theory. Our investigation has to be considered from this point of view.

In § 2, the main results of Landau's approximation are summarized and, in § 3, the asymptotic forms of the current operator are discussed. In § 4, we complete our arguments, using the results obtained in the preceding sections, and give some further discussion related to our conclusion.

§ 2. Survey of Landau's Method.

For large momenta $|p^2| \gg m^2$, m being the mass of the electron, the approximation method of LANDAU et al.[4)] consists in expanding any quantity in a series of the form

$$e_0^n \sum_{m=0}^{\infty} (e_0^2)^m f_m \left[e_0^2 \log \frac{|p^2|}{\Lambda^2} \right] \tag{1}$$

and in retaining only the first term (corresponding to m = 0) in this series. Here, n is the order of the first non-vanishing term in perturbation theory and Λ is the cut-off momentum. A characteristic feature of this approximation method lies in the point that the square of the charge e_0^2 is always accompanied by the logarithm of the cut-off parameter.

The most important result with which we shall be concerned in the following is the relation between the renormalized charge e and the bare one e_0 which is given by

$$e^2 = Z_3(e^2, \Lambda^2)\, e_0^2 = \left(1 - \frac{e^2}{3\pi} \log \frac{\Lambda^2}{m^2}\right) e_0^2 \equiv f(\Lambda^2)\, e_0^2 . \qquad (2)^1$$

The relation (2) has also been derived by TAYLOR who solved a functional equation, required from the renormalization transformation, on the assumption that the cut-off parameter always appears as a product

$$e^2 \log \Lambda^2/m^2 .^{5)}$$

As is immediately seen from (2), the cut-off parameter Λ^2 must be smaller than $\Lambda_c^2 = m^2 \exp(3\pi \times 137)$ so that we can avoid the difficulty connected with the ghost state. Consequently, we have to work within the energy region $|p^2| < \Lambda^2$.

Now, it is well known that Dyson's integral equation for the photon propagator[7)] can be written in the form

$$D'_F(p)_{\mu\nu} = D_F(p)\,\delta_{\mu\nu} + D_F(p)\,\Pi_F(p)_{\mu\nu}\,D_F(p) . \qquad (3)^2$$

Here, the causal kernel $\Pi_F(p)$ is given by

$$\Pi_F(p) = i \int d^4x e^{ip(x-x')} \langle P(j_\mu(x), j_\nu(x')) \rangle_0 , \qquad (4)^2$$

---

[1] Unless otherwise stated, notations and definitions are the same as in our previous papers, references 5) and 11).

[2] We are referring to the unrenormalized form.

where $j_\mu(x)$ means the current operator in the Heisenberg representation⁸⁾. It is also convenient to make use of Källén's kernel defined by

$$\Pi_K(p) = \frac{V}{-3p^2} \sum_{p(z)=p} \langle 0 | j_\nu | z \rangle \langle z | j_\nu | 0 \rangle . \tag{5}$$

These functions are connected with each other through the relation

$$\left.\begin{aligned} \Pi_F(p)_{\mu\nu} &= \int_0^{\Lambda^2} da\, \Delta_F(p^2, a)\, \Pi_K(-a)\,(-p^2\delta_{\mu\nu} + p_\mu p_\nu) \\ &= \int_0^{\Lambda^2} da \left[\frac{P}{p^2+a} + i\pi\delta(p^2+a) \right] \Pi_K(-a)\,(-p^2\delta_{\mu\nu} + p_\mu p_\nu), \end{aligned}\right\} \tag{6}$$

where $\Delta_F(p^2, a)$ means the free propagator for a particle of mass a. As is easily seen, the above relation meets the requirement of causality.[1]

On the other hand, as a general consequence of the renormalization cut-off¹¹⁾, we obtain from (2) the asymptotic form of $\Pi_F(p)$, i. e. for large $-p^2 \gg m^2$ it behaves like

$$\Pi_F(p)_{\mu\nu} = \frac{\dfrac{e^2}{3\pi}\log\dfrac{\Lambda^2}{-p^2}}{1 - \dfrac{e^2}{3\pi}\log\dfrac{-p^2}{m^2}}\,(-p^2\delta_{\mu\nu} + p_\mu p_\nu). \tag{7}$$[2]

The same result was obtained by Landau et al. by solving directly an integral equation.

We can proceed to discuss the properties of Π_K and Π_F by means of (5) and (6), only if we know something about the matrix elements of the current operator $\langle 0 | j_\mu | z \rangle$. Therefore, we shall next investigate the asymptotic behaviour of this matrix element.

§ 3. Asymptomic Behaviour of the Current Operator.

Let us start by recapitulating the main points concerning the discussion of the asymptotic forms of the S-matrix presented in the paper by Konuma

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[1] Rigorously speaking, the relation (6) holds only when $\Lambda^2 = \infty$. Stueckelberg and Wanders¹⁰⁾ have shown that, if we expect the cut-off factor to be a result of smearing effects of non-local interactions, the causality relation (6) does no longer hold. Nevertheless, we have to adopt this relation for the reason mentioned at the end of § 1.

Here, we use, for simplicity, the straight cut-off. The discussion in § 3, however, is essentially based on the renormalization cut-off, which we use as a mathematical tool only to obtain the asymptotic behaviour. Both methods give the same result in the asymptotic region⁵⁾, ¹¹⁾.

[2] While, in the references 4) and 5), the relations (2) and (7) were derived for the case of $p^2 > 0$ (space-like), we get the same result for $p^2 < 0$ (time-like) by applying the analytic continuation as suggested in reference 4) or by using the method of renormalization cut-off developed in ref. 5).

and UMEZAWA[12]. These authors showed that, from the invariance under the renormalization transformation (or renormalization group[13]), an element of the S-matrix is required to satisfy the following functional equation. For the transition amplitude such that its non-vanishing term first appears in the n^{th} order in perturbation expansion, the functional equation reads

$$\left.\begin{aligned} Z(\Lambda^2)\, g_0^n\, F\left(-\frac{k_i k_j}{m^2}, \ldots ; -\frac{k_i k_j}{\Lambda^2}, \ldots ; g_0^2\right) \\ = g^n\, F\left(-\frac{k_i k_j}{m^2}, \ldots ; -\frac{k_i k_j}{m^2}, \ldots ; g^2\right), \end{aligned}\right\} \tag{8}$$

where g_o and g are the bare and the renormalized charges, respectively, and Z is a product of $Z_2^{1/2}$ and $Z_3^{1/2}$, factors which come from respective external lines of momenta k_i's.

KONUMA and UMEZAWA have shown quite generally how to solve this equation in the asymptotic region if we accept relation (2). Since we now are concerned with matrix elements of the current operator $\langle 0 | j | z \rangle$, their arguments should be somewhat generalized in two points.

In the first place, it should be noted that, in the derivation of equation (8), it was most essential to realize that the charge renormalization could be carried out in the usual way, by extracting factors like Z. In the case of the general matrix elements of Heisenberg operators, the renormalization procedure is somewhat complicated in view of the fact that the "doubled Feynman diagram"[14], has to be used. On the other hand, for the special elements which are considered here, i. e. $\langle 0 | j | z \rangle$, the situation is not more complicated than for the S–matrix. In this case, the matrix element is equal to that obtained in the so-called mixed representation[7], viz. $\langle 0 | j_H | z \rangle = \langle 0 | S^{-1} j_F | z \rangle = \langle S 0 | j_F | z \rangle = \langle 0 | j_F | z \rangle$. The last equality is due to the fact that $S | 0 \rangle = | 0 \rangle$ except for a constant phase factor which is to be removed by renormalization.

Secondly, it has to be kept in mind that the quantity which appears in (8) is not the matrix element $\langle 0 | j | z \rangle$ itself, but the dimensionless scalar quantity $\frac{V}{-3p^2} Z_3^{-1} \sum_\mu | \langle 0 | j_\mu | z \rangle |^2$, since this quantity can be written as $[Z_3^{-1/2} D_F' (p^2)\, p^2\, e_0^{\nu+1}\, Z_3^{\nu/2}]^2\, h\, (S_F', D_F', \Gamma_\mu', e_0^2) = [D_{Fc}(p^2)\, p^2\, e^{\nu+1}]^2\, h\, (S_{Fc}, D_{Fc}, \Gamma_{\mu c}, e^2)$[14], where the first factor is the contribution from the external vertex.

Taking into account the above two points, we can set up the functional equation for the matrix element between the vacuum and the state $| z \rangle$ of ν-photons present with momenta k_i's ($i = 1, 2, \ldots \nu$; $\nu \geqslant 3$) in the following form:

$$\left.\begin{aligned} &[Z_3^{-1/2}\, e_0^{\nu+1}\, Z_3^{\nu/2}]^2 F\left(-\frac{k_i k_j}{m^2}, \ldots ; -\frac{k_i k_j}{\Lambda^2}, \ldots ;\, e_0^2\right) \\ &= (e^{\nu+1})^2 F\left(-\frac{k_i k_j}{m^2}, \ldots ; -\frac{k_i k_j}{m^2}, \ldots ;\, e^2\right), \ (i \neq j;\, p_\mu = \sum_i k_{i\mu}), \end{aligned}\right\} \quad (9)^1$$

where we have put $\dfrac{V}{-3\,p^2} Z_3^{-1} \sum_\mu |\langle 0 | j_\mu | z \rangle|^2 = [Z_3^{-1/2} e_0^{\nu+1} Z_3^{\nu/2}]^2 F.$

By virtue of relation (2), this formula may be rewritten in the form

$$Z_3^{-2} F\left(-\frac{k_i k_j}{m^2}, \ldots ; -\frac{k_i k_j}{\Lambda^2}, \ldots ;\, e_0^2\right) = F\left(-\frac{k_i k_j}{m^2}, \ldots ; -\frac{k_i k_j}{m^2}, \ldots ;\, e^2\right). \quad (10)$$

Now, it is rather complicated, though not impossible, to find the general solution to this functional equation, since many arguments $k_i\, k_j$ are contained in F. For our present purpose, however, it is necessary only to look for the expression for the sum of F over all the possible states of ν-photons which satisfy the condition $p_\mu = \sum_i k_{i\mu}$. If we put $\mathfrak{J} = \sum_{p=\Sigma k} F$, then $\mathfrak{J}$, now being a function of m^2, e_0^2, and $-p^2$ only, should satisfy the following simplified equation:

$$Z_3^{-2}\, \mathfrak{J}\left(-\frac{p^2}{m^2}; -\frac{p^2}{\Lambda^2};\, e_0^2\right) = \mathfrak{J}\left(-\frac{p^2}{m^2};\, -\frac{p^2}{m^2};\, e^2\right). \quad (11)^2$$

When solving this equation, it should be remembered that the Landau approximation makes the cut-off parameter appear together with the bare charge e_0 in the combination $e_0^2 \log \dfrac{|p^2|}{\Lambda^2}$ in the asymptotic region. Therefore, bearing in mind relation (2), we can rewrite (11) in the form

$$f(\Lambda^2)^{-2}\, \mathfrak{J}\left(-\frac{p^2}{m^2}; \frac{f(-p^2)}{f(\Lambda^2)}\right) = \mathfrak{J}\left(-\frac{p^2}{m^2};\, f(-p^2)\right), \quad (12)$$

---

[1] In our case, F depends only on a single parameter Λ which comes from the cut-off of the photon propagation function. It is also to be remarked that exactly speaking, in the last argument in F on the right hand side of (9), we must substitute the charge e_m defined by $e_m^2/e^2 = k^2 D_{Fc}\left(\dfrac{k^2}{m^2}, e^2\right)\Big|_{|k^2| = m^2}$. But, under our approximation, $k^2 D_{Fc} = 1$ in the domain $0 \leq |k^2| \leq m^2$ and so we can put $e_m^2 = e^2$. See in this connection the third paper of reference 4).

[2] The lower limit of each photon energy is conveniently taken as the elctron mass, so that the infrared divergence may be neglected. (Otherwise, another dimensional constant has to be introduced into F or $\mathfrak{J}$).

where we have used the relations $\frac{e^2}{f(\Lambda^2)} \log \frac{-p^2}{\Lambda^2} = 3\pi \left(1 - \frac{f(-p^2)}{f(\Lambda^2)}\right)$ and $e^2 \log \frac{-p^2}{m^2} = 3\pi\, (1 - f(-p^2))$ and where we have, moreover, redefined the function $\mathfrak{F}$ in such a way that $\mathfrak{F}\,(x;\, 3\pi\,(1-y)) \rightarrow \mathfrak{F}\,(x; y)$. Equation (12) clearly show sthat the only possible solution $\mathfrak{F}$ is given by

$$\mathfrak{F}\left(-\frac{p^2}{m^2};\, f\right) = \mathfrak{F}_0\left(-\frac{p^2}{m^2}\right) \times f^{-2}. \tag{13}$$

Here, it should be noted that the function $\mathfrak{F}_0$ does no longer contain the charge e^2 and, thus, is nothing but the so-called Born approximation. By this we mean conventionally the first non-vanishing term in the perturbation theory expansion.

In summarizing our results obtained so far, we get the following equation:

$$\frac{V}{-3p^2} \sum_z \langle 0 | j_\mu | z \rangle \langle z | j_\mu | 0 \rangle = \frac{V}{-3p^2} \frac{f(\Lambda^2)}{f(-p^2)^2} \sum_z \langle 0 | j_\mu^{Born} | z \rangle \langle z | j_\mu^{Born} | 0 \rangle \qquad (14)^1$$

---

[1] In some cases, it is still possible to get the concrete asymptotic expression for the current operator itself.

The most general matrix element $\langle 0 \,|\, j \,|\, z \rangle$, for the state in which c pairs of electrons and ν-photons are present, satisfies the following functional equation:

$$\left[Z_3^{-1/2}\, e_0^{\nu+2c-1}\, Z_3^{\nu/2}\, Z_2^{c}\right]^2 F\left(-\frac{k_i k_j}{m^2}, \ldots; -\frac{k_i k_j}{\Lambda^2}, \ldots; e_0^2\right)$$

$$= \left[e^{\nu+2c-1}\right]^2 F\left(-\frac{k_i k_j}{m^2}, \ldots; -\frac{k_i k_j}{m^2}, \ldots; e^2\right).$$

This equation can easily be solved in the case that one of the arguments $-k_i k_j$, say, is extremely large as compared with others, so that $-k_i k_j \approx -p^2$. The final expression then reads

$$\langle 0 \,|\, j_\mu \,|\, z \rangle = \frac{f(\Lambda^2)^{1/2}}{f(-p^2)^c} Z_2(-p^2)^c \langle 0 \,|\, j_\mu^{Born} \,|\, z \rangle.$$

Here, it is interesting to compare the result with the conjecture by Källén in his general discussion (without any approximation) [6])

$$\langle 0 \,|\, j_\mu \,|\, z \rangle = \frac{1}{f(-p^2)^{n/2}} Z_2(-p^2) \langle 0 \,|\, j_\mu^{Born} \,|\, z \rangle.$$

In this connection, it should further be remarked that the above functional equation has this solution if, and only if, the function $Z_2(x)$ is equal to some power of the function $f(x)$ or $Z_3(x)$. Landau's approximation meets this requirement in a special gauge, for $Z_2 = f^0 = 1$. See also reference 15).

§ 4. Completion of the Argument. Discussion.

We are now in a position to complete our argument. If we restrict the summation $|z\rangle$ in (5) to the states considered above, and substitute (14) into it, then we obtain an inequality for Π_K.

It has already been shown by Källén that the absolute square of $\langle 0 | j_\mu^{Born} | k_1 k_2 \ldots k_\nu \rangle$ gives the probability in lowest order perturbation theory[4], for the emission of ν-photons in a weak external field; thus, Gupta's[16] result can be used and gives the following expression in the asymptotic region

$$\frac{V}{-3p^2} \sum_{k_1 - k_\nu} \langle 0 | j_\mu^{Born} | k_1 \ldots k_\nu \rangle \langle k_\nu \ldots k_1 | j_\mu^{Born} | 0 \rangle = \frac{\alpha^\nu}{\nu\,!} \left[\log \frac{-p^2}{m^2} \right]^{2\nu} c \tag{15}$$

with a constant c which is of the order of magnitude unity.

By means of (5), (14), and (15) we now get the following inequality for Π_K

$$\Pi_K (p^2) > e^2 \frac{f(\Lambda^2)}{f(-p^2)} c \sum_{\nu = 3, 5,}^{\overline{N}} \frac{\alpha^\nu}{\nu\,!} \left[\log \frac{-p^2}{m^2} \right]^{2\nu}, \tag{16}$$

where $\overline{N}$, the upper limit of the sum, is not larger than $\sqrt{-p^2/E_0^2}$ with $E_0 \approx m$. If $\overline{N}$ and $\alpha \log^2 \left(\frac{-p^2}{m^2} \right)$ are very large, (16) may be rewritten in the form

$$\Pi_K (p^2) > \frac{c}{2} \frac{e^2 f(\Lambda^2)}{\left(1 - \frac{e^2}{3\pi} \log \frac{-p^2}{m^2} \right)^2} \left(\frac{-p^2}{m^2} \right)^{\alpha \log \left(\frac{-p^2}{m^2} \right)} . \tag{17}$$

From the relation (6), together with (16) and (17), we can immediately deduce the following results. Let us first consider the real part of $\Pi_F (p^2)$. If we take $\Lambda^2 \gg -p^2 \gg m^2$ we obtain the cut-off dependent term which increases much faster than any power of $\log \left(\frac{\Lambda^2}{m^2} \right)$, because in this case we have $\int^{\Lambda^2} \frac{da}{p^2 + a} \left(\frac{a}{m^2} \right)^{\alpha \log \frac{a}{m^2}} \approx \int^{\Lambda^2/m^2} \frac{dx}{x} e^{\alpha \log^2 x} \approx \left(1/\alpha \log \frac{\Lambda^2}{m^2} \right) e^{\alpha \log^2 \frac{\Lambda^2}{m^2}}$.

Secondly, we look at the imaginary part of $\Pi_F (p^2)$. If $-p^2 \gg m^2$ we find that a non-negligible imaginary part must exist, which strongly depends on $-p^2$ and which satisfies the same inequality as do (16) and (17). Therefore, it appears that the absolute value of $\Pi_F (p^2)$ must be very much larger than the value given by (7) (as far as the region $\Lambda_c^2 \gg \Lambda^2 > - p^2 \geqslant e^{100} m^2$ is concerned)[1].

These results are inconsistent with (2) and (7) which have been derived from the same starting point as (17). This puzzling situation can be explained if, and only if, Landau's approximation is incorrect. In spite of this, it is, of course, possible that other difficulties, independent of those found by LANDAU, exist within the framework of present field theory.

If the first alternative is true, it clearly means that there are appreciable contributions from terms neglected in Landau's approximation. This is not so inconceivable since, in the n^{th} order of perturbation expansion, we get, roughly speaking, a contribution $e^{2n}\left[n!\, c_0 + (n-1)!\, c_1 \log(\Lambda^2/m^2) + \ldots + c_n \log^n(\Lambda^2/m^2)\right]$ and all the terms, with the exception of the last one, are neglected in his approximation. The ratio of the former to the latter is approximately $n!\,/\log^n(\Lambda^2/m^2)$ or at least $n!\,/(137 \times 3\pi)^n$. Consequently, even if the approximation is good up to some orders, it would no longer be justified in higher orders, however large the cut-off may be. In other words, here it is not allowed to interchange the two kinds of limiting processes, viz. $\lim_{\Lambda\to\infty}\lim_{n\to\infty}$ and $\lim_{n\to\infty}\lim_{\Lambda\to\infty}$. The latter limit has recently been studied in great detail by several groups[5)]. On the other hand, it was pointed out by KÄLLÉN[6)] that our result (16) is consistent with every result obtained in perturbation theory.

Furthermore, if the second alternative is taken to be true, it would necessarily lead to the conclusion that present quantum field theory has no mathematically consistent solution at all.

Finally we like to add a few words about (ps) (ps) meson theory[5), 17)]. From the outset, it is evident that here Landau's approximation is not so powerful as in quantum electrodynamics. In this case, the cut-off momentum is of the order of the nucleon mass M because of the large value of the coupling constant. Consequently, we are no longer left with any asymptotic region $-p^2 \gg M^2$ in which this approximation is applicable. However, we might still make a formal argument, artificially supposing the coupling constant to be small and therefore using the same technique. If that is done, we get the same result for meson theories as for quantum electrodynamics.

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[1] As far as the renormalized kernel π_{Fc} is concerned, the above statement is true, irrespective of the region of Λ. (Landau's π_{Fc} is given by (7), but with replacement of $\Lambda^2 \to m^2$).

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CALCIUMORTHOPHOSPHATE

I. DIE FESTEN CALCIUMORTHOPHOSPHATE

II. KOMPLEXBILDUNG IN LÖSUNGEN VON CALCIUM- UND PHOSPHAT-IONEN

VON

NIELS BJERRUM

København 1958
i kommission hos Ejnar Munksgaard

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CALCIUMORTHOPHOSPHATE. I

DIE FESTEN CALCIUMORTHOPHOSPHATE

VON

NIELS BJERRUM

Synopsis.

Diese Abhandlung enthält eine Beschreibung der Darstellung und der Eigenschaften der festen Calciumorthophosphate als Vorarbeit zu einer Bestimmung der Löslichkeiten dieser Stoffe.

Es wird gezeigt, dass das wasserfreie 2-Calciumphosphat (mit dem Neutralisationsgrad 2, d. h. mit 2 Äquivalenten Calcium pro PO_4), ausgefällt aus wässriger Lösung immer etwa $^1/_{10}$ Mol H_2O enthält. Eingehend wird namentlich das $2^2/_3$-Calciumphosphat beschrieben.

Es wird eine Reihe von Calciumphosphaten untersucht, ausgefällt aus wässriger Lösung bei 100° C und bei pH-Werten variierend von 3,7 bis 11. Die Niederschläge besitzen alle Apatit-ähnliche Debyeogramme; der Neutralisationsgrad der Phosphorsäure in ihnen variiert aber von etwa 2,8 bis 3,4. Während das Hydroxylapatit mit dem Neutralisationsgrad $3^1/_3$ als eine wohl definierte chemische Verbindung in diese Reihe eingeht, repräsentiert der Niederschlag in dieser Reihe mit dem Neutralisationsgrad 3 nicht eine chemische Verbindung, sondern ist nur ein zufälliges Glied in dieser Reihe. Auf Grund aller bekannten Tatsachen wird die Auffassung vertreten, dass alle diese Niederschläge Hydroxylapatit-Gitter enthalten, und dass der variierende Neutralisationsgrad durch Aufnahme von Protonen an Hydroxyl-Ionen und Phosphat-Ionen im Gitter verursacht wird unter gleichzeitiger Austreibung von Ca-Ionen, die durch H_2O-Molekeln ersetzt werden. Diese Substitution findet statt teils im Inneren des Gitters und teils in Form einer Adsorption, indem in den Elementar-Zellen in oder nahe der Oberfläche eine stärkere Substitution als im Inneren vorhanden ist.

Bei 100° C sind (bei Partikeln etwa 1 μ gross) die Einflüsse der beiden Arten von Substitution von ähnlicher Grösse. Mit steigender Temperatur breitet die Substitution in der Oberfläche sich zu tiefer liegenden Schichten aus, und der Unterschied zwischen den beiden Arten von Substitution wird nach und nach ausgewischt, um an einer Stelle im Temperatur-Intervall 250°—450° ganz zu verschwinden.

Die von Tovborg Jensen beobachtete unerwartete Ausscheidung von wasserfreiem 3-Calciumphosphat im Harn und Speichel — unerwartet, weil wir bei unseren Versuchen im Laboratorium niemals eine solche Ausscheidung beobachtet haben — wird beschrieben und ihre Ursache diskutiert.

Zur analytischen Bestimmung von Calcium und Phosphat wird die sogenannte Apatit-Titrierung angewandt, und diese näher beschrieben.

INHALTSVERZEICHNIS

Einleitung.

In den Jahren 1930—36 wurden von mir und meinen Mitarbeitern P Damsgaard Sørensen und A. Tovborg Jensen ausführliche Untersuchungen über Calciumorthophosphate angestellt. Die wichtigsten der gewonnenen Resultate sind in kurzer Form auf der 19. skandinavischen Naturforscherversammlung in Helsingfors 1936 vorgetragen worden[1]. In der hier vorliegenden ausführlichen Darstellung dieser Untersuchungen werden auch ältere und neuere Arbeiten besprochen.

Bei Untersuchungen von Calciumphosphaten und namentlich ihrer Löslichkeiten stösst man auf viele Schwierigkeiten: Die Niederschläge sind oft schlecht definiert, die Löslichkeiten sind klein und der Eintritt der Sättigung langsam und oft unvollständig. Erst die Aufnahme von Debye-Scherrer Pulverdiagrammen mit Röntgenstrahlen hat eine genaue Kontrolle der Niederschläge, mit denen die Lösungen gesättigt sind, ermöglicht. Dazu kommt, dass man die Komplexbildung zwischen Calcium-Ionen und Phosphat-Ionen in den Lösungen nicht genau kennt.

In dieser ersten Abhandlung werden zuerst die untersuchten festen Phasen von Calciumphosphaten beschrieben. In einer zweiten Abhandlung wird angeführt, was man über die Komplexbildung zwischen Calcium- und Orthophosphat-Ionen in Lösungen sagen kann. Und in einer später zu publizierenden dritten Abhandlung werden die Resultate unserer Untersuchungen über die Löslichkeiten der Calciumorthophosphate beschrieben.

Es handelt sich in unseren Arbeiten nur um Orthophosphate von Calcium, und wir werden ein Orthophosphat mit dem Neutralisationsgrad N (Äquivalente Metall pro Moleküle H_3PO_4) als ein N-Phosphat bezeichnen. Wünschen wir im Namen auch einen Hydratwassergehalt n (H_2O pro PO_4) anzugeben, bezeichnen wir das Phosphat als ein (N, n)-Phosphat.

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[1] Auf dänisch im Bericht über die 19. skandinavische Naturforscherversammlung in Helsingfors 1936. Englische Übersetzung in: Niels Bjerrum, Selected papers, Einar Munksgaard, Copenhagen 1949.

1. Das $(1,{}^1/_2)$-Phosphat.

Das primäre Calciumphosphatmonohydrat $Ca(H_2PO_4)_2, H_2O$ haben wir nur wenig studiert. Seine Löslichkeitsverhältnisse werden aber auf Grund der Angaben in der Literatur diskutiert. Eine gute Darstellungsweise ist von A. Tovborg Jensen und J. Rathlev[2] angegeben.

2. Das (2,2)-Phosphat.

Darstellung. Das sekundäre Calciumphosphatdihydrat ($CaHPO_4$, 2 H_2O) wurde dargestellt durch Zutropfen (etwa 15 Minuten lang) bei gewöhnlicher Temperatur von einer Lösung von 50 g $CaCl_2$, 6 H_2O in 400 ml H_2O zu einer Lösung von 30 g Na_2HPO_4, 2 H_2O + 15 g KH_2PO_4 in 400 ml H_2O. Der Niederschlag war im Anfang amorph, wurde aber im Laufe einer Stunde in kleine, gut ausgebildete, monokline Kristallblätter umgewandelt. Am folgenden Tag wurden die Kristalle abgesaugt, chloridfrei gewaschen und mit Hilfe von Alkohol und Äther getrocknet. Der Zusatz von primärem Phosphat wurde vorgenommen, um eine Verunreinigung durch stärker basische Phosphate (mit $N > 2$) zu vermeiden. Mikroskopische Untersuchung zeigte, dass mit dem angegebenen Zusatz reine Kristalle zustande kamen. Es ist wichtig, dass die Fällung bei gewöhnlicher Temperatur vorgenommen wird, um die Bildung von wasserfreiem Salz zu verhindern.

Analyse. Im Präparat I wurde PO_4 kolorimetrisch und Ca mittels Fällung als Oxalat und Titrierung mit Permanganat bestimmt. Im Präparat II wurden Ca und PO_4 durch Apatit-Titrierung bestimmt (Titrierung zuerst zum Primärpunkt und danach zum Apatitpunkt. Siehe später Abschnitt 8).

	Gefunden		Berechnet für
	In Präp. I	In Präp. II	$CaHPO_4$, 2 H_2O
Ca	23,2 %	23,27 %	23,28 %
PO_4	55,1 %	55,22 %	55,20 %
Glühverlust	26,18 %		26,17 %

Bei Trocknen über konz. Schwefelsäure in Vakuum verlor das Salz nur sehr langsam Wasser (in 87 Tagen 0,11 %).

Vorkommen. In der Natur trifft man das Dihydrat des 2-Phosphats in Form vom Mineral Brushit und in Zahnstein[2a] an.

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[2] Inorganic syntheses IV. McGraw-Hill, New York 1953, S. 18.

[2a] A. Tovborg Jensen und Marianne Danø: J. Dental Research **33** (1954) 741.

3. Das (2,0)-Phosphat.

Darstellung von wasserfreiem sekundärem Calciumphosphat, $CaHPO_4$. Lösungen von 15 g Na_2HPO_4, 2 H_2O + 15 g NaH_2PO_4, 2 H_2O in 300 ml H_2O und von 30 g $CaCl_2$, 6 H_2O in 300 ml H_2O wurden zum Sieden erhitzt und unter Umrühren zusammengemischt. Der sogleich ausgeschiedene amorphe Niederschlag setzte sich nach kurzem Stehen zu Boden in Form eines kristallinischen Niederschlags, der unter dem Mikroskop gesehen aus kleinen stabförmigen Kristallen bestand. Die Kristalle wurden abgesaugt, mit Wasser gewaschen und drei bzw. 24 Stunden bei 100° getrocknet (Präp. I). Ein anderes Präparat (II) wurde mit Alkohol und Äther gewaschen und 24 Stunden an der Luft getrocknet. Ein drittes Präparat (III) wurde von nur halb so starken Lösungen gefällt. Dieses Präparat bestand unter dem Mikroskop gesehen aus kleinen, ein wenig schiefen Würfeln. Es wurde drei bzw. 24 Stunden bei 100° getrocknet.

Analysen. Die verschiedenen Präparate zeigten folgende Glühverluste:

Präp. I (3 Stunden bei 100° getrocknet) 7,83 $^0/_0$ (bei schwacher Glühhitze).
Präp. I (3 Stunden bei 100° getrocknet) 7,85 $^0/_0$ (bei starker Glühhitze).
Präp. I (24 Stunden bei 100° getrocknet) 7,83 $^0/_0$.
Präp. II (24 Stunden an der Luft getrocknet) 8,08 $^0/_0$.
Präp. III (3 Stunden bei 100° getrocknet) 7,85 $^0/_0$.
Präp. III (24 Stunden bei 100° getrocknet) 7,86 $^0/_0$.

Da der für $CaHPO_4$ berechnete Glühverlust 6,62 $^0/_0$ beträgt, besitzen die bei 100° getrockneten Präparate alle einen 1,21—1,24 $^0/_0$ zu grossen Glühverlust, entsprechend etwa 0,1 Molekül Wasser. (Die Angabe in der vorläufigen Mitteilung über einen Inhalt von $^1/_6$ Molekül Wasser beruht auf einem Rechenfehler). Titrierung von Präp. I mit Säure zum Primärpunkt und mit Base zum Apatitpunkt ergab folgende Resultate: Ca gefunden 29,08 $^0/_0$, berechnet nach $CaHPO_4$ 29,45 $^0/_0$. P gefunden 22,45 $^0/_0$, berechnet nach $CaHPO_4$ 22,79 $^0/_0$. Das Verhältnis zwischen Ca und P ist richtig; die Gehalte der beiden Stoffe sind aber zu klein. Ein Inhalt von 1,27 bzw. 1,51 $/_0$ eines Ca- und P-freien Stoffes kann die gefundenen Resultate erklären. Dieses Verhalten zusammen mit dem 1,24 $^0/_0$ zu grossen Glühverlust deutet darauf hin, dass die Kristalle wirklich etwa 1,3 $^0/_0$ Wasser entsprechend 0,1 Mol Wasser pro Mol $CaHPO_4$ enthalten. Sie verloren indessen nach drei Tagen über Phosphorsäureanhydrid nicht an Gewicht.

Auch andere Forscher haben bei der Darstellung von ganz wasserfreiem sekundärem Calciumphosphat Schwierigkeiten gehabt. Verbringer[3] hat ein Salz mit der Formel $CaHPO_4, {}^1/_6\, H_2O$ (entsprechend einem Glühverlust von 8,63 %) dargestellt, das erst bei 200° Wasser abgab. Birnbaum[4] meint indessen konstatiert zu haben, dass dieses Hydrat Wasser über konz. Schwefelsäure verliert. Rindell[5] fand für verschiedene Präparate von »wasserfreiem« Salz Glühverluste zwischen 7,54 und 7,87 %. A. Tovborg Jensen und Rathlev[6] fanden nach ihrem Darstellungsverfahren einen Glühverlust bei 900° von 7,13 % entsprechend 0,0416 Molekül Wasser. Bassett[7] erwähnt ein Produkt gefällt aus einer Lösung von $Na_2HPO_4 + NaH_2PO_4$ mit $CaCl_2$-Lösung bei ca. 95°, das beim Erhitzen 7,5 % verliert, entsprechend 0,072 Mol Hydratwasser, also auch etwas weniger als wir gefunden haben. Er glaubt, dass der zu grosse Gewichtverlust beim Glühen durch eine Abgabe von P_2O_5 verursacht sein kann. Birnbaum[4] gibt nämlich an, dass das primäre Calciumphosphat bei Glühen P_2O_5 verliert. Es scheint mir zwar möglich, dass das primäre Calciumphosphat (also in Wirklichkeit $Ca(PO_3)_2$) etwas P_2O_5 bei Glühen verliert. Es scheint mir aber kaum möglich, dass das sekundäre Calciumphosphat (also in Wirklichkeit $Ca_2P_2O_7$) bei Glühen P_2O_5 verliert. Die entsprechende Magnesiumverbindung $Mg_2P_2O_7$, gebildet bei starkem Glühen, ist lange Zeit zu exakten Phosphorbestimmungen angewandt worden, und es ist sehr unwahrscheinlich, dass die Magnesium-Verbindung sich in dieser Beziehung von der Calcium-Verbindung verschieden verhalten sollte.

Der Inhalt von 1,3 % Wasser im gefällten $CaHPO_4$ erinnert an den Inhalt von 1—2 % mitgefälltem Wasser in gefälltem Bariumsulfat. Nach G. Walton und G. H. Walden, jr.[7a] ist dieses mitgefällte Wasser im Bariumsulfat in fester Lösung vorhanden. Es ist nicht interstitial im Gitter aufgenommen, sondern Gruppen von $3\, H_2O$ mit dem normalen spezifischen Gewicht des Wassers substituieren im Gitter einzelne $BaSO_4$-Gruppen, die dasselbe Volumen einnehmen.

Wenn im folgenden von wasserfreiem sekundärem Calciumphosphat ((2,0)-Phosphat) gesprochen wird, werden darunter die oben besprochenen Präparate mit einem Glühverlust von etwa 7,85 % verstanden.

Vorkommen. In der Natur ist das wasserfreie 2-Phosphat als Mineral vorhanden (Monetit).

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[3] Zeitschr. anal. Ch. **9** (1870) 457.

[4] Zeitschr. f. Chemie **187** (1871) 137.

[5] Untersuchungen über die Löslichkeit einiger Kalkphosphate, Disp. Helsingfors 1899, S. 14, 19, 54, 65.

[6] Inorganic Syntheses IV. McGraw-Hill, New York (1953) S. 22.

[7] Zeitschr. anorg. Ch. **53** (1907) 35 und **59** (1908) 30.

[7a] Journ. Amer. Chem. Soc. **68** (1946) 1756.

4. Das $3^1/_3$-Phosphat (Hydroxylapatit).

a. Die Geschichte.

Bei seinen Untersuchungen über die hydrolytische Zersetzung der wenig löslichen Calciumphosphate durch Behandlung mit Wasser erhielt WARINGTON[8] Produkte, die mehr Calcium enthielten als das Tricalciumphosphat, und für den Niederschlag, der nach vielmaligen Behandlungen von Tricalciumphosphat mit Wasser zurückblieb, fand er die Zusammensetzung $3\,Ca_3(PO_4)_2, Ca(OH)_2$. O. FÖRSTER[9] erhielt dieselbe Verbindung aus Tricalciumphosphat durch Kochen mit verdünnter Lauge und zeigte, dass ihre fast vollständige Löslichkeit in Citronensäure durch starkes Glühen verloren ging. H. BASSETT[10] ist wohl der erste, der die wichtige Rolle dieser Verbindung in wässrigen Calciumphosphat-Systemen hervorgehoben hat. Er schreibt, dass sie die stabile Phase in einem grossen Reaktionsgebiet ist, indem sie in Gleichgewicht mit sowohl schwach sauren wie neutralen und alkalischen Lösungen sein kann, und sie ist vorhanden sowohl in Knochen und Zähnen wie in der Ackererde. Er nannte sie Oxy- oder Hydroxyapatit.

SCHLEEDE, SCHMIDT und KINDT[11] haben durch Röntgen-Strukturaufnahmen (Debyeogramme) gezeigt, dass BASSETT's Hydroxyapatit wirklich ein Körper mit Fluorapatit-Struktur ist, und sie haben es Hydroxylapatit genannt. Sie haben auch durch Aufnahmen von Debyeogrammen bestätigt, dass sowohl Dicalciumphosphat wie Tricalciumphosphat (KAHLBAUM's Handelsware) durch langdauernde Behandlung mit Wasser in Hydroxylapatit umgewandelt werden können. Zur Reindarstellung von Hydroxylapatit empfehlen sie, käufliches Tricalciumphosphat nach FÖRSTER[9] mit verdünnter Lauge längere Zeit zu kochen und das sorgfältig gewaschene Produkt auf 900° zu erhitzen. Getrocknet unterhalb dieser Temperatur enthält Hydroxylapatit noch Wasser, das bemerkenswert fest gebunden ist. Mit der Entfernung dieses Wassers verschwindet die Citronensäure-Löslichkeit des Stoffes (vgl. FÖRSTER[9]).

G. TRÖMEL und H. MÖLLER[12] haben gezeigt, dass bei der Umsetzung von Natriumphosphat mit Calciumnitrat in wässriger Lösung, bei Gegenwart von überschüssigem Ammoniak und bei 40°—50°, als primäre Kristall-Art stets nur Hydroxylapatit ausfällt und nicht Tricalciumphosphat, wie bisher

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[8] Journ. Chem. Soc. London **26** (1873) 983.
[9] Zeitschr. angew. Chem. Jahrgang 1892, 13.
[10] Journ. Chem. Soc. London **111** (1917) 620.
[11] Zeitschr. Elektrochem. **38** (1932) 633.
[12] Zeitschr. anorg. Chem. **206** (1932) 227.

angenommen wurde. Wenn dem Hydroxylapatit bei der Fällung Gelegenheit gegeben wird, überschüssiges P_2O_5 zu adsorbieren, werden Zusammensetzungen erreicht, die der des Tricalciumphosphats naheliegen.

Die geringe Teilchengrösse der Niederschläge macht sich auf den Röntgen-Aufnahmen bemerkbar. Die Linien der bei 110° getrockneten Proben sind sehr unscharf, und nur an den Stellen der starken Apatit-Linien sind Intensitätsmaxima zu erkennen. Diese sind aber genügend deutlich, um mit Sicherheit zu zeigen, dass Apatit-Struktur vorliegt.

Um schärfere Aufnahmen zu erhalten, wurden die Niederschläge langsam steigenden Temperaturen ausgesetzt. Dabei zeigte sich, dass bis zu etwa 600° Apatit-Struktur vorlag. Die Aufnahmen werden mit steigender Temperatur allmählich besser, erreichen aber nicht ganz die Schärfe derjenigen von Schmelzprodukten. Bei noch höheren Temperaturen (bei über 900°) treten aber Unterschiede auf. Bei einem Teil der Niederschläge ergeben sich sehr scharfe Apatit-Diagramme. Bei einem anderen Teil dagegen tritt jetzt das gänzlich verschiedene Diagramm des beta-$Ca_3P_2O_8$'s auf, mehr oder weniger vermischt mit demjenigen des Hydroxylapatits. Das adsorbierte P_2O_5 tritt also über 900° in das Hydroxylapatit-Gitter ein und wandelt es in das beta-$Ca_3P_2O_8$-Gitter um.

Zu derselben Zeit hatte TRÖMEL[13] auch Untersuchungen über das CaO, P_2O_5-System bei hohen Temperaturen im Gange. Er machte hierbei eine interessante Beobachtung, die die grosse Beständigkeit des Hydroxylapatit-Gitters anzeigt. RÖNTGEN-Aufnahmen von abgekühlten Schmelzen, die kalkreicher waren als das Tricalciumphosphat, zeigten ausser den erwarteten Tri- und Tetracalciumphosphat-Linien auch die Linien des Hydroxylapatits an. Diese Verbindung wurde während der Abkühlung bei 1050°—1200° aus dem Tetracalciumphosphat durch Reaktion mit der Luftfeuchtigkeit gebildet und konnte bei höheren Temperaturen (1400°) wieder in eine Mischung von Tri- und Tetracalciumphosphat umgewandelt werden[14].

KAZAKOV[15] und nach einer Modifikation seines Verfahrens P.W. ARNOLD[16] haben durch langsame Fällung Hydroxylapatit in gut ausgebildeten Kristal-

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[13] Mitt. Kaiser-Wilhelm-Inst. Eisenforschung, Düsseldorf **14** (1932) Abh. 198 und Zeitschr. physik. Chem. **158** (1932) 198.

[14] Vgl. auch SCHLEEDE, SCHMIDT und KINDT, Zeitschr. Elektrochem. **38** (1932) 639. — E. HAYEK, F. MÜLLNER und K. KOLLER, Sitzungsber. Akad. Wiss., Wien, math.-naturw. Kl. Abt. IIb, Bd. 160 (1951) 968, meinen in dem RÖNTGEN-Diagramm eines bei mehrstündigem Glühen bei 1100° zersetzten Hydroxylapatits die intensivsten Linien des Calciumoxyds beobachtet zu haben und nehmen deshalb an, dass das Hydroxylapatit beim Glühen in Tricalciumphosphat und Calciumoxyd ungewandelt wird.

[15] Trans. Sci. Inst. Fertilizers and Insectofungicides U.S.S.R. Nr. 139 (1937) 3–73 und Sovjetskaja Geologija, 8 Nr. **6** (1938) 33–47.

[16] Trans. Faraday Soc. **46** (1950) 1065.

len erhalten. W. Rathje[17] hat es durch langsame Fällung bei 95° in Drusen von bis 0,1 mm langen hexagonalen Nadeln gewonnen, und E. Hayek, Lechleitner und Böhmer[18] haben es 1955 durch Erhitzen mit 2 m NaOH auf 380 °C in 24 Stunden in bis zu 1 mm langen Kristallen erhalten. Yngve Ericsson[19] und E. Hayek und W. Stadlmann[19a] haben rationelle Darstellungsweisen von Hydroxylapatit beschrieben.

E. Hayek, F. Möllner und K. Koller[14] haben eine Reindarstellung von Hydroxylapatit aus Niederschlägen, gefällt sowohl aus sauren wie aus alkalischen Lösungen, durch Auskochen mit grossen Mengen reinsten Wassers beschrieben, und sie haben die gut definierte, kongruente Löslichkeit ihrer Produkte in reinem Wasser mit Recht als Zeichen dafür aufgefasst, dass es eine reine chemische Verbindung ist, und dass es bei 100° in Wasser der stabilste Bodenkörper ist.

Einen guten Beweis für die Existenz des Hydroxylapatits als eine stabile, wohl definierte chemische Verbindung gibt auch die im Abschnitt 8 dieser Arbeit beschriebenen Titrierung von Phosphorsäure[20]: Nach Zusatz von Calciumchlorid kann man eine sehr verdünnte 0,001 m Phosphorsäure-Lösung in der Siedehitze sehr scharf mit 0,1 m NaOH unter Anwendung einer Mikrobyrette zu dem Apatit-Punkt titrieren, wo genau $3^1/_3$ Äquivalente Natriumhydroxyd zugesetzt sind.

b. Eigene Präparate von Hydroxylapatit.

Als ein Beispiel für die Präparate, mit welchen unsere in einer später folgenden Abhandlung beschriebenen Löslichkeitsbestimmungen von Hydroxylapatit in den dreissiger Jahren ausgeführt wurden, sei das folgende genannt:

Präparat dargestellt und untersucht von Tovborg Jensen. Das Präparat wurde gefällt aus einer siedenden Lösung von 24 g Calciumchloridhexahydrat in 1,8 Liter Wasser durch langsames Zutropfen einer Lösung von 10,6 g Natriumphosphatdihydrat (etwas weniger als theoretisch notwendig) in 100 ml Wasser, indem während der Fällung die Lösung ständig durch Zusatz von 0,1 n NaOH schwach Phenolphthalein-rot gehalten wurde. Der Niederschlag wurde abzentrifugiert, 7 mal in Wasser aufgeschlemmt, abzentrifugiert und an der Luft getrocknet.

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[17] Ber. deut. chem. Ges. **74** (1941) 348.

[18] Angew. Chem. **67** (1955) 326.

[19] Acta odontologica scandinavica 8, Suppl. 3 (1949) 47.

[19a] Angew. Chem. **67** (1955) 327.

[20] Vgl. auch die Mitteilung von W. Rathje über die »acidimetrische Ausfällung« von Hydroxylapatit, Ber. deut. chem. Ges. **74** (1944) 343.

ANALYSEN.

	CaO	P_2O_5	H_2O	N
Gefunden bei Apatit-Titrierung....	52,8 %	40,25 %	6,95 %	3,342
Berechnet für $Ca_5(PO_4)_3OH$, 1,55 H_2O	52,88 %	40,20 %	6,96 %	3,333

Der Neutralisationsgrad kommt dem richtigen sehr nahe, und die Analysen stimmen zu einem Wassergehalt von 1,55 Mol H_2O.

c. Das Wasser in den Hydroxylapatit-Präparaten.

Der Wassergehalt in den Hydroxylapatit-Präparaten anderer Forscher ist ziemlich verschieden gewesen. SCHLEEDE[11] fand in einem Präparat, dargestellt nach FÖRSTER[9], durch Kochen von käuflichem Tricalciumphosphat mit 0,5 m Kalilauge und getrocknet bei 105°, 0,9 H_2O (Wasser bestimmt als Differenz, Hydroxyl-Wasser abgezogen). W. RATHJE[21] fand in einem Präparat, dargestellt aus 2-Phosphat und Calciumcarbonat durch Kochen mit Wasser und getrocknet in Vakuumexsikkator, 0,2 H_2O. Y. ERICSSON[19] fand in einem Präparat, gefällt in ähnlicher Weise wie das unsrige, nach Trocknen bei 110° 1,3 H_2O. ARNOLD[16] fand 1,5 H_2O in einem Präparat dargestellt nach KAZAKOW's Verfahren[15] (sehr langsame Fällung in $^1/_{20}$ m Ammoniumacetat bei gewöhnlicher Temperatur und pH >7; in 8 Stunden wurde 0,7 g pro Liter ausgeschieden; getrocknet bei 110°). Die 1,5 H_2O wurden über 110° bei steigender Temperatur langsam abgegeben, bis bei 750° alles Wasser abgegeben war. Die Hydroxylgruppen wurden erst bei 1250—1400° unter Abgabe von noch einem halben Mol Wasser zerstört. HAYEK[14] fand in einem Präparat, getrocknet mit Aceton und trockener Luft, 2,5 H_2O. Von diesen 2,5 H_2O wurde 1 H_2O bei 105° abgegeben, noch $^1/_2$ H_2O bei 200°, während das letzte H_2O erst bei 900° völlig abgegeben wurde.

Das von HAYEK, LECHLEITNER und BÖHLER[18] durch Erhitzen eines Calciumphosphat-Niederschlags mit 2 m NaOH auf 380 °C in 24 Stunden gewonnene Präparat verlor bei 600 °C nur 0,01 %, hatte analytisch genau die Zusammensetzung des Hydroxylapatits und ergab ein ganz scharfes Debyeogramm.

Bei der Abgabe des Wassers beim Erhitzen bis zu 750°—900° werden die Linien in den Debyeogrammen der Stoffe nicht verschoben, sondern nur verschärft, und es fällt deshalb schwer anzunehmen, dass die Wassermolekeln an bestimmten Plätzen im Kristall-Gitter angebracht sind. Es wird

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[21] Bodenkunde und Pflanzernährung **12** (1939) 124.

wohl auch im Allgemeinen angenommen, dass sie als hygroskopisches Wasser an der Oberfläche adsorbiert sind. Mit abnehmender Partikel-Grösse wird die Oberfläche wachsen, und man kann verstehen, dass der Wassergehalt in den verschiedenen Präparaten wechselt; und wenn die Partikeln kolloidale Dimensionen annehmen, kann man grosse Wassergehalte erklären. Es liegt nahe sich vorzustellen, dass die Ca^{++}-Ionen in der Oberfläche des Hydroxylapatits die H_2O-Molekeln binden können. Da Calciumchloridhydrate indessen alles Wasser schon bei 260° abgeben[22], ist es nach dieser Auffassung schwer zu verstehen, dass Hydroxylapatit sein letztes Molekel Wasser erst bei etwa 750° abgibt. Merkwürdig ist es auch, dass mit der Entfernung dieses Wassers die Citronensäure-Löslichkeit des Stoffes vermindert wird (Förster[9] und Schleede[11]). Ich glaube, wir müssen zugestehen, dass wir noch nicht wissen, in welcher Weise die Wassermolekeln in den Hydroxylapatit-Kristallen angebracht sind. Sie müssen aber sicher im Inneren des Gitters sitzen, und sie müssen sich im Gitter bewegen können, ohne das Gitter zu zerstören.

5. Das $2^2/_3$-Phosphat.

Von verschiedenen Seiten ist auf Anzeichen für die Existenz eines $2^2/_3$-Phosphats mit der Zusammensetzung $Ca_4H(PO_4)_3$, aq hingewiesen worden; die Hinweise waren jedoch wenig überzeugend, und das $2^2/_3$-Phosphat war nicht näher charakterisiert. Wir meinen indessen jetzt die Existenz einer solchen Verbindung nachgewiesen zu haben und haben sie genau beschrieben.

a. Die ersten Versuche, ausgeführt zusammen mit P. Damsgaard-Sørensen.

Darstellung. Bei einigen Untersuchungen über die Einwirkung von Wasser auf das sekundäre Calciumphosphatdihydrat (das (2,2)-Phosphat) stiessen wir auf ein kristallinisches $2^2/_3$-Calciumphosphat. Ich kann folgende Einzelheiten von einem unserer ersten Versuche mitteilen:

0,2 g $CaHPO_4$, 2 H_2O wurde mit 100 ml 0,001 m HCl bei 37° rotiert. (Um die Bildung von stärker basischen Phasen zu vermeiden, rotierten wir das sekundäre Calciumphosphat nicht mit Wasser, sondern mit 0,001 m HCl). Es stellte sich schnell ein pA_H-Wert 6,52 ein (pA_H ist ein nach

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[22] Abegg's Handbuch der anorg. Ch. II, 2 (1905) 98.

einer bestimmten Formel berechneter pH-Wert, siehe Abschnitt 8 dieser Abhandlung), und dieser Wert wurde sowohl 2 Stunden wie 20 Stunden nach dem Beginn des Versuches gefunden. Als dann mit einigen Kristallen von $CaHPO_4$, 2 H_2O, die durch Rotieren mit Wasser bei 37° unklar geworden waren, geimpft wurde, sank pA_H auf 5,89, und unter dem Mikroskop konnte man beobachten, dass eine neue Phase ausgeschieden war: Kleine Sphärolite, bestehend aus ganz kleinen, zu allen Seiten herausragenden, langen, schmalen, dünnen Blättchen. Fig. 1 gibt einige Mikrophotographien der Sphärolite wieder. Die Sphärolite sassen im Anfang gewöhnlich auf den grösseren Kristallen des 2-Phosphats fest, bis sie durch lang andauerndes Rotieren abgelöst und zu kleinen Einzelkristallen zerbrochen wurden[23]. Wir rotierten nun die Mischung der zwei Kristallformen, bis alle $CaHPO_4$, 2 H_2O-Kristalle verschwunden waren. Die Analyse des reinen Niederschlags von Sphäroliten, ergab dann eine Zusammensetzung entsprechend der Formel $Ca_4H(PO_4)_3$, 2 H_2O.

Analysen. Es wurden zwei Niederschläge (I und III) analysiert, die nach dem obigen Verfahren dargestellt waren. Ausserdem wurde ein Niederschlag (II) analysiert, dargestellt durch Rotieren von 100 ml 0,0005 m HCl und 0,2 g $CaHPO_4$, 2 H_2O bei 37° und geimpft mit (I).

ANALYSENRESULTATE.

	Subst.	Millimol P	Millimol Ca	N	Subst ber. nach $Ca_4(PO_4)_3H, 2H_2O$
Präp. I	15,2 mg	0,94	1,27	2,70	15,1 mg
— II	33,4	2,08	2,73	2,62	33,4 -
— II	58,0 -	3,57	4,74	2,65	57,4 -
— II	69,7 -	4,27	5,60	2,62	68,6 -
— III	62,9 -	3,93	5,23	2,67	63,1 -
— III	44,0 -	Glühverlust 4,4 mg. Ber. nach $Ca_4(PO_4)_3H$, 2 H_2O und Abgabe von $2^1/_2$ H_2O 4,1 mg			

»Millimol P« und »Millimol Ca« wurden bestimmt durch Titrierung zum Primärpunkt und zum Hydroxylapatitpunkt (vergleich Abschnitt 8). Die

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[23] Wir haben zuerst die herausragenden Kristalle als Nadeln aufgefasst. Nachdem aber ARNOLD (Trans. Faraday Soc. **46** (1950) 1066) sein Octocalciumphosphat als in dünnen Blättchen kristallisierend beschrieben hat ('the solid might possibly possess a platey structure'), haben wir unsere photographischen Aufnahmen einer erneuerten Untersuchung unterworfen, und besonders Fig. 1b und d scheinen uns deutlich zu zeigen, dass auch unsere »Nadeln« in Wirklichkeit lange, schmale, dünne Blättchen sind. Vgl. auch die elektronen-optischen Bilder von $2\,^2/_3$-Calciumphosphat auf Seite 28 (Fig. 2).

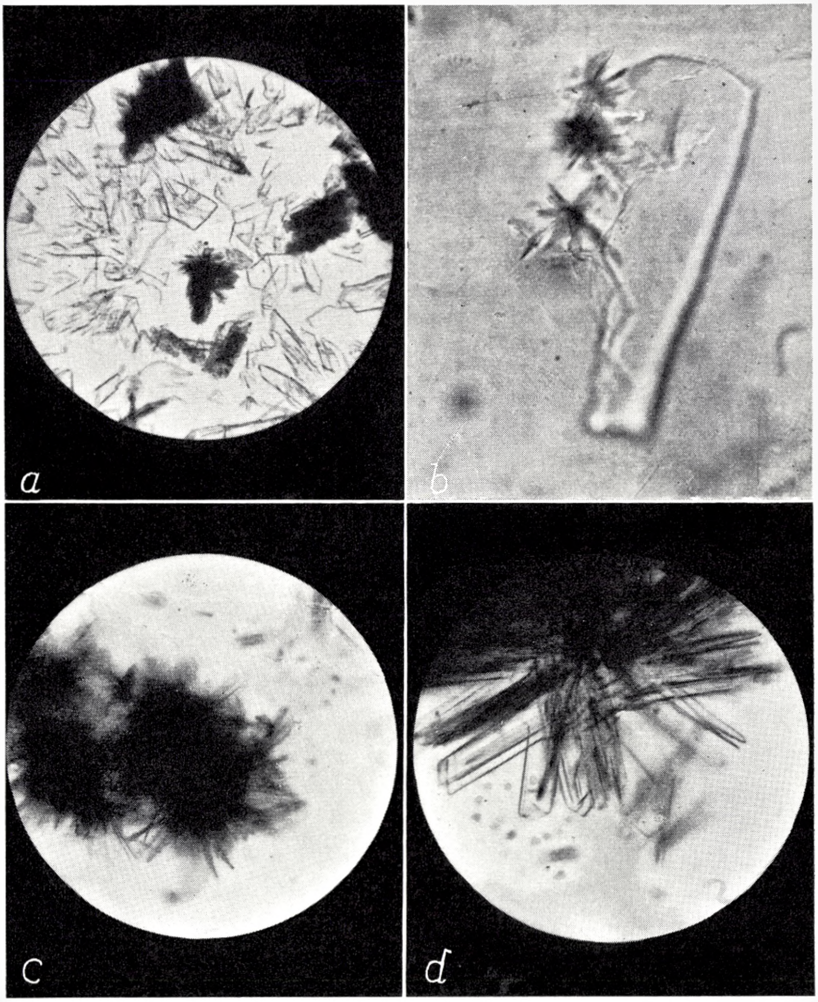

Fig. 1.

a 2-Phosphat in beginnender Umwandlung zu 2 $^2/_3$-Phosphat, Vergrösserung etwa 70 ×.
b 2-Phosphat in Umwandlung zu 2 $^2/_3$-Phosphat. Vergrösserung unbekannt.
c Typische Sphärolite von 2 $^2/_3$-Phosphat. Vergrösserung unbekannt.
d Schön ausgebildeter Sphärolit von 2 $^2/_3$-Phosphat. Vergrösserung 660 ×.

Zahlen für »Subst. ber. nach $Ca_4(PO_4)_3H, 2\,H_2O$« wurden berechnet nach dem Gehalt von Phosphor (Millimol P × 16,08). Der gefundene Neutralisationsgrad (N) schwingt innerhalb der Versuchsgenauigkeit um den Wert $2\,^2/_3$, und die Berechnung der abgewogenen Substanzmenge aus der Bestimmung des Phosphors nach der angenommenen Formel mit $2\,H_2O$ stimmt gut. Der Glühverlust ist ein wenig zu gross und entspricht ein wenig mehr Wasser als $2\,H_2O$.

b. Spätere Versuche ausgeführt von A. Tovborg Jensen.

Bei diesen (späteren) Versuchen wurde $CaHPO_4, 2\,H_2O$ mit 0,001 m oder schwächeren Lösungen von primärem Calciumphosphat bei 37° rotiert und in verschiedener Weise geimpft. In vielen Fällen erhielten sich die $CaHPO_4, 2\,H_2O$-Kristalle längere Zeit unverändert, und aus der Zusammensetzung der Lösung wurde dann die Löslichkeit des (2,2)-Phosphats berechnet. Nach längerer Zeit kam indessen spontan eine Ausscheidung von $2\,^2/_3$ Phosphat in Gang, was sowohl makroskopisch beobachtet werden konnte, indem der Niederschlag perlmutt-artig glänzend wurde und sich langsamer absetzte, wie — und besser — mikroskopisch, indem die leicht beobachtbaren Kristalle von 2-Phosphat nach und nach verschwanden und durch mehr oder weniger schöne Sphärolite von $2\,^2/_3$-Phosphat ersetzt wurden. Bei der Analyse der Lösungen konnte die eingetretene Umbildung immer bestätigt werden, indem der pA_H-Wert der Lösung kleiner geworden war und der $pI_{2\,^2/_3}$-Wert[24] grösser wurde. Nachdem die Kristalle des 2-Phosphates verschwunden waren, konnte man gewöhnlich auch konstatieren, dass die Lösungen in Bezug auf diese Kristalle ungesättigt geworden waren, indem der pI_2-Wert grösser als pL_2 (der pI_2-Wert in gesättigten Lösungen von $CaHPO_4, 2\,H_2O$) geworden war.

Die Analyse der abfiltrierten, ausgewaschenen und an der Luft getrockneten Niederschläge zeigte eine Zusammensetzung $Ca_4(PO_4)_3H, 3\,H_2O$ an. Wir betrachten diese neueren Analysen als sicherer als die älteren, die einen Wassergehalt von nur $2\,H_2O$ anzeigten.

c. Experimentelle Einzelheiten bei den von A. Tovborg Jensen ausgeführten Versuchen.

Darstellung. 1,000 g $CaHPO_4, 2\,H_2O$ wurde bei 37° mit 500 ml 0,0005 m $Ca(H_2PO_4)_2$ rotiert, nachdem mit 1 mg von einem älteren Präparat vom $2\,^2/_3$-Phosphat geimpft worden war. Im Laufe 24 Stunden wurde mikro-

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[24] $pI_{2\,^2/_3}$ ist eine Ionenprodukt-Funktion des $2\,^2/_3$-Phosphats, definiert durch $pI_{2\,^2/_3} = 4\,p\,[Ca] + 3\,p\,[HPO_4] - 2\,pA_H$, und pI_2 ist eine Ionenprodukt-Funktion des 2-Phosphats, definiert durch $pI_2 = p\,[Ca] + p\,[HPO_4]$.

skopisch festgestellt, dass die Bildung der Sphärolite gut im Gange war. pA_H war gleich 5,911, $pI_2 = 6{,}355$ und $pI_{2^2/_3} = 9{,}96$.

Der Wert $pI_2 = 6{,}355$ zeigt an, dass die Lösung noch annähernd mit dem 2-Phosphat gesättigt ist. Der Wert von pI_2 in einer gesättigten Lösung, pL_2, ist gleich 6,324.

Jetzt wurde die Lösung abdekantiert, durch 500 ml 0,000375 m $Ca(H_2PO_4)_2$ ersetzt und bei 37° weiter rotiert. 24 Stunden später war die Umbildung der Kristalle, mikroskopisch beobachtet, vollständig, und die Analyse der Lösung ergab $pA_H = 5{,}966$, $pI_2 = 6{,}382$, $pI_{2^2/_3} = 9{,}97$. Der höhere Wert von pI_2 deutet an, dass die Lösung nicht mehr mit dem 2-Phosphat gesättigt ist. Noch einmal wurde die Lösung abdekantiert und durch 500 ml 0,000375 m $Ca(H_2PO_4)_2$ ersetzt, und nach 48 Stunden Rotieren bei 37° ergab eine Analyse der Lösung: $pA_H = 6{,}480$, $pI_2 = 6{,}936$ und $pI_{2^2/_3} = 11{,}07$. Jetzt zeigt der pI_2-Wert deutlich an, dass die Lösung mit dem 2-Phosphat ungesättigt ist.

Dass $pI_{2^2/_3}$ 1,10 grösser als früher geworden ist, wird dadurch erklärt, dass am 2. Tage noch etwas $2^2/_3$-Phosphat ausgeschieden wurde, während an 3. und 4. Tage etwas $2^2/_3$-Phosphat in der (neuen) Lösung in Auflösung gegangen ist. Es scheint, als ob das $2^2/_3$-Phosphat in einem $pI_{2^2/_3}$-Gebiet von etwa 10 bis 11 weder in Lösung geht noch ausgeschieden wird (entweder gar nicht oder jedenfalls nur sehr langsam). Nachdem die Lösung noch 3 mal 24 Stunden, also im ganzen 7 Tage lang rotiert worden war, wurden gefunden: $pA_H = 6{,}476$, $pI_2 = 6{,}975$ und $pI_{2^2/_3} = 11{,}22$. Berechnet man den Neutralisationsgrad des Niederschlages, indem man berücksichtigt, was infolge der Analysen der dekantierten Lösungen in Lösung gegangen ist, findet man nach 1 mal 24 Stunden Rotieren $N = 2{,}226$, entsprechend einer Umbildung von $^1/_3$ des 2-Phosphats. Nach 2 mal 24 Stunden Rotieren mit einer neuen Lösung ist $N = 2{,}63$, entsprechend einer Umbildung von 95 %, und nach 7 tägigem Rotieren ist $N = 2{,}66$, entsprechend einer vollständigen Umbildung zu dem $2^2/_3$-Phosphat mit $N = 2{,}667$. Jetzt wurde der Niederschlag abfiltriert, mit Alkohol gewaschen und an der Luft getrocknet. Er bildete ein leichtes Pulver, unter dem Mikroskop schön gleichartig kristallinisch.

Analysen. Die gewonnenen Kristalle verloren selbst bei 100° nur langsam an Gewicht, und die Analyse ergab folgende Resultate:

	P_2O_5	CaO	N	H_2O
1. Analyse	42,3 %	44,7 %	2,658	13,0 %
2. Analyse	42,2 -	44,8 -	2,672	13,0 -
Berechnet nach $Ca_4(PO_4)_3H, 2H_2O$	44,2 %	46,5 %	2,667	9,3 %
Berechnet nach $Ca_4(PO_4)_3H, 3H_2O$	42,6 -	44,8 -	2,667	12,6 -

Der Inhalt von Wasser ist berechnet als Differenz: (100—% P_2O_5—% CaO).
Gewichtverlust bei 100°: 0,4 % und Glühverlust bei darauf folgendem Glühen 12,1 %.
Glühverlust: 12,5 % und 12,6 %.

Da Damsgaard-Sørensen's Analysen von früheren Präparaten darauf gedeutet hatten, dass nur 2 H_2O vorhanden waren, während Tovborg Jensen's Analysen 3 H_2O anzeigten, wurden noch 2 neue Präparate des $2^2/_3$-Phosphats dargestellt. Eins dieser Präparate zeigte bei der Titrierung einen Neutralisationsgrad 2,73 mit einem Wassergehalt 12,4 % und zeigte einen Glühverlust von 12,76 %. Das andere sehr schöne Präparat, das zweimal in einer neuen gesättigten Lösung von 2-Phosphat weiter gewachsen war, besass einen Neutralisationsgrad 2,67 mit einem Wassergehalt 11,0. Der Glühverlust war 12,5 %.

Bei einer neuen Analyse eines alten Präparats von Damsgaard-Sørensen fand Tovborg Jensen $N = 2{,}63$ und 11,1 % Wasser. Der Glühverlust war 13,3 %, bzw. 12,3 %. Für jede dieser letzten Analysen waren nur etwa 12 mg vorhanden, und die Bestimmungen sind deshalb nicht sehr zuverlässig. Die Zahlen deuten indessen darauf, dass dieses alte Präparat vielleicht auch 3 H_2O enthielt.

d. Erste Bestimmung des Debyeogramms ausgeführt von L. Misch.

Das $2^2/_3$-Phosphat besitzt eine grosse und vielleicht recht unregelmässige Elementarzelle. Denn sein Debyeogramm, genommen mit Eisenstrahlung, ergab nur schwache und diffuse Linien und eine starke allgemeine Schwärzung. Abkühlung der Kamera bis —70° während der Aufnahme half nur wenig. Die besten Aufnahmen wurden erzielt, wenn die Eisen-Strahlung (27 KV, 10 MA) durch einen Mangan-Filter filtriert wurde, um die beta-Strahlung zu entfernen, und 25 μ Aluminium-Folie auf dem Film angebracht wurde, um die Fluoreszenz-Strahlung von Calcium zu entfernen (vgl. G. Trömel und H. Møller, Z. anorg. Ch. **206** (1932) 230).

In Tabelle 1 sind die Lagen und die Intensitäten der Linien aufgeführt, die beobachtet wurden.

Die Lage der Linien wird durch den Abstand (in mm) der korrespondierenden Linien auf den beiden Seiten des direkten Strahles angegeben.

Die benutzte (steigende) Intensitätsskala ist: ss s^- s s^+ m^- m m^+ st.

TABELLE 1.

Debyeogramm des $2\,^2/_3$-Calciumphosphats, aufgenommen von L. MISCH.

1. Aufnahme		2. Aufnahme		1. Aufnahme		2. Aufnahme	
mm	Intensität	mm	Intensität	mm	Intensität	mm	Intensität
30,7	s	30,8	s	53,5	ss		
32,8	m^-	32,9	m^+	54,4	ss	54,6	s
35,2	s	35,6	s	59,5	s^+	59,7	m (diffus)
37,0	s	36,8	ss	63,5	s^+	63,7	m^+ (diffus)
39,9	st	40,1	st	67,9	m^-	68,0	m^+
		40,8	s	69,0	m	69,3	m^+-st
42,2	m^+	42,6	m^+-st			73,0	s-m
		43,6	ss			76,1	s-m
44,2	s	44,6	s^+	81,0	s	80,8	m^+
46,3	ss	46,4	s	82,0	s	82,4	m^+
51,5	ss	51,9	m^+	83,9	s	83,9	m^+

Die benutzte Kamera hatte einen Durchmesser von 57,3 mm.

Glüht man das $2\,^2/_3$-Phosphat, erhält man eine Mischung, die die Linien von beta-Tricalciumphosphat und, schwächer, von Calciumpyrophosphat ergibt.

e. Neue Bestimmung des Debyeogramms ausgeführt von KROGH ANDERSEN.

Um die Haltbarkeit des $2\,^2/_3$-Phosphats zu untersuchen, hat KROGH ANDERSEN auf meine Veranlassung 1955 eine neue Debye-Aufnahme aufgenommen von einem alten, 1935 dargestellten Präparat von $2\,^2/_3$-Calciumphosphat. Wir wünschten zu untersuchen, ob es sich unverändert gehalten hatte, oder mehr oder weniger umgewandelt war. Die neuen Aufnahmen wurden gemacht teils mit Co-Strahlung, filtriert durch einen 0,017 mm Eisen-Filter, und in einer BRADLEY-Kamera mit einem Durchmesser von 190 mm und mit Wasserstoff gefüllt, teils mit monochromatischer CuK_α-Strahlung in einer GUINIER-Kamera[26]. Um mit den alten Aufnahmen von L. MISCH, die mit Eisen-Strahlung ausgeführt waren, vergleichen zu können, wurden aus allen Linienlagen die Gitterabstände (d) in Ångström berechnet. In Tabelle 2 sind diese d-Werte der neuen (3. und 4. Kolonne) und der alten (2. Kolonne) Aufnahmen zusammengestellt.

In Anbetracht der verschiedenen Technik und der, namentlich in den

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[26] Radiocristallographie par ANDRÉ GUINIER, Paris, Dunod (1945) s. 136.

TABELLE 2.

Debye-Aufnahmen von $2^2/_3$-Calciumphosphaten.

Präparat von 1955 Aufnahme 1955 (Co-Strahlung, Fe-Filter, Kamera Durchmesser 190 mm, H_2)		Präparat von 1935 Zwei Aufnahmen 1935 (Fe-Strahlung, Mn-Filter, Al-Folie, Kamera Durchmesser 57,3 mm)		Präparat von 1935 Aufnahme 1955 (Co-Strahlung, Fe-Filter, Kamera Durchmesser 190 mm, H_2)		Präparat von 1935 Aufnahme 1957 (CuK_α-Strahlung in Guinier-Kamera)	
d	I	d	I	d	I	d	I
						18,6	st
						9,46	m
						9,07	m
						5,52	s^{+}
						5,08	s
						4,46	s
						4,27	s^{-}
						3,91	s
						3,85	s
						3,74	s^{+}
3,644	m^{-}	3,66–3,65	s–s			3,65	m^{+}
						3,48	s
3,401	m	3,43–3,42	m^{-}–m^{+}	3,364	st	3,43	st
						3,38	s
						3,32	s
						3,27	s
						3,22	s
3,175	ss	3,20–3,16	s–ss	3,121	m^{-}	3,17	s
3,050	ss	3,05–3,07	s–ss			3,05	s^{+}
						3,02	s
						2,99	s^{-}
				2,953	m^{+}	2,95	s^{-}
						2,85	s
2,835	st	2,84–2,83	st–st	2,826	s	2,84	st
2,813	st	2,79	s			2,83	st
						2,77	s^{+}
2,778	m^{-}			2,748	ss	2,75	s^{+}
				2,72	ss	2,69	ss
2,665	m^{+}	2,69–2,66	m^{+}–m^{+}			2,67	m
2,639	s					2,64	s^{+}
		2,61	ss^{-}			2,60	s^{+}
2,552	ss	2,57–2,54	s–s^{+}			2,55	s
		2,46–2,45	ss–s	2,482	ss	2,45	s
						2,33	st
				2,302	ss	2,29	s
				2,246	ss	2,26	s^{-}
2,208	s	2,23–2,21	s–m^{+}	2,198	ss	2,21	s^{+}

Fortsetzung der Tabelle 2.

d	I	d	I	d	I	d	I
		2,15	ss	2,156	s	2,15	s +
2,102	ss	2,12–2,11	ss–s			2,10	s
2,078	ss					2,08	s
						2,01	s
1,985	s	1,95–1,94	s^+–m	1,990	s	1,95	s
1,922	ss			1,911	s		
				1,866	ss	1,86	st
1,844	ss	1,84–1,84	s^+–m^+	1,846	m^-	1,84	s^+
1,83	s			1,832	s		

alten Aufnahmen, nicht scharfen Linien glaube ich, dass die Zahlen der Tabelle zeigen, dass das alte Präparat von 1935 sich im Laufe von 20 Jahren nicht umgewandelt hat. Unter dem Mikroskop gesehen hat es sich auch nicht geändert.

Die Guinier-Aufnahme (Kolonne 4) enthält zwar eine Reihe früher nicht beobachteter Linien, und andere Linien treten mit verstärkter Intensität auf. Die Technik ist ja aber auch bedeutend verfeinert. Nur die Guinier-Technik erlaubt Linien zu beobachten, denen d-Werte grösser als 3,65 Å entsprechen. Vergleicht man die d-Werte der neuen Aufnahme in der dritten Kolonne mit den alten Aufnahmen in der zweiten Kolonne, die mit mehr gleichartiger Technik ausgeführt sind, und namentlich mit den Zahlen in der ersten Kolonne, die mit einem frischen Präparat von $2^2/_3$-Phosphat (Darstellung vergleiche unten) und mit genau derselben Technik aufgenommen sind wie die Aufnahme in der dritten Kolonne, so findet man nur kleinere Unterschiede. In der Aufnahme des 20 Jahre alten Präparats sind keine starken Linien vorhanden, die nicht auch in der Aufnahme des frisches Präparates vorhanden sind. In der dritten Kolonne tritt zwar eine Linie bei 3,364 Å auf, deren Intensität als st angegeben ist. In der Guinier-Aufnahme in der vierten Kolonne ist die Intensität der Linie bei 3,38 Å nur als s angeben. Eine starke Linie liegt aber bei $d = 3{,}43$. Auch die Linie bei 2,953 Å mit Intensität m^+, besitzt in der Guinier-Aufnahme nur die Intensität s^-.

Um die Sachlage näher zu beleuchten, stellte Krogh Andersen neue Proben des $2^2/_3$-Phosphats dar.

Er rotierte einige Proben von 1 g $CaHPO_4$, $2\,H_2O$ mit 500 ml 0,0005 m $Ca(H_2PO_4)_2$ bei 37°. Da im Laufe einer Woche die Kristalle des 2-Phosphats sich nicht in Sphärolite umgewandelt hatten, und pH sich dauernd in der Nähe von 7 hielt, selbst nach Impfung mit einer Probe eines alten $2^2/_3$-Phosphats, rotierte er einige Proben von 1 g $CaHPO_4$, $2\,H_2O$ mit 500 ml destilliertem Wasser bei 37°. Hier wurde im Laufe einiger Tagen das 2-Phosphat anscheinend vollständig in die charakteristischen Sphärolite des $2^2/_3$-Phosphats umgewandelt, und pH sank bis auf 6,2 herunter[26a]. Es wurden von zwei solchen frischen Präparaten von $2^2/_3$-Phosphat DEBYE-Aufnahmen gemacht mit K_α-Cobalt-Strahlung, filtriert durch 0,017 mm Eisen, und in einer BRADLEY-Kamera mit Durchmesser 190 mm und mit Wasserstoff-Füllung. Die Glas-Pflöcke, auf die die Präparate mit Canada-Balsam in einer Schichtdicke von 0,1 mm aufgeklebt waren, hatten einen Durchmesser von 0,2 mm. Die beiden Aufnahmen waren ganz identisch, und es war KROGH ANDERSEN bei Vergleich der Filme mit guten Aufnahmen von Hydroxylapatit und von 2-Phosphatdihydrat nicht möglich, Linien zu finden, die diesen Stoffen entsprachen. Die Lagen der Linien nach Ausmessungen an einer der Aufnahmen sind in Tabelle 2, Kolonne 1 angeführt.

Die Aufnahme des neuen 1955-Präparates ist den alten Aufnahmen der 1935-Präparate ganz ähnlich. Sie enthält einige neue schwache Linien, und man kann Veränderungen der Lagen und der Intensitäten einiger Linien konstatieren. Die Veränderungen sind aber nicht grösser, als zu erwarten ist auf Grund der verbesserten Technik, und weil die Intensitätsbestimmungen von verschiedenen Personen ausgeführt worden sind.

f. Ältere und neuere Angaben in der Literatur über die Existenz eines $2^2/_3$-Phosphats.

J. J. BERZELIUS beschreibt in der 3. Auflage seines Lehrbuchs der Chemie (**4** (1935) 274) ein $2^2/_3$-Calciumphosphat, das er erhält bei Fällen einer Lösung von 2-Natriumphosphat mit Calciumchlorid in kleinen Anteilen und in Unterschuss. Es war gallertartig und zeigte unter dem Mikroskop gesehen keine Spur einer bestimmten Gestalt. Wenn er 2-Calciumphosphat in einer Säure aufgelöst und mit Ammoniak in Überschuss niederschlägt, so erhält er denselben Niederschlag.

[26a] Schon bei der Ausführung unserer älteren Versuche in den dreissiger Jahren hatte es uns verwundert, dass die Kristalle des $2^2/_3$-Phosphats oft lange Zeit ausbleiben konnten und recht unregelmässig auftauchten. S. R. ROWLES, der in unserem Laboratorium zusammen mit meinem Nachfolger A. TOVBORG JENSEN über Calciumphosphate neulich gearbeitet hat, kam auf den Gedanken, dass vielleicht ein geringer Kupfer-Gehalt in unserem in verzinnten Kupfer-Apparaten gekühlten und herumgeleiteten destillierten Wasser hierbei von Bedeutung sein könne, und er hat jetzt (April 1957) an TOVBORG JENSEN geschrieben, dass er nach seiner Rückkehr nach England konstatiert habe, dass sich das $2^2/_3$-Phosphat leicht (im Laufe von 1 oder 2 Tagen) bildet, wenn man mit glasdestilliertem Wasser arbeitet. Macht man aber durch Zusatz von Kupfervitriol das Wasser 10^{-5} molar, ja selbst nur 10^{-6} molar in bezug auf Kupfer, ist die Bildung des $2^2/_3$-Phosphats verlangsamt oder möglicherweise verhindert. In unserem destillierten Wasser haben wir schon vor vielen Jahren Kupfer in Mengen von über 10^{-6} molar konstatieren können.

In der 5. Auflage seines Lehrbuches (**3** (1945) 406) schreibt er über dieselbe Verbindung: »Am sichersten wird das Salz frei von einer Einmengung von einem andern Sättigungsgrade erhalten, wenn man eine Lösung von Chlorcalcium in ein mit kaustischem Ammoniak vermischtes phosphorsaures Ammoniak tropft.« Da seine Angaben über die Zusammensetzung dieses Calciumphosphats indessen bezweifelt wurden, so wiederholte BERZELIUS die Untersuchung, und in einer kleinen Arbeit von 1945[27] teilt er mit, dass wenn man einer Lösung von Ammoniumphosphat und Ammoniak eine Lösung von Calciumchlorid tropfenweise zusetzt, bis etwa die Hälfte des Phosphors ausgefällt ist, dann den Niederschlag abfiltriert, und wieder mit Calciumchlorid fällt, so findet man im ersten Niederschlag 8 Ca pro 3 P (entsprechent $N = 2^2/_3$), während der zweite Niederschlag weniger Phosphor enthält.

Man muss sagen, dass die Angaben unseres grossen Chemikers BERZELIUS hier einen recht zuverlässigen Eindruck machen; man wird aber doch etwas bedenklich, wenn er in der 3. Auflage seines Lehrbuches (**4** (1835) 275) schreibt: »Diese Verbindung (d.h. das $2^2/_3$-Phosphat) ist es, welche einen so hauptsächlichen Bestandteil der tierischen Knochen ausmacht«, denn diese Behauptung ist, wie wir heute wissen, jedenfalls nicht richtig. Es ist kaum wahrscheinlich, dass BERZELIUS wirklich ein wohl definiertes $2^2/_3$-Phosphat in seinen Händen gehabt hat, und jedenfalls hat er es nicht näher beschrieben.

WARINGTON[28] konnte BERZELIUS' Darstellung eines $2^2/_3$-Phosphats durch Fällung einer ammoniakalischen Lösung von Ammoniumphosphat mit Calciumchlorid nicht wiederholen. Dagegen erhielt auch er ein $2^2/_3$-Phosphat, wenn er eine Lösung von sekundärem Natriumphosphat mit einem Unterschuss von Calciumchlorid fällte, so dass die Lösung dauernd alkalisch blieb.

TISSIER[29] erhielt einen Niederschlag mit derselben Zusammensetzung bei der Fällung von Calciumphosphat-Lösungen mit Natriumborat-Lösung.

RINDELL[30] hat in seinen Untersuchungen über die Löslichkeit einiger Calciumphosphate durch vielmalige Behandlung von kleinen Mengen $CaHPO_4$, $2\,H_2O$ mit grösseren Mengen von Wasser bei 30° Bodenkörper erhalten, in welchen der Neutralisationsgrad bis auf 3 und noch höher gestiegen war. Seine Analysen deuten darauf, dass nicht nur tertiäres Calciumphosphat (mit $N = 3$) und vielleicht auch mehr basische Produkte gebildet worden waren, sondern auch Zwischenprodukte mit $N < 3$, die sich

[27] Lieb. Anm. **53** (1845) 286.

[28] Journ. chem. Soc. London (2) **4** (1866) 302.

[29] Compt. rend. Paris **39** (1854) 192.

[30] Untersuchungen über die Löslichkeit einiger Kalkphosphate, Helsingfors 1899.

unter der fortgesetzten Einwirkung von Wasser weiter umgewandelt hatten. Um diese Erscheinungen näher zu untersuchen, hat K. Buch[31] auf Veranlassung von Rindell eine neue Untersuchung der hydrolytischen Zersetzung des sekundären Calciumphosphats ausgeführt. Es gelang ihn indessen nicht, bestimmte Zwischenprodukte nachzuweisen. Die Untersuchung wurde bis zur Bildung von tertiärem Calciumphosphat durchgeführt. Ob diese Stufe die Grenze der Zersetzung darstellt, oder ob die Zersetzung noch bis zu einer basischen Verbindung weiterzuführen ist, so dass das Tricalciumphosphat nur als eine verhältnismässig stabile Zwischenstufe zu betrachten ist, darüber war es Buch schwer zu entscheiden. Mehrere Umstände, insbesondere die zahlreichen in der Natur vorkommenden basischen Phosphorsäureverbindungen, sprechen nach ihm für letztere Annahme.

Die ausgedehnten Versuchsreihen von Rindell und von Buch scheinen auch mir nach einer Durchsicht nicht auf wohl definierte Zwischenprodukte, ja nicht einmal auf ein wohl definiertes tertiäres Calciumphosphat zu deuten. Man kann aber doch sagen, dass die Versuchsreihen mit der Existenz eines $2^2/_3$-Phosphats und mit Hydroxylapatit als Endprodukt gut vereinbar sind.

In neuerer Zeit hat Jolibois[32] mitgeteilt, dass er ein kristallinisches Calciumphosphat mit der Formel $Ca_5(PO_4)_4H_2, 9\,H_2O$ (also mit $N = 2{,}5$) dargestellt hat. Die Verbindung wurde jedoch nicht näher beschrieben. A. Sanfourche und J. Henri[33] meinen später bei ihren Versuchen über das Verhalten von $CaHPO_4, 2\,H_2O$ bei Behandlung mit vielmals wiederholten Portionen von Wasser Anzeichen gefunden zu haben, die auf die Existenz des von Jolibois gefundenen intermediären Phosphats hindeuten.

Die experimentellen Belege, die Tissier, und Sanfourche und Henri für die Existenz einer Verbindung mit $N = 2^2/_3$ bzw 2,5 anführen, scheinen mir indessen nicht überzeugend zu sein.

In neuester Zeit (1950) hat P. A. Arnold[34] Anzeichen für die Existenz des $2^2/_3$-Phosphats beobachtet. Er konnte Berzelius' und Warington's alte Beobachtungen bestätigen, indem er bei Zusatz von 0,1 m Calciumchlorid-Lösung zu einer 0,1 m Lösung von sekundärem Natriumphosphat Niederschläge mit Neutralisationsgraden in der Nähe von $2^2/_3$ erhielt, wenn er nur nicht so viel Calciumchlorid zusetzte, dass die Lösung sauer wurde ($pH > 7$). Er verwendet für diese Verbindung Warington's alten, nicht besonders guten Namen Octocalciumphosphat. Er erhielt das $2^2/_3$-Phosphat bei Versuchen, in

[31] Zeitschr. anorg. Chem. **52** (1907) 325.
[32] Compt. rend. Paris **169** (1919) 1095.
[33] Bull. Soc. chim. France **52** (1933) 1213.
[34] Trans. Faraday Soc. **46** (1950) 106.

welchen er das Verhältnis $CaCl_2/Na_2HPO_4$ von $^1/_{12}$ bis zu $^1/_3$ variierte. In einer Tabelle, in welcher er angibt, wie sich das Verhältnis Ca/P im Niederschlag ändert, wenn er die Niederschläge (erhalten, wenn das Verhältnis $CaCl_2/Na_2HPO_4$ gleich $^1/_{12}$ war) verschiedene Zeiten (von 5 Minuten bis zu 8 Tagen) nach der Fällung in den Lösungen in Bewegung hielt, ehe er sie analysierte, finden sich jedoch Werte für Ca/P, die recht beträchtlich und unregelmässig variieren (von 1,34 zu 1,46; der Wert für das $2^2/_3$-Phosphat ist 1,33). ARNOLD schreibt, dass diese zu hohen und schwankenden Werte davon herrühren, dass die Niederschläge mehrmals mit Wasser gewaschen wurden.

ARNOLD hat Debyeogramme von einer Reihe seiner Niederschläge aufgenommen, und er gibt die Resultate wieder in Form von Diagrammen mit den aus der Lage der Linien berechneten d-Werten in Å als Abszissen und den Intensitäten der Linien als Ordinaten. Aus den Diagrammen zieht er die folgenden Schlüsse: Die Niederschläge mit Zusammensetzungen in der Nähe des $2^2/_3$-Phosphats zeigen Linienspektren, die denen des Hydroxylapatits ähnlich sind. Sie enthalten jedoch auch einige (schwache) Linien des 2-Phosphatdihydrats und ausserdem Linien, denen d-Werte von 2,31, 3,60, 5,86, 9,33, 11 und 22 Å entsprechen. ARNOLD schliesst hieraus, dass diese Niederschläge mit N in der Nähe von $2^2/_3$ ein $2^2/_3$-Phosphat mit Apatit-ähnlicher Gitter-Struktur neben etwas 2-Phosphat als Verunreinigung enthalten. Die grossen d-Werte 9,33, 11 und 22, die mit der gewöhnlichen Apatit-Struktur nicht vereinbar sind, setzt er in Verbindung mit »the platey nature of dried octocalcium phosphate«, und er sucht sie in folgender Weise zu erklären: Während das Hydroxylapatit-Gitter aus Schichten aufgebaut ist, die von zwischen ihnen eingeschobenen Ca^{++}-Ionen zusammengehalten werden, so sind im $2^2/_3$-Phosphat in jedem zweiten dieser Zwischenräume zwischen den Schichten die Ca^{++}-Ionen gegen H_2O-Molekeln umgetauscht, indem gleichzeitig H^+-Ionen in das Gitter aufgenommen worden sind, um die Elektroneutralität aufrecht zu erhalten.

Die Linien, die ARNOLD seinem Octocalciumphosphat zuschreibt, stimmen einigermassen mit den Linien überein, die wir von unserem $2^2/_3$-Phosphat erhalten haben. Dies geht aus Tabelle 3 hervor, in welcher die d-Werte seiner Aufnahmen mit den unsrigen zusammengestellt sind. Sein Octocalciumphosphat ist daher sicher mit unserem $2^2/_3$-Phosphat identisch. Von seiner Behauptung, dass das Debyeogramm des $2^2/_3$-Phosphats Apatit-ähnlich sei, muss ich dagegen Abstand nehmen.

In 1953 hat KURMIES[35] in einigen kristallinischen Bodenkörpern, die er

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[35] Die Phosphorsäure **13** (1953) 88.

beim Zusatz von $CaCl_2$-Lösung zu einer Lösung von Na_2HPO_4 erhalten hatte, in Elektronen-optischen Aufnahmen ausser den Kristall-Nadeln von Hydroxylapatit und den charakteristischen Kristallen von $CaHPO_4$, $2\,H_2O$ auch blättchen-artige Gebilde ganz unregelmässiger Form gefunden, die sich vor allem durch ihre äusserst geringe und anscheinend gleichartige Dicke von den Kristallen des Dicalciumphosphates unterscheiden. Er nimmt an, dass es sich bei den blättchen-artigen Gebilden um das von Arnold beschriebenen Octophosphat handelt, und es ist meine Überzeugung, dass er darin recht hat. Wenn man die Kristalle, aus denen unsere »Sphärolite« zusammengesetzt sind, durch kräftiges Rotieren der Lösung, in welcher sie aufgeschlemmt sind, von einander trennt und Elektronen-optisch photographiert, so erhält man Bilder (siehe Fig. 2), auf welche Kurmies' Beschreibung ausgezeichnet zutrifft.

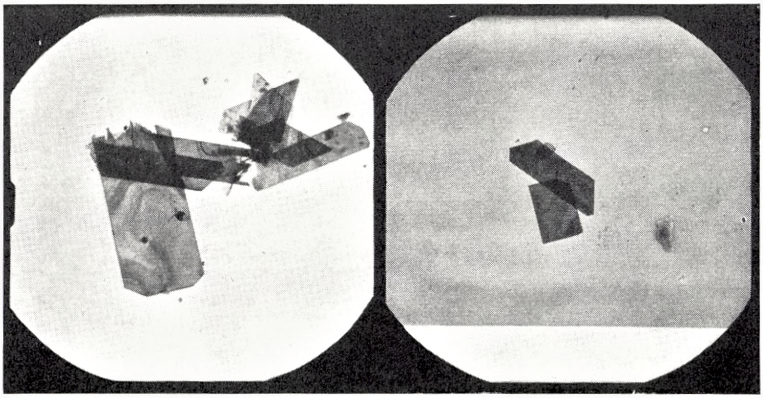

Fig. 2. Elektronen-optische Photographien von $2\,^2/_3$-Calciumphosphat. Vergrösserung 3500 ×. Aufgenommen von Carlsen und Krogh Andersen 1956.

Diego Carlström[36] hat neulich eine Kritik von Arnold's Arbeit veröffentlicht. Er meint, dass es nicht berechtigt sei, eine wohl definierte Verbindung in dem CaO-P_2O_5-H_2O-System mit der Zusammensetzung eines $2\,^2/_3$-Phosphats anzunehmen. Er kennt meine vorläufige Mitteilung von 1936 nicht, und jedenfalls konnte er nicht die Grundlage für meine Annahme der Existenz eines $2\,^2/_3$-Phosphats kennen, da sie erst in dieser Arbeit veröffentlicht wird.

Carlström hat selbst ein Calciumphosphat untersucht, dass er durch Mischung verdünnter Lösungen von Calciumchlorid und sekundärem Na-

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[36] Acta Radiologica, Supplementum 121, Stockholm 1955, 15—17.

TABELLE 3.

d-Werte in Å, berechnet aus der Lage der Linien in Debyeogrammen von Calciumphosphat-Niederschlägen, ausgefällt aus wässrigen Lösungen.

Arnold		Carlström		Trautz	Bjerrums $2\ ^2/_2$-Phosphat (nur die starken Linien)	
d	I	d	I	d	d	I
22	m	18,36	st	18,87	18,6	st
11	s	—	—	..	—	—
9,33	m	9,34	st	..	9,46	m
—	—	8,94	st	..	9,07	m
—	—	6,49	s	..	—	—
5,86	s	5,52	m	..	5,52	s+
—	—	4,49	ss	..	—	—
3,60	s	3,66	m	..	3,65	m+
—	—	—	—	3,412	3,43	st
—	—	—	—	2,847	2,84	st
—	—	—	—	..	2,83	st
—	—	—	—	..	2,67	m
2,31	s	2,22	m	..	2,21	s+
—	—	—	—	..	2,15	s+

triumphosphat bei gewöhnlicher Temperatur erhalten hatte[37]. Der Niederschlag war kristallinisch und zeigte in seinem Debyeogramm ausser den gewöhnlichen Hydroxylapatit-Linien (korrespondierend mit einer der gewöhnlichen gegenüber etwas veränderten Elementarzelle: $a = 9{,}44$Å statt 9,42 und $c = 6{,}84$ Å statt 6,88) eine kleine Anzahl recht wohl definierter Linien, die mit den von ARNOLD in einem Präparat mit $N = 2{,}68$ beobachteten ziemlich gut und die mit den Linien in unserem $2\,^2/_3$-Phosphat gut übereinstimmen. Auch O. R. TRAUTZ[37a] hat aus wässrigen Lösungen Niederschläge von Calciumphosphat erhalten mit N-Werten von etwa 2,66 und mit einer Linie in ihrem Debyeogramm, dem der grosse *d*-Wert 18,87 Å entspricht, und die er als identisch mit WARRINGTON's und ARNOLD's Octocalciumphosphat betrachtet. In der Tabelle 3 sind die *d*-Werte der von ARNOLD, von CARLSTRÖM und von TRAUTZ beobachteten Linien mit denen der stärksten Linien in dem von uns untersuchten $2\,^2/_3$-Phosphat zusammengestellt. Die Übereinstimmung zwischen den Zahlen der vier Beobachter ist ganz gut, namentlich zwischen den CARLSTRÖM'schen und den unsrigen. Nur fehlen bei CARLSTRÖM (und auch bei ARNOLD) die Linien, denen *d*-Werte von 2,67, 2,83

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[37] Nach dem Verfahren von Watson und Robertson, Am. Journ. Anat. **93** (1933) 25.

[37a] Ann. New York Acad. of Sci. **60** (1955) 699.

und 2,84 Å entsprechen. In diesem Gebiete liegen indessen starke Hydroxylapatit-Linien, die die $2^2/_3$-Phosphat-Linien verdeckt haben können. Die Übereinstimmung zwischen den *d*-Werten zeigt, dass sowohl Arnold wie Carlström und Trautz Präparate in Händen gehabt haben, die $2^2/_3$-Phosphat enthielten.

Die Existenz des $2^2/_3$-Phosphats ist in neuerer Zeit jedoch von anderer Seite bezweifelt worden. Zum Beispiel schreibt E. Hayek[14] 1951: »Durch Gleichgewichtsuntersuchungen im System CaO-P_2O_5-H_2O bei 40°, insbesondere Röntgen- und Elektronenmikroaufnahmen, wird für das neutrale und alkalische Gebiet die ausschliessliche Existenz der Bodenkörper $CaHPO_4$, $2\,H_2O$, Hydroxylapatit und $Ca(OH)_2$ nachgewiesen«. Nach einem Briefwechsel, in welchem ich ihm meine Unterlagen für die Existenz des $2^2/_3$-Phosphats mitgeteilt habe, schrieb er mir 1955: »Es geht daraus sicherlich eindeutig hervor, das die Existenz dieses Salzes nachgewiesen ist. Offensichtlich hat es aber ein recht schmales Existenzgebiet zwischen dem sekundären Phosphat und dem Hydroxylapatit.«

g. Vorkommen von $2^2/_3$-Phosphat in der Natur.

α. Mineralanalysen, die auf die Existenz eines $2^2/_3$-Calciumphosphat-haltigen Minerals hingedeutet haben.

Das Mineral Martinit hat infolge Kloos[38] die Zusammensetzung $Ca_5(PO_4)_4H_2, {}^1/_2\,H_2O$, also $N = 2{,}5$. Mehrere andere Forscher haben in Guano-Lager Calciumphosphat-Minerale getroffen, in welchen der Neutralitätsgrad N zwischen 2 und 3 lag. Zeugit ist ein von Julien[39] analysiertes Umlagerungsprodukt von Metabrushit-Kristallen, gefunden in »Sombrero«-Guano. In diesem Mineral ist nach Julien $N = 2{,}64$. Da das Mineral indessen 3,57 % MgO, 0,66 % $(Fe, Al)_2O_3$ und andere Unreinheiten enthielt, ist dieser Wert wohl ohne grössere Bedeutung. Clifford Frondel[40] meint, dass die Minerale Zeugit und Martinit mit dem von ihm beschriebenen und benannten Mineral Whitlockit, einem Magnesium-haltigen Tricalciumphosphat, identisch seien.

β. Biologisches Vorkommen von $2^2/_3$-Phosphat in Zahnstein.

A. Tovborg Jensen und K. Gebhard Hansen[41], die die Zusammensetzung von Zahnsteinen untersucht haben, haben in 48 von im Ganzen

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[38] Jahrbuch d. Min. **1** (1888) 41.
[39] Am. J. Sc. **40** (1865) 373.
[40] The American Mineralogist, **28** (1943) 228.
[41] A. Tovborg Jensen und K. Gebhard Hansen. Experientia, Basel **13** (1957) 311.

124 Zahnstein-Proben, stammend von Kopenhagener Patienten, Röntgenspektrographisch einen kleinen Inhalt von $2^2/_3$-Calciumphosphat nachweisen können.

6. Das hypothetische 3-Phosphathydrat.

a. Die Geschichte.

Über die Existenz eines 3-Calciumphosphathydrats ($Ca_3(PO_4)_2$, aq) als eine wohl definierte chemische Verbindung sind die Meinungen lange Zeit sehr geteilt gewesen.

In der ersten Hälfte des 19. Jahrhunderts wurden die Niederschläge, die durch Zusatz von Calciumchlorid zu alkalischen Lösungen von Phosphaten gefällt wurden, als Tricalciumphosphat angesehen (J. J. Berzelius[42], E. Mitscherlich[43]).

Als Resultat ausgedehnter Untersuchungen über die Löslichkeit der Calciumphosphate kamen F. K. Cameron und seine Mitarbeiter indessen zu einer anderen Auffassung. Cameron und Bell[44] schreiben 1907: »That the so-called tricalcium phosphate ($Ca_3(PO_4)_2$) is not a definite chemical compound, but is one of a series of solid solutions of which series it is a member. The behavior of this tricalcium phosphate at ordinary temperatures and in contact with water or aqueous solutions does not exclude, however, the possibility that under other conditions, such as high temperature, there may be a compound of the above formula which may exist over a considerable range of concentration in a molten magma.« Diese Auffassung hat sich in den folgenden Jahren vollständig bestätigt. Cameron, Seidell und Bell[45] haben auch geäussert, dass zwischen dem sekundären Dicalciumphosphat und Calciumhydroxyd nur eine Reihe von festen Lösungen existiere. Diese letzte Behauptung hat sich nicht als richtig erwiesen.

1917 schreibt H. Bassett[46] bei seinen Isothermenbestimmungen im System CaO-P_2O_5-H_2O: »It is true that one still finds statements in textbooks to the effect that these substances (d. h. Knochenphosphate und Phosphorit-Mineralen) consist of tricalciumphosphate. This is far from being the case, however. Even laboratory preparations of so-called tricalcium phosphate vary considerably in composition and seldom have the correct CaO-

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[42] J. J. Berzelius, Lehrbuch d. Chem. 3. Aufl. **4** (1835) 275.
[43] E. Mitscherlich, Lehrbuch d. Chem. **2** (1840) 135.
[44] U.S. Department of Agriculture, Bureau of Soils, Bull. No. 41 (1907).
[45] Journ. Amer. Chem. Soc. **27** (1905) 1512.
[46] Journ. chem. Soc. London **111** (1917) 620.

P_2O_5 ratio«. In derselben Abhandlung schreibt BASSETT jedoch später (S. 642): »Two, and only two, phosphates of calcium more basic than dicalcium phosphate exist which can be in stable equilibrium with an aqueous solution at 25° (and probably at any temperature). These are tricalcium phosphate, $Ca_3P_2O_8$, and hydroxyapatite, $(Ca_3P_2O_8)_3$ $Ca(OH)_2$«. Etwas später schreibt er: »Hydroxyapatite is the stable phase over a range of acidity of great practical importance, as it can exist in contact with faintly acid, neutral, and alcaline solutions«, und er schreibt auch: »It is probable that hydroxyapatite is the only calcium phosphate that can permanently exist under normal soil conditions«.

Zu ähnlichen Resultaten wie CAMERON und wie BASSETT sind später H. DANNEEL und K.W. FRÖLICH[47] gekommen. Ein Präparat mit der Zusammensetzung $Ca_3(PO_4)_2$, aq kann nach ihnen aus wässriger Lösung nur unter ganz bestimmten, näher angegebenen Bedingungen ausgefällt werden und wird deshalb von ihnen nicht als eine bestimmte chemische Verbindung aufgefasst. In 1932 schliessen sich BREDIG, FRANCK und FÜLDNER[48] dieser Auffassung an. Sie meinen röntgenographisch nachgewiesen zu haben, dass die bereits früher durch chemisch-analytische Befunde nahegelegte Folgerung richtig ist, wonach man in gefälltem Tricalciumphosphat nicht das Individuum $Ca_3P_2O_8$, sondern eine apatitähnliche Substanz vor sich hat. Auch die käuflichen Handelswaren von tertiärem Calciumphosphat zeigten variierende Zusammensetzungen.

SCHLEEDE, SCHMIDT und KINDT[49] beobachten zu derselben Zeit, dass die gewöhnlichen Tricalciumphosphate nach ihren Debyeogrammen Mischungen von Hydroxylapatit und Dicalciumphosphat sind.

TRÖMEL[50] hat nachgewiesen, dass man aus einer bei hoher Temperatur geschmolzenen Masse mit der Zusammensetzung 3 CaO, P_2O_5 bei Abkühlung eine wohl definierte, kristallisierte alpha-Form von wasserfreiem Tricalciumphosphat erhält, die bei schneller Abkühlung zu gewöhnlicher Temperatur gewonnen werden kann, die aber bei langsamer Abkühlung (langsam besonders bei etwa 1150°) in eine bei tiefer Temperatur beständige beta-Form übergeht. Beide Formen besitzen charakteristische Debyeogramme mit scharfen Linien und gut definierten optischen Eigenschaften.

Über die Resultate seiner Untersuchungen von wässrigen Systemen schreibt TRÖMEL[51]: »Es wurde gezeigt, dass bei der Umsetzung von Natrium-

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[47] Zeitschr. Elektrochem. **36** (1930) 302.

[48] Zeitschr. Elektrochem. **38** (1932) 158, vgl. auch **39** (1933) 959.

[49] Zeitschr. Elektrochem. **38** (1932) 633.

[50] Mitt. Kaiser-Wilh. Inst. Eisenforschung **14** (1932) Abh. 198.

[51] TRÖMEL und MÖLLER, Zeitschr. anorg. Chem. **206** (1932) 240.

phosphat mit Calciumnitrat bei Gegenwart von überschüssigem Ammoniak in wässriger Lösung als primäre Kristallart stets nur Hydroxylapatit $Ca_{10}(PO_4)_6(OH)_2$ ausfällt und nicht Tricalciumphosphat, wie bisher angenommen wurde. Für das weitere Verhalten des Niederschlags beim Trocknen und für seine Zusammensetzung ist ausschlaggebend, ob bei der Fällung Gelegenheit gegeben war, überschüssiges P_2O_5 zu adsorbieren. Wenn das der Fall ist, so werden Zusammensetzungen erreicht, die der des Tricalciumphosphats naheliegen. Diese Verbindung selbst kommt erst zustande, wenn die Adsorptionsverbindung durch Glühen zerstört wird. Dabei entstehen dann entsprechend der Zusammensetzung durch Reaktion im festen Zustand Gemenge von beta-Tricalciumphosphat und Hydroxylapatit, vielfach auch mehr oder weniger reines beta-Tricalciumphosphat.

In einigen Arbeiten aus den Jahren 1931—42 beschreibt S. B. Hendricks[52] die Darstellung eines 3-Calciumphosphathydrats mit Hydroxylapatit-ähnlichem Debyeogramm. Es wurde gewonnen (1931) durch langsames Zufügen einer Lösung von Trinatriumphosphat zu einer Lösung mit einem Überschuss von Calciumnitrat als ein Niederschlag, der, nachdem er mit einer gesättigten Lösung von Tricalciumphosphat nitratfrei gewaschen und bei 50° getrocknet war, eine Zusammensetzung, entsprechend der Formel $Ca_3P_2O_8, 2\,H_2O$ besass. Das Hydrat besitzt nach seinem Debyeogramm zu urteilen eine Hydroxylapatit-ähnliche Struktur, und Hendricks nimmt an, dass die Struktur des Hydrats, das feste Lösungen mit Hydroxylapatit bildet, am besten mit der Formel $Ca_9(H_2O)_2(PO_4)_6$ (oder $Ca_3(PO_4)_2, {}^2/_3\,H_2O$) wiedergeben wird. Wenn man in dieser Formel die zwei H_2O mit $Ca(OH)_2$ umtauscht, so erhält man ja die Formel des Hydroxylapatits. Später gibt Hendricks als gutes Herstellungsverfahren für das Tricalciumphosphathydrat Hydrolyse von 2-Phosphatdihydrat in Wasser bei 100° und $pH < 5$ an. Das 3-Phosphat wird dann als eine kristallinische Substanz in Kristallen bis zu $2\,\mu$ lang und mit der Formel $Ca_9(PO_4)_6, 2\,H_2O$ gewonnen[53].

Nach den Erfahrungen vieler anderer Forscher führen indessen die angegebenen Darstellungsverfahren nicht zu wohl definierten Hydraten eines 3-Calciumphosphats, und Hendricks selbst ist auch später[54] für die Auffassung eingetreten, dass sein Tricalciumphosphathydrat als Hydroxylapatit mit adsorbierten phosphorsäurereicheren Verunreinigungen aufzufas-

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[52] S. B. Hendricks, W. L. Hill, K. D. Jacob und M. E. Jefferson, Industrial and Engineering Chemistry **23** (1931) 1413. S. B. Hendricks, M. E. Jefferson und V. M. Mosley, Zeitschr. f. Kristallographie **81** (1932) 352 und Science **96** (1942) 255.

[53] S. B. Hendricks und W. L. Hill, Proc. Nat. Acad. Sci. U.S.A., **36** (1950) 731.

[54] Proc. Nat. Acad. Sci. U.S.A. **36** (1950) 731. Trans. of the 3. and 4. Conference on Metabolic Interrelations with special reference to calcium, 1951 und 1952, sponsored by Josiah Macy jr. Foundation.

sen ist. Die Kalksubstanz der Knochen und der Zähne betrachtet er jetzt nicht mehr als Tricalciumphosphathydrat, sondern als Hydroxylapatit mit an äusseren und inneren Oberflächen *adsorbierten* phosphorsäurereicheren Calciumphosphaten und Calciumcarbonat. Hendricks meint, dass das Debyeogramm der Kalksubstanz der Knochen mehr Apatit-ähnlich ist, als es mit einer Substitution von $Ca(OH)_2$ mit $2\,H_2O$ vereinbar sei, und die Oberfläche (äussere und innere) der Hydroxylapatit-Kristalle ist so gross, dass genügende Mengen adsorbiert werden können, um die analytisch gefundenen Zusammensetzungen der Kalksubstanz erklären zu können. Und 1955 schreibt Hendricks[55a], dass wir jetzt wissen, dass andere Bestandteile, die in Knochen und Phosphoriten neben Hydroxyl- und Fluor-Apatit vorhanden sind (CO_3^{--}, HCO_3^-, H^+, Überschuss von OH^+ und F^-, H_2O, Na^+, Mg^{++}, $MgOH^+$, Citrat), sich in den Grenzflächen der Kristalle befinden. Diese Bestandteile können 10 $^0/_0$ der ganzen Knochen-Masse betragen, was viel mehr ist, als was für andere Substanzen gefunden worden ist.

Die Existenz eines 3-Calciumphosphathydrats und sein Auftreten in Knochen und Zähnen wird aber von Dallemagne[55] und seinen Mitarbeitern weiterhin verteidigt. Dallemagne hat käufliche Proben von gefälltem 3-Calciumphosphat untersucht. Sie ergaben Debyeogramme mit unscharfen, Apatit-ähnlichen Linien. Bei Erwärmung zu 105° gaben die Proben verschiedene Mengen adsorbierten Wassers ab, ohne ihre Debyeogramme zu ändern. Wurden sie aber weiter bis 700° erhitzt, gaben alle Proben $2\,H_2O$ pro $Ca_9(PO_4)_6$ ab, und gleichzeitig änderten sich ihre Debyeogramme, indem sie jetzt die schärferen Linien des wasserfreien 3-Calciumphosphats zeigten. Hydroxylapatit dagegen ändert sein Debyeogramm erst bei einer weit höheren Temperatur. Auch die Niederschläge mit der Zusammensetzung $Ca/P = 1{,}94$, entsprechend $N = 3$, die Dallemagne bei Einwirkung von Calciumnitrat auf 2-Natriumphosphat in einer grossen Menge Wasser erhalten hatte, zeigten dasselbe Verhalten. Er benutzt als Namen für dieses ausgefällte Tricalciumphosphathydrat die Bezeichnung *alpha-Tricalciumphosphathydrat*. 1949 (l.c.) fasst Dallemagne seine Erfahrungen mit folgenden Worten zusammen: »Le phosphate tricalcique éxiste réellement sous la forme hydratée, que nous avons décrite, mais sa préparation à l'état pur exige des conditions bien definies. Précipité en milieu trop alcalin, il adsorbe du

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[55a] Ann. New York Acad. Sci. 60 (1955) 660 (Abstract).

[55] Dallemagne und Brasseur: Bull. Soc. Roy. Liège, **11** (1942) 451, 488. Dallemagne, Thesis for Appointment of Higher Teaching, Gordimer, Liège (1943). Dallemagne und Brasseur: Experimentia, **3** (1947) 469. Dallemagne, Brasseur und Melon: Bull. Soc. chim. France **3** (1949), Documentations 138; Bull. Soc. chim. biol., **31** (1949) 425. Dallemagne: Journ. Physiologie (Paris), **43** (1951) 425. Dallemagne: Trans. 4. Conf. on Metabolic Interrelations (1952) 154. Sponsored by Josiah Macy jr. Foundation. Dallemagne, Fabry und Posner: Bioch. et Bioph. Acta, **15** (1954) 304.

chaux. Abandonné à lui-même dans les eaux-mères pendant les heures qui suivent sa formation, il se décompose. Précipité à partir de chaux il adsorbe une partie de ce dernier, même s'il se forme en milieu finalement neutre«.

Dass ein Niederschlag mit der richtigen stöchiometrischen Zusammensetzung von Dallemagne nur unter ganz bestimmten Bedingungen gewonnen wird, spricht indessen entschieden dafür, dass es sich nicht um eine wohl definierte chemische Verbindung handelt (vgl. Danneel und Frölich[47]); und dass die Substanz von Dallemagne schon bei 700° Wasser verliert unter gleichzeitiger Änderung ihres Apatit-ähnlichen Debyeogramms zu demjenigen des wasserfreien beta-Tricalciumphosphats, trotzdem das reine Hydroxylapatit Wasser erst bei 1300° abgibt, ist nicht damit unvereinbar, dass es aus kleinen Hydroxylapatit-Partikeln mit adsorbierten säurereicheren Verunreinigungen besteht. Die Wasserabgabe bei 700° erscheint dann als eine natürliche Folge der Umsetzung des Hydroxylapatits mit den adsorbierten Verunreinigungen bei dieser Temperatur.

In einer interessanten Arbeit von 1950 hat auch P. W. Arnold[56] sich über die Existenz des Tricalciumphosphathydrats ausgesprochen. Auf Grund gewisser von ihm entwickelter Vorstellungen über die Gitterstrukturen von $2\,^2/_3$-Calciumphosphat und von Hydroxylapatit kommt er zu der Auffassung, dass eine ununterbrochene Reihe von Niederschlägen mit Apatit-ähnlichen Gittern zwischen diesen Verbindungen existieren kann, und dass das 3-Calciumphosphathydrat als ein Glied in diese Reihe eingeht.

Diego Carlström[57] ist in einer Arbeit von 1955 auf dieselbe Frage eingegangen. Er gibt eine ausführliche Darstellung der verschiedenen Auffassungen, die über die Calciumphosphate mit Apatit-ähnlichen Strukturen vorgebracht worden sind. Seine eigene Auffassung vom 3-Calciumphosphathydrat kleidet er in die folgenden Worte (l. c. S. 20): »The observed differences in the physical characteristics of TCPH and HA cannot, however, be taken as definite evidence for the existence of TCPH as a single phase«, und in »The Summary« S. 44: »The varying opinions on the nature of apatite-like tertiary calcium phosphate are discussed. The earlier evidence for the existence of tricalcium phosphate hydrate seems to be inconclusive.«

Auch Hayek[58] weist auf Grund der vorliegenden Daten die Existenz dieser Verbindung entschieden zurück.

Um die Frage zu beleuchten, haben A. P. Posner und S. E. Stephenson[59] grössere und besser entwickelte Kristalle vom 3-Calciumphosphat-

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[56] Trans. Faraday Soc. **46** (1950) 1061.

[57] X-Ray Crystallographic Studies on Apatites and Calcified Structures, Acta Radiologica, Supplementum 121 (1955).

[58] E. Hayek, F. Möllner und K. Koller, Monatsheft f. Chemie **22** (1951) 959. Sitz. ber. Akad. Wien, Math.-naturwiss. Kl., Abt. IIb **160** (1951) 959.

[59] Journ. Dental. Research **31** (1952) 371.

hydrat dargestellt. Aus einer schlecht kristallisierten, käuflichen Probe von Tricalciumphosphathydrat (mit Partikeln von etwa 500 Å) haben sie durch Erhitzung mit Wasser auf 250° bis 450°C in einer mit Platin bekleideten hydrothermalen Bombe Kristalle von derselben Zusammensetzung erhalten, die eine Länge von 2—3 Mikron besassen. Diese grossen Kristalle zeigten Debyeogramme, die denjenigen des Hydroxylapatits ganz ähnlich waren, sowohl in Bezug auf Linienschärfe wie auf Linienlage ($a = 9{,}42$—$9{,}44$; $c = 6{,}87$—$6{,}88$; für Hydroxylapatit ergab sich $a = 9{,}45$; $c = 6{,}89$). Das spezifische Gewicht und der Refraktionskoeffizient weichen etwas von denjenigen des Hydroxylapatits ab. Die Verfasser schreiben, dass diese Unterschiede »can possibly be explained by postulating a 6 per cent phosphate ion inclusion in the entrapped surfaces of the hydroxy apatite crystal«. Als mögliche Formel für ihre Kristalle schlagen sie deshalb vor:

$$Ca_{10}(PO_4)_6(OH)_2, \text{ occluded } 0{,}67\ H_3PO_4.$$

b. Eigene Versuche über die Eigenschaften von bei 100° C ausgefällten Calciumphosphaten mit Apatit-ähnlichen Debyeogrammen.

α. *Beschreibung des angewandten Verfahrens.*

Wir haben schon 1935/36 eine Versuchsreihe durchgeführt, in welcher die Niederschläge untersucht wurden, die aus einer Calciumsalz-Lösung bei langsamem Zutropfen einer Lösung von Natriumphosphat bei 100°C ausgeschieden wurden, wenn man während der Fällung durch Zusatz von NaOH, bzw. HCl dafür sorgte, dass *die Fällung die ganze Zeit bei demselben pH-Wert stattfand.* Die Versuchsreihe wurde von A. Tovborg Jensen geplant und ausgeführt.

Die näheren Einzelheiten bei der Ausführung der Versuche waren die folgenden: 23,8 g $CaCl_2$, $6\,H_2O$ (0,1 Mol + 2 g extra) wurden in 1800 ml Wasser mit zugesetztem Farbstoffindikator in einem Rundkolben zum Sieden erhitzt und einige Zeit gekocht, um Kohlendioxyd auszutreiben. Im Laufe von anderthalb Stunden wurde danach eine Lösung von 0,06 Mol Na_2HPO_4, $2\,H_2O$ (10,63 g) + 0,06 oder 0,08 Mol NaOH in 100 ml Wasser zugetropft, indem ständig gekocht wurde. Während der ganzen Zeit wurde durch Zusatz von 0,1 m NaOH, bzw. 0,1 m HCl, dafür gesorgt, dass der Farbstoffindikator in der Lösung immer denselben Farbton zeigte, und nach der Fällung wurde gewöhnlich eine Stunde weiter gekocht.

In vielen der Versuche wurden jedoch doppelt so grosse Mengen von $CaCl_2$ und von Na_2HPO_4 + NaOH angewandt. Die Versuchsnummern sind in diesen Fällen mit einem * versehen. In diesen Versuchen sind die Konzentrationen von NaCl und von $CaCl_2$ in den Mutterlaugen somit doppelt so gross wie in den anderen. Die grössere Konzentration von $CaCl_2$ führte in Versuch 12* (mit einen kleinen pH-Wert) zu einer Ausscheidung von wasserfreiem 2-Calciumphosphat, die zu einem unangenehmen Stossen während des Kochens führte. Dieser Versuch wurde nicht zu Ende geführt. In Versuch 7 wurde das $CaCl_2$ gegen eine äquivalente Menge von $Ca(NO_3)_2$ ausgetauscht, um eine Bildung von etwas Chlorapatit sicher zu vermeiden. Eine Bildung von Chlorapatit-haltigen Niederschlägen wurde jedoch in den $CaCl_2$-Versuchen niemals konstatiert.

In den Versuchen 14 und 15 wurden statt $CaCl_2, 6H_2O$ und Na_2HPO_4, $2\ H_2O + NaOH$ festes primäres Calciumphosphat und eine gesättigte Lösung von Calciumhydroxyd angewandt. Das primäre Calciumphosphat wurde in ganz kleinen Portionen mit einem Spatel zu 500 ml mit Indikator versehenem siedendem Wasser zugesetzt, und durch Zusatz der $Ca(OH)_2$-Lösung wurde ständig der gewünschte Indikator-Farbton festgehalten. In Tabellen und Übersichten sind diese Versuche mit »(ohne NaCl)« bezeichnet. In diesen Versuchen ist es sicher, dass die ausgefällten Niederschläge weder Na noch Cl enthalten können. Die Ionenstärke in der Mutterlauge ist in diesen Versuchen weit kleiner als in den anderen Versuchen.

Als Indikatoren wurden angewandt: Methylorange (MO), Methylrot(MR), Bromthymolblau (BTB), Phenolphtalein (Ph) und Thymolphtalein (Th). Die später angegebenen Werte für die pH-Werte, bei welchen die Fällungen vorgenommen wurden, sind nur geschätzt. Sie repräsentieren die pH-Werte, bei welchen die Indikatoren bei gewöhnlicher Temperatur den Farbton besitzen, der während der Fällung bei 100° durch Zusatz von HCl oder NaOH angestrebt wurde. Da es sich um Aufschlemmungen handelt, konnte ein bestimmter Farbton nur recht ungenau festgehalten werden.

In den Mutterlaugen wurden in mehreren Fällen der Gehalt an Phosphorsäure ($[PO_4]$) und der Neutralisationsgrad der Phosphorsäure (N) durch Titrierungen von herausgenommenen Proben zum Primärpunkt und zum Apatitpunkt nach den Angaben in Abschnitt 8 bestimmt. In den Mutterlaugen, in welchen keine Phosphorsäure gefunden wurde, konnte der Gehalt an freier Base ($[OH^-]$) aus den Titrierungsresultaten berechnet werden.

Wenn in der Mutterlauge noch Phosphorsäure vorhanden war (was in den Versuchen mit kleinen pH-Werten der Fall war), erlaubte die Bestimmung des Neutralisationsgrades der Phosphorsäure eine gewisse Kontrolle der geschätzten pH-Werte.

In den Niederschlägen wurde der Neutralisationsgrad der Phosphorsäure durch Titrierungen zum Primärpunkt und zum Apatitpunkt nach dem Verfahren in Abschnitt 8 bestimmt. Wenn der *N*-Wert als »(direkt)«, bezeichnet ist, wurde der Niederschlag zuerst mit Hilfe einer Zentrifuge mit Wasser gut ausgewaschen. Die Niederschläge waren alle so feinkörnig, dass sie tonartig waren. Durch Zentrifugierung (mit 5500 bis 6000 Umdrehungen) wurden sie als eine stark wasserhaltige Paste (mit etwa 75 $^0/_0$ Wasser) gewonnen. Von dieser Paste konnte man die Mutterlauge abgiessen. Es war nicht leicht, diese Paste in dem Waschwasser aufzuschlemmen. Es war notwendig, die Paste zuerst in dem Waschwasser aufzurühren und danach einige Zeit in einer Schüttelmaschine zu schütteln. Einige *N*-Werte, die mit »(indirekt)« bezeichnet sind, wurden durch Analyse einer Aufschlemmung des ungewaschenen Niederschlags in Mutterlauge gewonnen, indem die Analyseresultate von einer entsprechenden Menge Mutterlauge abgezogen wurden. Einige wenige *N*-Werte, die als »(berechnet)« bezeichnet sind, wurden aus den angewandten Mengen von Ausgangsmaterialen und einer Analyse der Mutterlauge berechnet.

Einige der Analysen wurden von LINDHARD ausgeführt. Sie sind mit (L) bezeichnet. Wurden Parallel-Analysen von TOVBORG JENSEN ausgeführt, sind sie mit (T.J.) bezeichnet. Ein Vergleich dieser Bestimmungen gibt eine Vorstellung von der Genauigkeit, die man den gefundenen *N*-Werten zulegen kann.

Von einer Reihe der Niederschläge wurden von Frl. L. MISCH sogleich nach ihrer Herstellung Debyeogramme aufgenommen. Sie verwendete eine kleine Kamera mit 57 mm Durchmesser und arbeitete mit Fe-Strahlung, und die erhaltenen Aufnahmen waren wegen dieser unvollkommenen Technik nicht gut. L. MISCH's Beschreibungen der erhaltenen Debyeogramme sind bei der Besprechung der einzelnen Versuche angeführt. Von den Niederschlägen, die in 6 der Versuche erhalten wurden, sind viele Jahre später neue und bessere Debyeogramme von TOVBORG JENSEN aufgenommen worden.

β. *Die Resultate der einzelnen Versuche.*

Die Versuche Nr. 1 bis Nr. 3 betrachten wir nur als Vorversuche, da sie nicht so exakt ausgeführt wurden wie die späteren. Es soll von diesen Versuchen nur angeführt werden, dass sie bei pH ~ 8,5 (Phenolphthalein schwach rot) ausgeführt wurden. In den mit Wasser nur unvollständig ausgewaschenen Niederschlägen wurden *N*-Werte von 3,31 bis zu 3,34 gefunden. Gelöst in Salpetersäure ergaben die ausgewaschenen Niederschläge nur eine schwache Opaleszenz, und an der Luft getrocknet enthielten sie recht variirende Wassermengen (Glühverluste von 4,2 bis 6,6 $^0/_0$).

Versuch Nr. 4, pH ~ 8,5 (Ph schwach rot). Nach der ersten Zentrifugierung (6000 Umdrehungen) war die Mutterlauge noch unklar, und der ausgefällte, etwa 10 g grosse Niederschlag bildete eine kompakte Paste mit einem Volumen von etwa 80 ml. Das Volumen der Paste sank jedoch nach drei Auswaschungen mit warmem Wasser nach Zentrifugierung auf etwa 40 ml herab. Der Niederschlag (sowohl noch feucht, als auch an der Luft getrocknet) ging in der Kälte nur langsam in Lösung in einem Überschuss von 0,1 m Salzsäure (im Laufe von 3—4 Stunden). Für N im Niederschlag ergab sich: 3,330, 3,328, 3,342; im Mittel $N = 3{,}333$ (direkt).

Versuch Nr. 5*. pH ~ 5 (MR ganz rot). Die Mutterlauge enthielt reines primäres Phosphat mit $N = 1{,}0$ und $[PO_4] = 0{,}0024$ m. Nach 6-maliger Auswaschung (das letzte Waschwasser war fast chloridfrei) und Zentrifugierung ergab sich: $N = 3{,}189$ (L) und 3,176 (T. J.); im Mittel $N = 3{,}182$ (direkt).

Versuch Nr. 6*. pH ~ 6,5 (MR und BTB rein gelb). In der Mutterlauge war $[PO_4] = 0{,}00030$ und $N = 1{,}57$. Im Niederschlag wurde gefunden: $N = 3{,}210$ (indirekt) und nach Auswaschung $N = 3{,}247$ (L) und 3,264 (T.J.); im Mittel 3,255 (direkt).

Kocht man eine Probe vom Niederschlag und Mutterlauge mit mehr Calciumchlorid, wird die Lösung stark sauer, und bei Zusatz von Natriumhydroxyd zu der siedenden Mischung, bis sie Phenolphthalein-rot wurde, stieg N im Niederschlag auf 3,32 (L) und 3,31 (T.J.). Beim Auswaschen stieg somit N im Niederschlag von 3,210 auf 3,255; und beim Kochen mit $CaCl_2$ und Zusatz von NaOH, bis die Lösung Phenolphthalein-rot wurde, erhielt man nahezu reines Hydroxylapatit.

Versuch Nr. 7. Um sicher zu sein, dass Chlorapatit nicht gebildet werden konnte, wurde in diesem Versuch $CaCl_2$ gegen $Ca(NO_3)_2$ ausgetauscht. pH ~ 3,7 (MO ganz rot). In der Mutterlauge war $[PO_4] = 0{,}0174$ und $N = 0{,}953$. Im Niederschlag wurde gefunden: $N = 2{,}79$ (berechnet aus der Menge der Ausgangsmaterialen und der Zusammensetzung der Mutterlauge) und $N = 2{,}82$ (indirekt). Das Mittel von diesen zwei Bestimmungen, die beide die Zusammensetzung des ungewaschenen Niederschlags angeben, ist $N = 2{,}805$. Nach 7 maliger Auswaschung mit heissem Wasser wurde gefunden: $N = 3{,}116$ (L) und 3,090 (T.J.); im Mittel $N = 3{,}103$ (direkt).

Wurde der Niederschlag mit $CaCl_2$ gekocht und langsam NaOH zugesetzt, stieg N auf 3,24, bevor die Lösung Phenolphthalein-rot wurde. Der Neutralisationsgrad stieg also von 2,805 auf 3,103 beim Auswaschen und auf 3,24 bei Zusatz von NaOH. Die Zusammensetzung des Niederschlags nähert sich bei diesen Behandlungen derjenigen des Hydroxylapatits, die jedoch nicht erreicht wird.

L. Misch schliesst aus ihrem Debyeogramm dieses Niederschlags, dass das Verhältnis c/a der hexagonalen Achsenlängen in ihm etwa 0,5 $^0/_0$ kleiner ist als im reinen Hydroxylapatit.

Versuch Nr. 8*. pH ~ 9 (Ph und Th rot, nicht blaurot). In der Mutterlauge war kein Phosphat vorhanden ($[PO_4] < 0{,}00002$) und [OH] war 0,0004 (100 ml verbrauchte 0,4 ml 0,1 n NaOH, um farblos zu werden). Im Niederschlag wurde gefunden: $N = 3{,}348$ (indirekt) und nach 7 maliger Auswaschung mit ausgekochtem Wasser: $N = 3{,}330$ (L) und 3,315 (L), im Mittel 3,323 (direkt).

Nach L. Misch ist das Debyeogramm des Niederschlags ein reines Apatit-Diagramm ($c/a = 0{,}731$).

Versuch Nr. 9*. pH ~ 11 (Th blau). In der Mutterlauge war kein Phosphat vorhanden ($[PO_4] < 0{,}00002$) und $[OH] = 0{,}001$. Im Niederschlag wurde gefunden: $N = 3{,}395$ und $N = 3{,}400$; im Mittel 3,397 (indirekt). In dem ausgewaschenen Niederschlag wurde gefunden: $N = 3{,}397$ (direkt).

Versuch Nr. 10*. pH ~ 8 (BTB und Ph blau). Die Mutterlauge enthielt weder Phosphat noch Base nachweisbar bei der Titrierung. Im Niederschlag wurde gefunden: $N = 3{,}268$, 3,270, 3,266; im Mittel 3,268 (L) (indirekt) und nach 7 maliger Auswaschung $N = 3{,}271$, 3,269, 3,265, 3,265; im Mittel 3,267 (L) (direkt).

Versuch Nr. 11. pH ~ 6.9 (MR und BTB grün). Die Mutterlauge enthielt weder Phosphat noch Base nachweisbar bei Titrierung. Im Niederschlag wurde gefunden: $N = 3{,}189$ (indirekt).

Versuch Nr. 12*. pH ~ 3,8 (MO fast rein rot). Die Lösung kochte während der Fällung mit Stössen, und der Niederschlag enthielt mikroskopisch sichtbare Kristalle von wasserfreiem 2-Phosphat, und für seinen Neutralisationsgrad wurde gefunden: $N = 2{,}38$ (indirekt). Dieser Versuch wurde kassiert und durch Nr. 13 ersetzt, bei dem nur halb so viel von den Ausgangsmaterialen angewandt wurde. Die Ausscheidung von wasserfreiem 2-Phosphat in Versuch Nr. 12 zeigt, dass wir bei pH ~ 3,8 an der Grenze des pH-Gebietes angelangt sind, in welchem Calciumphosphate mit Apatit-ähnlichen Debyeogrammen ausgefällt werden können.

Versuch Nr. 13. pH ~ 4 (MO rotgelb). In diesem Versuch wurde kein Kochen mit Stössen beobachtet, und Kristalle vom wasserfreien 2-Phosphat waren mikroskopisch nicht sichtbar. In der Mutterlauge wurde gefunden: $[PO_4] = 0{,}021$ m und $N = 0{,}955$. Der Niederschlag setzte sich schnell zu Boden und nach 5 Minuten Zentrifugierung mit 5500 Umdrehungen wurde eine Paste mit etwa 1 g Niederschlag in 13 ml gewonnen. In dem Niederschlag wurde gefunden: $N = 3{,}00$ (berechnet) und $N = 3{,}015$ und 2,967, im Mittel $N = 2{,}991$ (indirekt).

L. Misch gibt an, dass das Debyeogramm des nicht ausgewaschenen, nur abzentrifugierten und an der Luft getrockneten Niederschlags ein stark ausgewischtes und etwas verschobenes Apatit-Diagramm war. Die Linien waren so diffus, dass die Gitterkonstanten nicht genau berechnet werden konnten.

Versuch Nr. 14 (ohne NaCl). In diesem und in Versuch Nr. 15 wurde der Niederschlag in 500 ml Wasser durch Zusatz von 3,15 g festem 1-Calciumphosphat und von etwa 1000 ml gesättigter Calciumhydroxyd-Lösung dargestellt (um nicht Na^+- und Cl^--Ionen in der Mutterlauge zu haben). pH ~ 4,5 (MO schwach rot). In der Mutterlauge wurde gefunden: $[PO_4] = 0{,}00492$ und $N = 0{,}984$. In dem Niederschlag wurde gefunden: $N = 3{,}06$ (indirekt).

L. Misch gibt an, dass das Debyeogramm zwar ausgewischt ist, aber ohne planmässige Verschiebungen der Linien von ihren Lagen in einem Apatit-Diagramm. Nach Glühen ergab der Niederschlag ein Debyeogramm mit den scharfen Linien des beta-Tricalciumphosphats und mit den stärksten Linien des Hydroxylapatits, ganz in Übereinstimmung mit dem gefundenen N-Wert.

Nachdem der Niederschlag bei 98° C 24 Stunden in der Mutterlauge verblieben war, wurde gefunden: $N = 3{,}10$, und L. Misch gibt an, dass das Debyeogramm jetzt »wirklich anständig aussieht«. Der Niederschlag scheint also nach 24 Stunden in der Mutterlauge bei 98° C etwas mehr grobkristallinisch geworden zu sein und hat gleichzeitig damit seinen Neutralisationsgrad von 3,06 auf 3,10 vergrössert.

Versuch Nr. 15 (ohne NaCl). pH ~ 9 (Ph rot). Die Mutterlauge enthielt kein Phosphat und $[OH^-]$ wurde bei der Titrierung = 0,00097 gefunden. In dem Niederschlag war $N = 3{,}34$ (indirekt).

Nach Kochen des Niederschlags mit einer Lösung von 1-Calciumphosphat in vier Stunden wurde im Niederschlag $N = 3{,}32$ (indirekt) gefunden. Der Niederschlag hat somit von der Lösung mit $N \sim 1{,}0$ jedenfalls nur sehr wenig adsorbiert.

Versuch Nr. 16 und Versuch Nr. 17 wurden nicht durchgeführt.

Versuch Nr. 18. pH ~ 9,5 (Ph und Th rot nicht violett. Nach Abkühlung wurde die Mutterlauge violett). Der Niederschlag sank in der Mutterlauge schnell zu Boden. Nach 7-maliger Auswaschung wurde in ihm $N = 3{,}339$ (L) (direkt) gefunden.

γ. Diskussion der erhaltenen Resultate.

In Tabelle 4 sind die in den Niederschlägen gefundenen N-Werte in ihrer Abhängigkeit von den bei den Fällungen vorhandenen pH-Werten zusammengestellt.

TABELLE 4.
Die Neutralisationsgrade (N) in den bei festgehaltenen pH-Werten ausgefällten Niederschlägen von Calciumphosphaten.

Versuch Nr.	pH	N direkt (nach Auswaschung)	N indirekt oder berechnet (also in nicht ausgewaschenem Niederschlag)
7 ($Ca(NO_3)_2$)	3,7	3,103	2,805
13	4		2,991
14 (ohne NaCl)	4,5		3,06
5*	5	3,182	
6*	6,5	3,255	3,210
11	6,9		3,189
10*	8	3,267	3,268
4	8,5	3,333	
15 (ohne NaCl)	9		3,34
8*	9	3,323	3,348
18*	9,5	3,339	
9*	11	3,397	3,397

In der letzten Kolonne in der Tabelle 4 sind sowohl die indirekten wie die berechneten N-Werte beide aufgeführt. Sie repräsentieren ja beide den N-Wert in dem nicht ausgewaschenen Niederschlag, während die direkten N-Werte in der vorletzten Kolonne die N-Werte in dem mit Wasser gewaschenen Niederschlägen repräsentieren. Ein über die Versuchsfehler hinausgehender Unterschied zwischen den Zahlen in diesen zwei Kolonnen ist für $N > 3{,}27$ nicht vorhanden. Die Niederschläge mit N-Werten in der Nähe von $3^1/_3$ haben also beim Auswaschen ihre Zusammensetzungen nicht verändert. In den Niederschlägen mit $N < 3{,}27$ dagegen wird N beim Auswaschen grösser und um so mehr, je kleiner N ist. Diese Niederschläge scheinen an ihrer Oberfläche adsorbierte, säurereichere Verunreinigungen zu enthalten, die sie beim Auswaschen mehr oder weniger abgeben.

Wenn sich pH von 8,5 zu 9,5 verändert, liegt N innerhalb der Versuchsgenauigkeit sowohl in den gewaschenen wie in den ungewaschenen Niederschlägen bei $3^1/_3$, entsprechend der Bildung der reinen chemischen Verbindung Hydroxylapatit. Es ist aber kein pH-Intervall vorhanden, innerhalb welchem $N \sim 3$ ist. Wenn sich pH von 3,7 zu 4,5 verändert, so ändert N sich von 2,80 zu 3,06 in dem nicht ausgewaschenen Niederschlag, und in den ausgewaschenen Niederschlägen sinkt N überhaupt nicht unter 3,103. Unsere Versuche ergeben also dasselbe Resultat, das andere Forscher erzielt haben (CAMERON, SEIDELL und BELL[45], TRÖMEL und MÖLLER[51], Arnold[56] und Carlström[57]). Es existiert zwar eine kontinuierliche Reihe von Calciumphosphat-Niederschlägen mit N-Werten variierend von über $3^1/_3$ bis zu unter 3. In dieser Reihe spielt aber der Niederschlag mit $N = 3$ keine besondere Rolle und ist deshalb nicht als eine reine chemische Verbindung zu betrachten.

δ. Die Debyeogramme der bei festgehaltenen pH-Werten ausgefällten Niederschläge von Calciumphosphat.

Wie schon früher angeführt, haben wir längere Zeit nach der Ausfällung der Calciumphosphat-Niederschläge mit einer verbesserten Technik neue Debyeogramme von 6 der ausgefällten Niederschläge aufgenommen. Die Diagramme wurden mit einer Bradley-Kamera mit Durchmesser 190 mm und mit Wasserstoff-Füllung aufgenommen, und die angewandte Strahlung war K_α-Strahlung von Kupfer. Die 6 Debyeogramme sind in Fig. 3 reproduziert.

Die Reproduktion der Diagramme zeigt, dass sie alle recht ähnlich sind. Die Intensitäts-Verhältnisse zwischen ihren Linien ändern sich nur wenig mit N. Die Breite und die Unschärfe der Linien werden mit abnehmenden N-Werten vielleicht etwas grösser, aber jedenfalls nur wenig. Wir können deshalb schliessen, dass die Grösse der Kristalle, die die Linien hervorrufen, mit abnehmenden N-Werten jedenfalls nur wenig abnimmt. Eine kleine Verschiebung in den Lagen der Linien mit abnehmenden N-Werten ist aber vorhanden. Krogh Andersen hat auf meine Veranlassung hin die Länge der a- und der c-Achsen der hexagonalen Kristalle aus der Lage der Linien in den Debyeogrammen berechnet. Zu der Berechnung wurden die neun Linien angewandt, die in dem Diagramm Nr. 6 auf Fig. 3, unten mit kleinen Strichen markiert sind. Ihre Indizierung ist von links nach rechts: (203), (222), (312), (320), (213), (321), (410), (402) und (004). Mit Hilfe dieser Linien wurden für jede der 6 Niederschläge vier von einander unabhängige Werte der a- und der c-Achse berechnet. Die Mittelwerte der berechneten Werte sind in Tabelle 5 zusammengestellt. Die Abweichungen der Einzelbestimmungen vom Mittelwert lagen gewöhnlich unter 0,01 Å, und nur bei der Berechnung der c-Achse in dem Niederschlag mit $N = 3{,}06$ war die Abweichung einer Einzelbestimmung grösser als 0,02 Å. Bei der Berechnung wurde als Wellenlänge für die angewandte Strahlung als Mittelwert der Wellenlängen von K_{α_1} und K_{α_2} 1,5418 Å benutzt.

In der Literatur findet man für synthetische, reine Präparate von Hydroxylapatit recht variierende Achsen-Längen angegeben. In der letzten

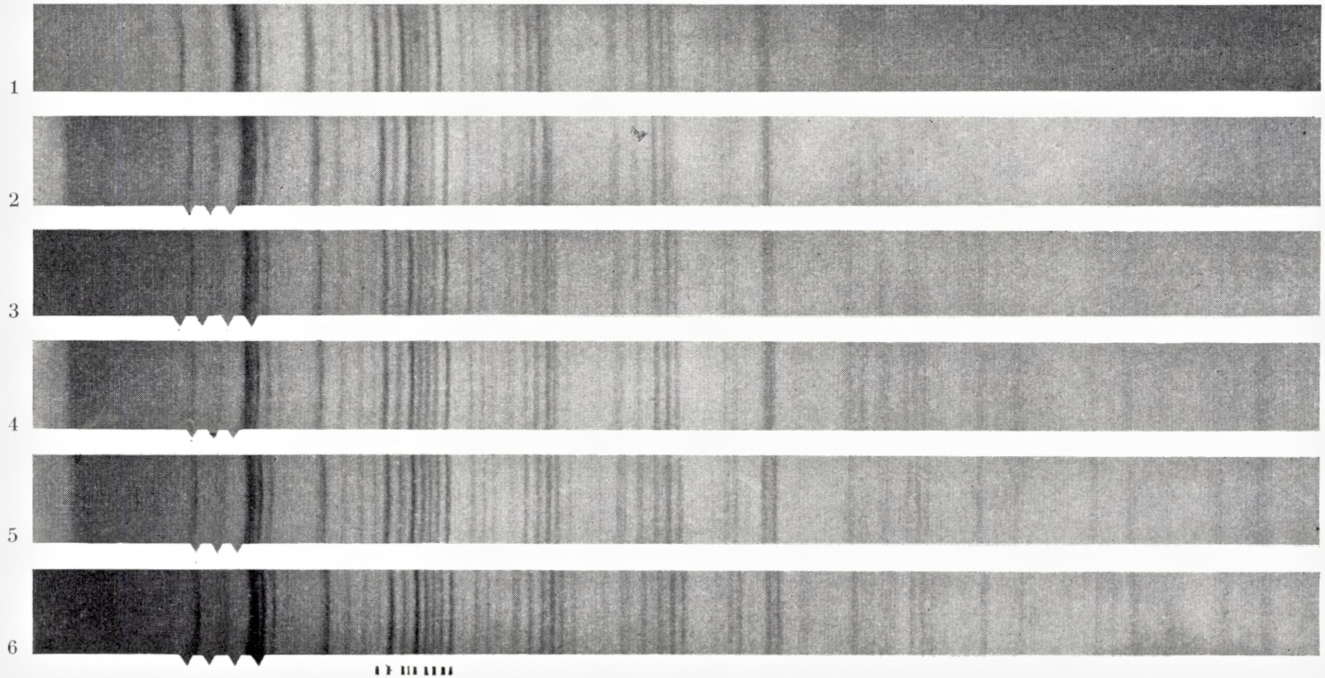

Fig. 3. Debyeogramm von Calciumphosphat-Niederschlägen, langsam gefällt bei 100° C. und verschiedenen pH-Werten. Die N-Werte sind die N-Werte im nichtgewaschenen Niederschlag.

Nr. 1.	Niederschlag vom Versuch 7.	Gefällt bei pH = 3,7.	N = 2,805
Nr. 2.	„ „ „ 13.	„ „ pH = 4 .	N = 2,991
Nr. 3.	„ „ „ 14 (ohne NaCl).	„ „ pH = 4,5.	N = 3,06
Nr. 4.	„ „ „ 11.	„ „ pH = 6,9	N = 3,189
Nr. 5.	„ „ „ 8.*	„ „ pH = 9.	N = 3,348
Nr. 6.	„ „ „ 15 (ohne NaCl).	„ „ pH = 9.	N = 3,34

Tabelle 5.

Die Länge der *a*- und der *c*-Achse in den bei festgehaltenen pH-Werten ausgefällten Niederschlägen von Calciumphosphat.

Diagram Nr.	Versuch Nr.	pH	*N* direkt	*N* indirekt oder ber.	*a* in Å	*c* in Å
1	7 ($Ca(NO_3)_2$)	3,7	3,103	2,805	9,481	6,879
2	13	4		2,995	9,511	6,878
3	14 (ohne NaCl)	4,5		3,06	9,458	6,894
4	11	6,9		3,189	9,462	6,870
5	8*	9	3,323	3,348	9,435	6,904
6	15 (ohne NaCl)	9		3,34	9,428	6,891
Reines Hydroxylapatit nach anderen Forschern					9,42–9,49	6,872–6,94.

Zeile der Tabelle 5 sind nach einer Zusammenstellung von Carlström[57] (Seite 21) die kleinsten und die grössten der gefundenen Werte zusammen gestellt. Die von uns gefundenen Änderungen der Achsen-Längen mit *N* liegen mit einer einzigen Ausnahme in diesem Intervall.

Betrachtet man unsere Werte für die *c*-Achse (die sechszahlige Achse) in der letzten Kolonne der Tabelle 5, sieht man, dass die Länge dieser Achse von dem *N*-Wert recht unabhängig ist und sich jedenfalls nicht regelmässig mit ihm ändert. Dagegen zeigen die Werte für die *a*-Achse mit fallendem *N*-Wert eine kleine, wenn auch ziemlich unregelmässige Steigerung. Von $N = 3\,{}^1/_3$ (in Nr. 5 und Nr. 6) bis $N = 3$ (in Nr. 1 und Nr. 2) handelt es sich um eine Steigerung von 9,431 zu 9,496, also um eine Steigerung von etwa 0,7 %. Von L. Misch wurde auf Grund ihrer nicht guten Debyeogramme geschätzt, das im Niederschlag von Versuch 7, gefällt bei pH = 3,7, das Achsen-Verhältnis a/c etwa 0,5 % grösser war als im reinen Hydroxylapatit. Posner und Stephenson[59] fanden in den von ihnen dargestellten grossen Kristallen mit N = etwa 3 $a = 9{,}43$ und $c = 6{,}875$, während sie für Hydroxylapatit mit $a = 9{,}45$ und $c = 6{,}89$ rechnen. Diesen Zahlen entsprechen eine Steigerung in *a* von 0,2 % und eine Verminderung in *c* von etwa 0,2 %.

Die von uns gefundene *Änderung in der Länge der a-Achse* mit fallendem *N*-Wert scheint uns zwar unzweideutig zu zeigen, dass eine gewisse Substitution im Hydroxylapatit-Gitter mit sinkendem *N*-Wert stattgefunden hat. Die Änderung ist aber so klein, dass sie gegen die von Hendricks[52] ursprünglich postulierte Substitution der ganzen Menge des $Ca(OH)_2$'s im Hydroxylapatit-Gitter durch $2\,H_2O$ spricht. Es handelt sich ja bei einer solchen Substitution nicht nur um eine Raumfrage, sondern auch um eine Kraftfrage. Die elektrostatischen Kräfte, die das Ionen-Gitter zusammenhalten, werden ja sehr geschwächt, wenn ein Ca^{++}-Ion und zwei OH^{-}-Ionen verschwinden und durch zwei H_2O (oder vielleicht drei H_2O) ersetzt werden. Es wäre auch merkwürdig, wenn eine so grosse Änderung in dem Aufbau des Gitters ohne bedeutende *Intensitätsänderungen* der Linien stattfinden könnte.

Es wäre von Bedeutung, einmal eine Monographie über die bei Gitter-Substitutionen stattfindenden Änderungen von Gitter-Konstanten zu bekommen. Ich möchte hier nur auf folgende Daten hinweisen: A. TOVBORG JENSEN und S. L. ROWLES[60] haben nachgewiesen, dass eine Substitution von 9,5 % der Calcium-Atome im wasserfreien 3-Calciumphosphat (Whitlockit) mit Magnesium-Atomen eine Verkleinerung der Gitter-Zelle von 1179 Å³ zu 1146 Å³, also von etwa 3 %, bewirkt. Und substituiert man F durch HO, die nahezu gleich gross sind, und wodurch die elektrostatischen Kräfte nicht geändert werden, in Fluorapatit, so ändert sich die a-Achse von 9,42—9,49 zu 9,369—9,394 (nach der Zusammenstellung von CARLSTRÖM[57] (Seite 28), also um etwa 0,8 %. Die Achsen-Änderungen, die G. WALTON und G. H. WALDEN, jr.[60a] in ausgefällten $BaSO_4$-Kristallen gefunden haben, wenn 4 % $Ba^{++} + SO_4^{--}$ mit K^+, Na'' oder $NH_4^+ + HSO_4$ substituiert wird, sind jedoch kleiner und nur von der Grössenordnung 1 p.m.

Es wäre denkbar, das bei der Substitution im Gitter die in der Mutterlauge anwesenden Na^+-Ionen eine Rolle spielen könnten. Um zu untersuchen, inwieweit die Anwesenheit von Natriumchlorid in der Mutterlauge einen Einfluss auf die Gitter-Konstanten der Niederschläge hat, kann man Versuch 15 (ohne NaCl) mit Versuch 8* vergleichen. In diesen Versuchen ist $pH = 9$, und N ist 3,348, bzw. 3,34. Sowohl für die a-Achse wie für die c-Achse sind in diesen Versuchen innerhalb der Versuchsgenauigkeit dieselben Werte gefunden. Man kann auch Versuch 14 (ohne NaCl) mit Versuch 13 vergleichen. In diesen Versuchen sind die Niederschläge bei $pH = 4,5$, bzw. bei $pH = 4$ ausgefällt, und die N-Werte sind nur wenig verschieden (3,06 bzw. 2,991). In diesen Versuchen bewirkt die Abwesenheit von NaCl eine Verminderung der a-Achse von 9,511 auf 9,458, also von 0,56 %, und eine Vergrösserung der c-Achse von 6,878 auf 6,894, also von 0,23 %. Diese Änderungen liegen innerhalb des von uns geschätzten Versuchsfehlers, und wir dürfen aus ihnen nicht schliessen, dass die Anwesenheit von Natriumchlorid in der Mutterlauge eine Gitter-Änderung mit sich führt.

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[60] Nature (1957) Nr. 170. Eine ausführliche Arbeit wird in Acta Odont. Scand. **15** (1957) 121 erscheinen.

[60a] Journ. Am. Chem. Soc. **68** (1946) 1742.

c. Die innere Natur des sogenannten Tricalciumphosphathydrats. (DALLEMAGNE'S alpha-Tricalciumphospathydrat).

Es kann wohl jetzt als recht sicher angesehen werden, dass HENDRICKS's und DALLEMAGNE's Tricalciumphosphathydrat nicht eine reine chemische Verbindung ist, sondern nur ein Glied in einer Reihe von aus wässrigen Lösungen erhaltenen Substanzen mit Hydroxylapatit-ähnlichen Debyeogrammen und mit Neutralisationsgraden, die von $3^1/_3$ (entsprechend Hydroxylapatit) bis weit unter den Wert 3 (entsprechend 3-Calciumphosphat) heruntergehen. Man ist sich aber noch nicht über die innere Natur dieser Reihe von Substanzen einig geworden: Sind sie, wie TRÖMEL[51] zuerst vorgeschlagen hat, Hydroxylapatit-Kristalle mit adsorbierten Verunreinigungen an der Oberfläche, oder sind sie, wie HENDRICKS[52] vorgeschlagen hat, feste Lösungen, d.h. Hydroxylapatit-Kristalle, in deren Gitter Substitutionen stattgefunden haben. Die Natur dieser Calciumphosphate mit Hydroxylapatit-ähnlichen Debyeogrammen haben ein besonderes Interesse, da die Kalksubstanzen in den Knochen und den Zähnen von derselben Natur sind.

α. Die Aussage der Debyeogramme betreffend Substitution.

Wie schon besprochen (S. 45) sind die Debyeogramme dieser Substanzen so Hydroxylapatit-ähnlich, dass wir schliessen zu müssen glauben, dass die Herabsetzung des Neutralitätsgrades auf 3 in diesen Substanzen nicht allein durch Substitution im Gitter geschehen sein kann. Eine kleine Änderung in der a-Achse ist doch sicher nachzuweisen, und diese kleine Änderung zeigt uns, dass eine gewisse, wenn auch vielleicht nur kleine, Substitution stattgefunden hat.

O. R. TRAUTZ[61] hat auch Debyeogramme von Calciumphosphat-Niederschlägen mit verschiedenen Zusammensetzungen, alle aber mit Apatitähnlichen Diagrammen aufgenommen. Die Herstellungsweisen seiner Niederschläge sind nicht näher angegeben und scheinen recht verschieden gewesen zu sein. Die Achsen-Werte, die er aus seinen Aufnahmen berechnet, liegen vielleicht auch deshalb recht zerstreut. Mann kann aber aus seinen Angaben ersehen, dass die c-Achse sich mit dem Neutralisationsgrad der Niederschläge nur wenig ändert, wie auch wir gefunden haben. Für die a-Achse stellt TRAUTZ eine kleine Abnahme mit sinkendem Neutralisationsgrad fest. Die Abnahme ist aber kleiner als diejenige, die wir gefunden haben. Auch er schliesst jedoch aus der von ihm beobachteten Abnahme, dass eine gewisse Substitution im Gitter stattgefunden hat.

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[61] Ann. New York Acad. Science **60** (1955) 696.

β. Die Art der Substitution.

Es liegt am nächsten anzunehmen, dass eine eventuell stattgefundene Substitution von dem von Hendrick's vorgeschlagenen Typus ist: Austausch von $Ca(OH)_2$ gegen $2\,H_2O$ oder, wie Trautz es ausdrückt: Ersatz von Ca^{++} durch $2\,H^+$. Trautz diskutiert, ob die aufgenommenen H^+-Ionen als H^+-Ionen oder als H_3O^+-Ionen vorhanden sind, oder ob die Niederschläge durch Mitfällung (coprecipitation) von sekundärem Phosphat (Brushit oder Monetit) zusammen mit dem Hydroxylapatit ihre Zusammensetzung erhalten haben. Meiner Meinung nach können die H^+-Ionen unmöglich als freie Protonen anwesend sein, es ist auch nicht möglich, dass in demselben Gitter gleichzeitig stark saure Ionen wie H_3O^+ und stark basische Ionen wie HO^- oder PO_4^{3-} anwesend sind, und mit der Annahme einer Mitfällung verlassen wir die Hypothese einer Substitution. Die H^+-Ionen können aber in das Gitter aufgenommen werden, indem sie sich mit HO^--Ionen zu H_2O-Molekeln oder mit PO_4^{3-}-Ionen zu HPO_4^{2-}- oder $H_2PO_4^-$-Ionen verbinden.

A. Tovborg Jensen hat mich darauf aufmerksam gemacht, dass auch eine Substitution von $Ca^{++} + PO_4^{3-}$ durch $Na^+ + SO_4^{--}$ möglich wäre. Eine solche Substitution würde von dem von Feldspat-Mineralen her bekannten Typus sein, wo $Na_2O + 2\,SiO_2$ durch $2\,CaO + Al_2O_3$ substituiert wird oder, wie man es auch ausdrücken kann, $Na^+ + SiO_4^{4-}$ durch $Ca^{++} + AlO_4^{5-}$. In den von uns dargestellten Niederschlägen kann indessen nach ihrer Darstellungsweise Sulfat nicht vorhanden sein. Eine Substitution von Ca^{++} durch Na^+ unter gleichzeitiger Aufnahme eines Protons, wäre auch denkbar. Bei unseren titrimetrischen Bestimmungen des Neutralisationsgrads (nach Abschnitt 8) kann man zwischen Äquivalente Calcium und Äquivalente Natrium nicht unterscheiden. Wir haben leider nicht auf die Anwesenheit von Natrium in den von uns dargestellten und untersuchten Niederschlägen acht gegeben. Unsere Versuche bei Anwesenheit von NaCl und bei Abwesenheit von NaCl (S. 46) scheinen uns indessen zu zeigen, dass anwesende Na^+-Ionen keine Rolle bei einer eventuellen Substitution spielen können.

γ. Die Adsorptions-Hypothese.

Wir werden nun etwas näher diskutieren, ob es möglich ist, den grössten Teil der Herabsetzung des Neutralisationsgrades in den Calciumphosphat-Niederschlägen durch Adsorption von fremden Stoffen an der Oberfläche zu erklären.

Rein qualitativ sprechen für eine solche Adsorptions-Hypothese eine Reihe Beobachtungen, die wir bei Darstellung und Untersuchung solcher Niederschläge gemacht haben. Es soll zuerst angeführt werden, dass wir konstatiert haben, dass Calciumphosphat-Niederschläge, deren Neutralitätsgrad weit von $3^1/_3$ entfernt liegt, und die somit nach der Adsorptions-Hypothese eine grössere Menge von adsorbiertem Stoff an der Oberfläche enthalten, durch Auswaschung mit Wasser immer ihre Zusammensetzung änderten. Ihre Neutralisationsgrade näherten sich $3^1/_3$, wenn auch dieser Wert bei weitem nicht erreicht wurde. Nach HAYEK's Erfahrungen[14] wissen wir indessen, dass es beim Auskochen von solchen Niederschlägen mit grossen Mengen von Wasser möglich ist, reines Hydroxylapatit zu erhalten. Bei HAYEK's kräftigerer Behandlung handelt es sich jedoch vielleicht nicht nur um Entfernung von adsorbierten Substanzen, sondern auch um eine Umkristallisation.

Zweitens spricht für die Annahme einer Adsorption, dass es im Allgemeinen möglich ist, durch Kochen unserer Niederschläge mit $CaCl_2$-Lösung unter Zusatz von NaOH, bis die Lösung dauernd Phenolphthalein-rot wird, schnell den Neutralisationsgrad bis auf $3^1/_3$ zu erhöhen (Versuch 6*). Unser in Abschnitt 8 beschriebenes Titrierungs-Verfahren, wonach Phosphorsäure in $CaCl_2$-Lösung bei 100° C scharf zum Hydroxylapatit-Punkt titriert werden kann, sagt ja dasselbe aus. Denn beim anfänglichen Zusatz von NaOH muss ein Niederschlag mit kleinem N-Wert ausgefällt werden, und in dem weiteren Verlauf der Titrierung muss dieser Niederschlag seinen Neutralisationsgrad bis auf $3^1/_3$ erhöht bekommen haben.

In Versuch 7, wo bei $pH \sim 3{,}7$ ganz langsam im Laufe von anderthalb Stunden ein Niederschlag mit N = etwa 3,1 ausgefällt wurde, gelang es jedoch beim Kochen mit $CaCl_2$ unter Zusatz von NaOH, bis die Lösung Phenolphthalein-rot wurde, nur einen Neutralisationsgrad 3,24 zu erreichen. In den in diesem Versuch ausgefällten Kristallen scheint neben einer Adsorption eine Substitution im Gitter stattgefunden zu haben, die nicht schnell durch Zusatz von $CaCl_2$ und NaOH rückgängig gemacht werden konnte. Würden wir damit rechnen, dass die Herabsetzung in N von 3,33 zu 3,24 durch Substitution im Gitter verursacht gewesen sei, dagegen die Herabsetzung von 3,24 auf 3,1 durch Adsorption, so würden wir zu dem Resultat kommen, dass $^9/_{23}$ der ganzen Erniedrigung durch Substitution im Gitter zu erklären wäre. Wir glauben jedoch nicht, dass es erlaubt ist, diese Berechnung als ganz sicher zu betrachten. Bei unseren Apatit-Titrierungen haben wir nie solche irreversiblen Substitutionen angetroffen. Die Niederschläge, die während der Titrierung im Laufe von Minuten ausgefällt werden, müssen aber auch aus sehr kleinen Partikeln bestehen, und man kann sich leicht vorstellen, dass in solchen ganz kleinen Partikeln später im Laufe der Titrierung Ausbesserungen im Ionen-Gitter stattfinden können.

Gegen die Annahme einer Adsorption als die Hauptursache der Herabsetzung des Neutralisationsgrades der Calciumphosphat-Niederschläge spricht nur Versuch 15 (ohne NaCl). In diesem Versuch wurde bei $pH \sim 9$ ein Niederschlag mit $N = 3{,}34$ ausgefällt. Dieser Niederschlag wurde nachher mit einer Lösung von 1-Calciumphosphat vier Stunden lang gekocht, und hierdurch wurde sein Neutralisationsgrad nur auf $N = 3{,}32$ gesenkt, also kaum verändert. Ein ausgefällter, fertig gebildeter Niederschlag von Hydroxylapatit scheint hiernach nach Kochen mit einer Lösung von primärem Calciumphosphat, in welcher $N = 1$ ist, phosphorsäurereichere Verbindungen nicht in seine Oberfläche aufnehmen zu können.

Wir wollen nun diskutieren, ob es überhaupt möglich ist, an der Oberfläche der ausgefällten Kristalle eine so grosse Adsorption anzunehmen, dass dadurch der Neutralisationsgrad bis zu unter 3 erniedrigt werden kann. Um diese Frage beantworten zu können, werden wir zuerst auf die atomistische Natur der Adsorption an einer Kristallfläche etwas näher eingehen.

δ. *Die elektrostatische Auffassung der Adsorption an einer Kristallfläche.*

Es liegt nahe sich vorzustellen, dass die Gitter-Ionen in der Grenzfläche eines Kristall-Gitters entgegengesetzt geladene Ionen binden können, namentlich wenn die Ionen schwerlösliche Salze mit einander bilden. Es ist z. Beisp. wahrscheinlich, dass Ca^{++}-Ionen in der Oberfläche eines Hydroxylapatit-Gitters Anionen wie PO_4^{3-}, HPO_4^{--}, CO_3^{--}, OH^- und Citrat-Ionen binden können. Um die Elektroneutralität des Hydroxylapatit-Kristalls mehr oder weniger genau aufrecht zu erhalten, muss sich dann eine entsprechende Menge der Kationen in der Lösung in der Nähe der Oberfläche anhäufen (die Gegenionen) und mit den adsorptiv gebundenen Anionen eine elektrische Doppelschicht bilden. Sind die Kationen in der Lösung Ca^{++}- und Na^+-Ionen, werden beide diese Ionen als Gegenionen gebunden. Beim Auswaschen ist zu erwarten, dass die Na^+-Ionen zusammen mit den adsorptiv gebundenen Anionen leichter abgegeben werden als die Ca^{++}-Ionen, die mit den adsorptiv gebundenen Anionen schwerer lösliche Salze bilden. In der Weise würde man erklären können, wenn die adsorbierten Salze sich nicht alle gleich leicht auswaschen liessen. Wenn ein Kation in der Lösung auch Neigung hätte, sich adsorptiv an ein Anion im Kristall-Gitter zu binden, z. Beisp. ein Ca^{++}-Ion an die PO_4^{3-}-Ionen im Gitter, würde dies eine stärkere adsorptive Bindung verursachen können. Nach der hier geschilderten hauptsächlich elektrostatischen Auffassung der Adsorption muss man die Abhängigkeit der Adsorption an Hydroxylapatit-Kristallen vom pH-Wert der

Lösung dadurch erklären, dass mit sinkendem pH-Wert die Proton-reicheren Phosphat-Ionen in der Mutterlauge mehr und mehr vorherrschen. Wegen der kleineren elektrischen Ladung dieser Proton-reicheren Ionen und der grösseren Löslichkeit ihrer Calciumsalze sollte man aber andererseits von ihnen eine kleinere Neigung zur Adsorption erwarten.

Es ist schwer, sich nach dieser elektrostatischen Theorie eine Vorstellung von der möglichen Grösse der Adsorption und von ihrem Einfluss auf den Neutralitätsgrad eines Niederschlags zu bilden.

ε. Die Adsorption aufgefasst als eine Substitution in der Oberfläche.

Man kann sich aber auch denken, dass die Adsorption an der Oberfläche eines Kristall-Gitters dadurch stattfindet, dass in denjenigen Elementarzellen des Gitters, die in der Grenzfläche des Kristalls liegen, Substitutionen stattfinden, die in den inneren Zellen verboten sind. Die Bedingungen in bezug auf Ähnlichkeit zwischen einem substituierenden Ion oder Molekel und dem substituierten Ion oder Molekel werden in der Grenzfläche ohne Zweifel nicht so streng sein wie im Inneren des Gitters.

Das Kristall-Gitter des Hydroxylapatits ist, wenn auch kompliziert, doch recht beständig (energiearm), und es erfordert eine grosse Ähnlichkeit zwischen dem Substituenten und dem Substituierten, um Substitution zu erlauben. Dies geht daraus hervor, dass man mit grosser Genauigkeit Phosphorsäure bis zu dem Apatit-Punkt titrieren kann (vgl. Abschnitt 8 dieser Arbeit), und man kann es auch daraus schliessen, das Mg^{++}-Ionen die Ca^{++}-Ionen in Hydroxylapatit nach A. Tovborg Jensen und Rowles nicht substituieren können, trotzdem sie doch den Ca^{++}-Ionen recht ähnlich sind. A. Tovborg Jensen und Aase Möller[62] haben nämlich konstatiert, dass Magnesium nicht in das Hydroxylapatit-Gitter aufgenommen wird, wenn man das Hydroxylapatit in Anwesenheit von Magnesiumoxyd durch Zusammensintern seiner Bestandteile bei hoher Temperatur synthetisiert.

Die grosse Stabilität der Hydroxylapatit-Zelle und ihre geringe Neigung zu Substitutionen sind jedoch wahrscheinlicherweise nur vorhanden, wenn die Zelle an allen Seiten von Hydroxylapatit-Zellen umgeben ist. Man darf erwarten, dass die Zellen an der Oberfläche des Gitters, die an einer oder mehreren Seiten keine Nachbar-Zellen haben, eine weit grössere Neigung zu Substitutionen zeigen werden.

Die Adsorption an einem Hydroxylapatit-Kristall kann deshalb darin

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[62] Noch nicht gedruckt. Referiert in einer Arbeit von Tovborg Jensen und Rowles, Acta odont. scand. **15** (1957) 132.

bestehen, dass in den Elementar-Zellen in der Oberfläche des Kristalls Protonen aufgenommen werden, die mit den anwesenden HO^--Ionen H_2O Molekeln oder mit den anwesenden PO_4^{3-}-Ionen HPO_4^{--}-Ionen bilden, indem gleichzeitig, um die Elektroneutralität aufrecht zu erhalten, etwa die halbe Menge von Ca^{++}-Ionen ausgetrieben und gegen H_2O-Molekeln ausgetauscht wird. Es ist einleuchtend, dass diese Aufnahme von Protonen mit sinkendem pH-Wert steigen muss. Werden alle HO^-- und PO_4^{3-}-Ionen in einer Zelle in dieser Weise umgewandelt, ist der Inhalt der Zelle $6\,CaHPO_4 + 6\,H_2O$ und ihr Neutralisationsgrad N ist 2. Eine mehr oder weniger durchgeführte Substitution von dieser Art in den Elementar-Zellen in der Oberfläche des Kristalls bedeutet somit eine Adsorption von $CaHPO_4$ an dem Kristall. Nimmt man an, dass die HPO_4^{--}-Ionen in den Zellen in der Oberfläche durch Protonen-Aufnahme weiter zu $H_2PO_4^-$-Ionen umgebildet und gleichzeitig eine entsprechende Anzahl von Ca^{++}-Ionen gegen H_2O-Molekeln ausgetauscht werden, so wird der Inhalt der Zelle $3\,Ca^{++} + 6\,H_2PO_4^- + 9\,H_2O$ und ihr Neutralisationsgrad $N = 1$. Eine solche Substitution in den Oberflächen-Zellen bedeutet somit eine Adsorption von $Ca(H_2PO_4)_2$ an der Kristall-Oberfläche. Eine so weitgehende Protonen-Aufnahme ist, wenn auch nicht sehr wahrscheinlich, so doch nicht unmöglich. In der Mutterlauge sind die $H_2PO_4^-$-Ionen bei $pH < 6$ vorherrschend.

Die hier geschilderte Auffassung von der Natur der Adsorption an einer Kristall-Fläche kann man eine adsorptionsartige Substitution nennen. Sie repräsentiert eine Art Vereinigung der Substitutions-Hypothese mit der Adsorptions-Hypothese.

Wir wollen nun versuchen, eine höhere Grenze für eine Adsorption durch Substitution in den Elementar-Zellen in der Grenzfläche zu berechnen. Um eine solche Berechnung ausführen zu können, müssen wir die Grösse und die Form der betreffenden Hydroxylapatit-Kristalle kennen. Nach den Debyeogrammen in Fig. 3 zu urteilen, bestehen alle die Niederschläge, die bei 100° und bei festgehaltenen pH-Werten ausgefällt sind, unabhängig vom angewandten pH-Wert, aus Partikeln ähnlicher Grösse. Jedenfalls sind die Linien in allen Diagrammen von ähnlicher Breite.

ζ. Die Grösse der Oberfläche der Partikeln in den bei 100° C gefällten Niederschlägen von Calciumphosphat.

Um eine Vorstellung von der Grösse und Form dieser Partikeln zu erhalten, haben wir einige Elektronen-optische Mikrophotographien von einem Niederschlag, gefällt bei 100° und bei $pH \sim 9$ (Phenolphthalein schwach rot) aufgenommen. Fig. 4 zeigt zwei von diesen Photographien. Sie wurden von Carlsen und Sigurd Larsen in dem biophysikalischen Institut der Universität Kopenhagen aufgenommen. Die angewandte Vergrösserung war 7500 ×. Die Bilder zeigen die Kristalle als lange, dünne Blätter etwa 3 μ lang und 0,3 μ breit. Die Dicke der Blätter ist schwer zu beurteilen. Einige der Blättchen, die senkrecht stehen, ermöglichen jedoch zu schätzen, dass die Dicke kaum mehr als etwa 0,03 μ = 300 Ångström betragen kann.

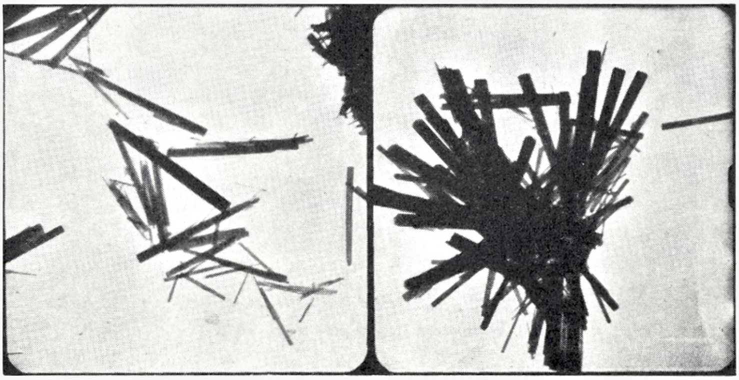

Fig. 4. Elektronenmikroskopische Bilder von einem Calciumphosphat-Niederschlag, gefällt bei 100° C. und bei pH = 9 (Phenolphtalein schwach rot). Vergrösserung 7500 ×.

Es wurden später auch Elektronen-optische Mikrophotographien vom Präparat Nr. 13 (mit $N = 2{,}995$ und gefällt bei 100° und pH ~ 4) und vom Präparat Nr. 14 (ohne NaCl) (mit $N = 3{,}06$, und gefällt bei 100° C und pH ~ 4,5) aufgenommen. Sie wurden von Carlsen und Krogh Andersen in dem biophysikalischen Institut der Universität zu Kopenhagen aufgenommen. Die Bilder zeigten Kristalle, die etwas schlechter ausgebildet und etwas kleiner waren als die Kristalle in Fig. 4. Es wurde geschätzt, dass die kleinen Kristallblättchen durchschnittlich etwa 0,4 μ lang, 0,1 μ breit und 0,02 μ dick waren. Die Schätzung der Dicke ist jedoch recht unsicher. Wir werden indessen nichtsdestoweniger für die Dicke der Blättchen im folgenden mit dem Wert 0,02 μ = 200 Å rechnen.

Wir können damit rechnen, dass die Kristallblätter sich der Basis-Ebene (0,0,1) ihres Kristall-Gitters entlang entwickelt haben. Diese Ebene ist ja die einzige singuläre Ebene in dem hexagonalen Kristall. Folglich muss die c-Achse des Kristall-Gitters senkrecht auf der Ebene der Blätter stehen. Wenn wir als Länge der c-Achse mit 6,9 Å rechnen, so entsprechen der geschätzten Dicke der Blätter etwa 200/6,9 = 29 Elementar-Zellen. Diese

Anzahl ist in guter Übereinstimmung mit der Breite und der Deutlichkeit der Linien in den Debyeogrammen. Hätten die Blätter eine wesentlich kleinere Dicke gehabt, so wären ihre Debyeogramme nicht so linienreich und die Linien in ihnen nicht so scharf gewesen. F. Carlsen, E. Jensen und G. Johansen[63] haben gefunden, dass ein nicht bei 100° C, sondern bei gewöhnlicher Temperatur ausgefälltes Präparat von Hydroxylapatit ein Debyeogramm ergab, in welchem nur 5 Apatit-Linien zu sehen waren, alle sehr diffus. Elektronen-optisch bestimmten sie die Partikel-Grösse in diesem Präparat auf etwa 100 Å und bei Vergleich ihres Diagramms mit Diagrammen von Hydroxylapatiten (Zahnemaille und Zahndentin), für welche A. Tovborg Jensen und Aase Møller[64] aus den Linien-Verbreitungen mittlere Partikel-Grössen berechnet hatten, kamen sie für ihre Partikeln auf eine Partikel-Grösse 140 ± 30 Å. Ein anderes Präparat, das auch bei gewöhnlicher Temperatur, nur schneller, ausgefällt worden war, gab ihnen Debyeogramme, in welchen nur die allerstärkste der Hydroxylapatit-Linien zu sehen war, und selbst diese Linie war schwach und sehr diffus. In diesem Präparat waren die Partikeln so klein, dass ihre Grösse elektronenoptisch nicht beobachtet werden konnte.

In unserem Präparat mit Blättchen, deren Dicke wir auf 200 Å geschätzt haben, entsprechend 29 Elementar-Zellen, liegen nur etwa $^2/_{29}$ der Zellen in der Oberfläche, wenn wir von den Zellen in den Seitenflächen der Blättchen absehen. Wird durch Protonen-Aufnahme in allen ihren Oberflächen-Zellen der Neutralisationsgrad der Phosphorsäure in ihnen auf 2, bzw. auf 1 erniedrigt, so sinkt der Neutralisationsgrad der Phosphorsäure in dem ganzen Kristall nur auf $n = 3{,}24$, bzw. auf $N = 3{,}17$, also bei weiten nicht auf den Wert 3,00, der ein 3-Phosphat charakterisiert. Um im ganzen Kristall einen Neutralisationsgrad 3 zu bekommen, muss eine Substitution auch in tiefer liegenden Oberflächen-Zellen stattgefunden haben. Je nachdem durch Protonen-Aufnahme der Neutralisationsgrad in den Zellen auf 2, bzw. auf 1 erniedrigt wird, müssen fast alle Zellen in den 4, bzw. in den 2, obersten Schichten der Kristalle Protonen aufgenommen haben. Nicht nur der hier geschilderte Adsorptions-Mechanismus, sondern überhaupt jede Adsorptions-Hypothese muss, um Neutralisationsgrade von 3 in den ausgefällten Kristall-Blättchen zu erklären, mit Adsorptions-Schichten rechnen, die eine Dicke von mehreren Molekülen besitzen.

Nach den früher gegebenen Daten von Versuch 7 (Seite 49) schätzte ich, dass in einem Niederschlag von Apatit-ähnlichem Calciumphosphat mit

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[63] Compt. rend. Lab. Carlsberg, série chem. **29** Nr. 1 (1953).
[64] Journ. Dental Research, **27** (1948) 524.

$N = 3{,}1$ etwa $^9/_{23}$ von N's Abweichung von $3^1/_3$, dem Wert für reines Hydroxylapatit, von Substitutionen im Inneren des Gitters herrührt. Der Rest der Abweichung von $3^1/_3$ (etwa $^{14}/_{23}$), muss dann durch Adsorption erklärt werden, und diese Adsorption kann nicht nur durch Substitution in den äussersten Zellen erklärt werden, sondern die Erklärung erfordert auch Substitution in Zellen, die durch eine oder mehrere Zellen von der Oberfläche getrennt sind.

η. Die Beweglichkeit der Gitterbausteine in dem Hydroxylapatit-Gitter.

Die Annahme einer adsorptionsartigen Substitution auch in etwas tiefer liegenden Zellen kann vielleicht im ersten Augenblick etwas befremdend und unwahrscheinlich vorkommen. Bedenkt man aber das Verhalten des Wassers in den Hydroxylapatit-Präparaten (S. 14), so wird man sich kaum darüber verwundern. Der ziemlich unbestimmte Gehalt von H_2O-Molekülen in diesen Präparaten und die langsame Abgabe dieses Wassers beim Erhitzen, die erst bei über 700° vollständig wird, und die ohne wesentliche Änderung in dem Debyeogramm vor sich geht, führen zu dem Schluss, dass die H_2O-Moleküle nicht nur an der Oberfläche sitzen können. Sie können auch nicht als Gitterbausteine sitzen, sondern sie sind vielleicht interstitial zwischen den Gitterbausteinen angebracht. Die Abgabe dieser H_2O-Moleküle bei Erhitzen zeigt, dass sie sich im Gitter bewegen können, ohne das Gitter zu zerstören. Die viel kleineren Protone müssen sich noch leichter im Gitter bewegen können, ohne es zu zerstören. Etwas schwieriger werden die Ca^{++}-Ionen sich wahrscheinlicherweise im Gitter bewegen können. Sie sind ja grösser als die Protone, kleiner aber als die H_2O-Moleküle.

Wenn Protone in das Gitter aufgenommen werden, entstehen elektrostatische Kräfte, die die Ca^{++}-Ionen aus dem Gitter auszutreiben suchen. Bei 100° C scheinen die Ca^{++}-Ionen sich jedoch so langsam im Gitter zu bewegen, dass sie sich nur ganz oberflächlich austreiben lassen und deshalb das Eindringen von Protonen elektrostatisch verhindern (Versuch 15, Seite 50). Die Dicke der Adsorptionsschicht bei 100 °C muss als das Resultat eines Gleichgewichts aufgefasst werden zwischen dem Bestreben der Protone, in das Gitter einzudringen, und der Verfestigung der Elementar-Zellen, wenn sie tiefer im Kristall liegen. Bei höheren Temperaturen wird die Stabilität der reinen Hydroxylapatit-Zelle wahrscheinlicherweise verkleinert und die Beweglichkeit der Ionen im Gitter vergrössert; die Dicke der Adsorptionsschicht wird deshalb grösser, und es ist verständlich, dass wenn man die Versuche bei

250—450° C in einer hydrothermalen Bombe ausführt (POSNER und STEPHENSON's grosse Kristalle[59]), der Unterschied zwischen Substitution im Inneren und in der Oberfläche der Hydroxylapatit-Kristalle ausgewischt wird.

ϑ. Die Natur der grossen Kristalle von 3-Calciumphosphathydrat.

Für die Anhänger der Adsorptions-Hypothese ist es eine grosse Schwierigkeit gewesen, dass es mehreren Forschern gelungen ist, recht grosse Kristalle von Calciumphosphat mit N-Werten in der Nähe von 3 und mit Apatitähnlichen Debyeogrammen darzustellen (HENDRICKS[53], DALLEMAGNE[55], POSNER und STEPHENSON[59]). Von DALLEMAGNE wurde die Existenz solcher grossen Kristalle als ein entscheidender Beweis gegen die Adsorptions-Hypothese betrachtet. HENDRICKS nahm, um ihre Existenz zu erklären, seine Zuflucht zur Annahme von Adsorption in »inneren« Oberflächen, und POSNER und STEPHENSON betrachteten sie als Hydroxylapatit-Kristalle mit »occludierter« Phosphorsäure. Wir wollen etwas näher auf die mögliche Existenz solcher Adsorptions-fähigen inneren Oberflächen oder occludierter Phosphorsäure eingehen.

Unter solchen Umständen, wo eine so starke Adsorption vorhanden ist, dass die Adsorptionsschicht mehrere Schichten von Elementar-Zellen (oder von Molekülen) umfasst, ist das Wachsen von Apatit-Kristallen und namentlich die Bildung von Keimen von Hydroxylapatit (mit z. Beisp. nur 8 oder 27 Elementar-Zellen) schwer zu verstehen, wenn man nicht annimmt, dass Zellen in der Oberfläche, die wegen Substitution nicht die richtige Zusammensetzung haben, durch Bedeckung mit neuen Zellen, die auch nicht die richtige Zusammensetzung haben, dadurch eine Umgebung erhalten, die sich derjenigen der inneren Zellen so stark nähert, dass sie zu einer richtig zusammengesetzten Hydroxylapatit-Zelle aufgebaut werden. Nimmt man indessen an, dass eine solche Vervollständigung stattfinden kann, so ist es anderseits leicht sich vorzustellen, dass beim Wachsen eines Kristalls diese Vervollständigung nicht immer erreicht wird, ehe die unvollständige Zelle im Gitter so tief liegt, dass sie nicht mehr vervollständigt werden kann, und wir haben dann eine »Adsorption an inneren Oberflächen«.

Es ist in dieser Beziehung von Interesse, dass die makroskopischen Kristalle von Apatit, die man in der Natur als Minerale trifft, nur selten durchsichtig sind. Gewöhnlich sind sie ganz opak. Wir können daraus schliessen, dass sie Gitterunregelmässigkeiten oder Verunreinigungen enthalten, über die der Kristall hinübergewachsen ist. Diese Tendenz des Apatit-Gitters zum Überwachsen macht es plausibel anzunehmen, dass das Wachsen eines Hydroxylapatit-Kristalls oft über Zellen stattfinden kann, die noch nicht die richtige Hydroxylapatit-Zusammensetzung erhalten haben. Diese Zellen können die inneren Oberflächen repräsentieren, die HENDRICKS zur Hilfe gerufen hat, um die Adsorptions-Hypothese aufrecht erhalten zu können.

Ich bin jedoch geneigt anzunehmen, dass für grosse Kristalle, die bei einer hohen Temperatur dargestellt sind (POSNER und STEPHENSON[59]), die Substitution in der Oberfläche sich zu einer Substitution in dem ganzen Kristall entwickelt hat.

In einer Arbeit von 1955[61] schildert TRAUTZ eingehend das Phänomen, dass man als Mitfällung (coprecipitation) bezeichnet. Es besteht darin, dass man bei der Fällung eines kristallinischen Niederschlages Stoffe oder Ionen mitgefällt bekommt, die mit dem Niederschlag nicht isomorph oder zur Substitution nicht fähig sind. Wenn die mitgefällten Stoffe (oder Ionen) sich an bestimmten inneren Flächen sammeln, hat man die von HENDRICKS zur Hilfe genommene Adsorption an inneren Oberflächen. Wenn die mitgefällten Stoffe mehr zufällig in dem ausgefällten Niederschlag verteilt sind, so werden die Dimensionen der Elementar-Zellen und das Debyeogramm geändert. Vielleicht spielt eine solche Mitfällung bei der Ausfällung von Calciumphosphaten eine bedeutende Rolle. TRAUTZ schreibt, dass nach WALTON und WALDEN[65] H_2O-Moleküle durch Mitfällung in Bariumsulfat-Niederschläge aufgenommen werden, und er meint, dass die Unregelmässigkeiten in den Eigenschaften der Calciumphosphat-Niederschläge darauf deuten, dass auch in ihnen H_2O-Moleküle mitgefällt werden.

Wenn bei der Bildung eines langsam kristallisierenden Niederschlags zuerst ein amorpher Niederschlag von recht unbestimmter Zusammensetzung gebildet wird, und dann dieser amorphe Niederschlag eine kristallinische Struktur annimmt, sind die Möglichkeiten von Mitfällungen sowohl in Form von optisch sichtbaren Inclusionen wie in Form von submikroskopisch verteilten Verunreinigungen sicher gross.

ι. *Zusammenfassung.*

Nach den auf den vorangehenden Seiten geschilderten Versuchen und Betrachtungen sind wir somit zum folgenden Resultat gekommen:

Das sogenannte 3-Calciumphosphathydrat enthält ein Hydroxylapatit-Gitter, in dessen Inneren eine gewisse Substitution stattgefunden hat (Aufnahme von Protonen an Hydroxyl-Ionen und Phosphat-Ionen und gleich-

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[65] J. Am. Chem. Soc. **68** (1946) 1742.

zeitige Austreibung von Calcium-Ionen, die durch H_2O-Moleküle ersetzt sind) und an dessen Oberfläche eine Adsorption vorhanden ist, indem in den Elementar-Zellen in oder nahe der Oberfläche eine stärkere Substitution von derselben Natur wie die oben beschriebene im Inneren des Gitters stattgefunden hat.

Die Substitutionen im Inneren und namentlich die in der Oberfläche sind temperaturabhängig. Bei 100° C sind bei Partikeln von der Grössenordnung 1 μ die Einflüsse der beiden Arten von Substitution auf die Zusammensetzung der Kristalle von ähnlicher Grösse. Mit steigender Temperatur wachsen die Substitutionsmöglichkeiten, und namentlich breitet sich die Substitution in der Oberfläche zu tiefer liegenden Schichten aus, der Unterschied zwischen den beiden Arten der Substitution wird nach und nach ausgewischt und scheint ganz zu verschwinden an einer Stelle in dem Temperatur-Intervall 250°—450° C.

7. Das wasserfreie 3-Phosphat.

a. Die Geschichte.

Durch die vielen, im wesentlichen gleichartigen Resultate anderer Forscher (abgesehen von den ursprünglichen Hendricks'schen), die mit den experimentellen Erfahrungen von meinen Mitarbeitern und mir übereinstimmten, waren wir 1936 in unserem Laboratorium, als ich die Resultate unserer Arbeiten über Calciumphosphate auf einer skandinavischen Naturforscherversammlung in Helsingfors vortrug, zu der recht festen Überzeugung gekommen, dass ein wohl definiertes 3-Calciumphosphat aus einer wässrigen Lösung nicht ausgefällt werden könne. Es machte daher einen starken Eindruck auf mich, als einer meiner damaligen Mitarbeiter, A. Tovborg Jensen, in einer selbständigen Untersuchung, die er über die Zusammensetzung von Blasensteinen eingeleitet hatte, über einen Fund von zwei Blasensteinen berichten konnte[66], die die Zusammensetzung eines 3-Calciumphosphats besassen, und die charakteristische linienreiche Debyeogramme ergaben, die mit den Diagrammen des nach Trömel[50] aus einer Schmelze erhaltenen wasserfreien beta-Tricalciumphosphats identisch waren.

Nachdem Tovborg Jensen in 1938 die zwei Blasensteine gefunden hatte, die das wasserfreie beta-3-Phosphat enthielten, ist diese Verbindung

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[66] A. Tovborg Jensen und J. E. Thygesen, Zeitschr. f. Urologie **32** (1938) 659. Zusammenfassung auf dänisch: J. Thygesen, Ugeskrift f. Læger **101** (1939) 115.

später oft an Stellen gefunden worden, wo sie aus wässriger Lösung ausgeschieden sein muss. H. MATHIS[67] hat sie in Zahnstein beobachtet, BRANDENBURGER und SCHENZ[68] haben sie in einer verkalkten tuberkulösen Lunge beobachtet, ALBERTINI, BRANDENBURGER und RÄTTNER[69] in einer verkalkten Lymphdrüse in einer Lunge nach Silicosis und FRONDEL und PRIEN[70] in einer kranken verkalkten appendix testis. TOVBORG JENSEN hat sie selbst in 14 Speichelsteinen[71] und in 41 Proben von Zahnstein[72] nachgewiesen.

Als Mineral ist das beta-3-Phosphat von CLIFFORD FRONDEL[73] gefunden, ausgeschieden in Granit-Pegmatit, bei höherer Temperatur in Anwesenheit von Wasser gebildet.

FRONDEL hat das Mineral *Whitlockit* genannt und hat seine Eigenschaften ausführlich beschrieben. FRONDEL glaubt, dass auch die Minerale Zeugit, Pyrophosphorit und Martinit, denen ihre Entdecker andere Zusammensetzungen zuschrieben, mit seinem Whitlockit identisch sind. In diesen Mineralen scheint das Whitlockit aus wässrigen Lösungen bei gewöhnlichen atmosphärischen Temperaturen und Drucken gebildet zu sein. In zwei Fällen war das Whitlockit Pseudomorphosen nach den wasserhaltigen Mineralen Brushit, $CaHPO_4$, 2 H_2O, und Gips, $CaSO_4$, 2 H_2O. FRONDEL ist über das Vorkommen seines Whitlockit in der Natur verwundert, weil, wie er schreibt, alle Versuche, tertiäres Calciumphosphat aus wässrigen Lösungen ausgeschieden zu bekommen, zur Ausscheidung von Hydroxylapatit geführt haben. Er scheint die Beobachtungen von TOVBORG JENSEN nicht gekannt zu haben.

b. Die Versuche zu Erklärung der unerwarteten Ausfällung von wasserfreiem 3-Calciumphosphat (Whitlockit) aus wässrigen Lösungen unter gewissen Umständen.

Bei unseren Versuchen über die Löslichkeit der verschiedenen Calciumphosphate ist es uns nicht gelungen, aus geeigneten Lösungen durch Impfung mit wasserfreiem 3-Calciumphosphat von einem Blasenstein eine weitere Ausscheidung dieses Phosphats zu erhalten. Diese wasserfreie und harte, recht mineralähnliche Verbindung scheint sich sehr langsam zu lösen und auszuscheiden, und es ist uns nicht gelungen, diese Substanz in Lösungs-

[67] Deutsch. Zahn-, Mund- und Kieferheilkunde **5** (1938) 114.
[68] Helv. Med. Acta, Serie A **12** (1945) suppl. 16.
[69] Zeitschr. Unfallmed. in Berufskr. **39** Nr. 4 (1946).
[70] Science **103** (1946) 326.
[71] A. T. JENSEN und MARIANNE DANØ, Journ. Dental Research **31** (1952) 620.
[72] ib. **33** (1954) 741.
[73] The Amer. Mineralogist **26** (1941) 145 und **28** (1943) 215.

gleichgewicht mit einer wässrigen Lösung zu bringen. Wir wollen jedoch nicht behaupten, dass es nicht möglich sein sollte, diesen Zweck durch neue, wesentlich länger dauernde Versuche zu erreichen.

Um ihre für uns daher unerwartete, häufige Bildung im Speichel und Harn zu erklären, hat Tovborg Jensen[71] den Gedanken geäussert, dass vielleicht im Speichel und Harn ein Faktor vorhanden sei, der die Ausscheidung und das Wachstum von Hydroxylapatit verhindert und der dadurch die Ausscheidung des (wahrscheinlicherweise) weniger stabilen wasserfreien 3-Calciumphosphats möglich macht.

K. J. Pedersen[74] hat in ähnlicher Weise (auf Grundlage gewisser Beobachtungen von Branner über die Bildung von Calciumoxalatdihydrat in Harn) gezeigt, dass im Harn ein Faktor vorhanden ist, der die Ausscheidung des stabilen Monohydrats von Calciumoxalat verhindert oder jedenfalls verzögert und der deshalb im Harn die Ausscheidung vom metastabilem Dihydrat ermöglicht. Er fand, dass Zusatz von unter 10 % Harn genügte, um die Ausscheidung des stabilen Monohydrats zu verhindern. Es gelang ihm jedoch nicht, die Natur dieses Faktors zu erhellen.

In neuester Zeit ist Tovborg Jensen[75] auf die Natur des Faktors, der die Ausscheidung vom wasserfreien 3-Calciumphosphat hervorrufen kann, näher eingegangen. Er wurde dazu veranlasst durch eine Arbeit von O. R. Trautz[76]. Trautz und seine Mitarbeiter haben eine Whitlockit-ähnliche Substanz dargestellt, indem sie Elephantenzahn mit Dampf bei 300° und 200 Atm. autoklavierten. Der Elephantenzahn enthält etwas Magnesium. Unter denselben Umständen wurde Magnesium-freies Whitlockit in Hydroxylapatit und Calciumpyrophosphat umgewandelt. Frondel's Analysen seiner Whitlockit-Mineralen zeigen auch, dass diese Mineralen Magnesium enthalten. Die Anwesenheit von Magnesium scheint deshalb für die Ausscheidung Whitlockit-ähnlicher Kristalle von Bedeutung zu sein. Es gelang denn auch Trautz, Whitlockit auszufällen, wenn eine sehr verdünnte Lösung von Calciumphosphat einer Lösung von Magnesiumphosphat bei 100° zugefügt wurde. Die bei diesen Versuchen erhaltenen Whitlockit-Kristalle besassen Gitterdimensionen, die etwas variierten, die aber alle ein wenig kleiner waren als die des beta-Tricalciumphosphats. Diese Verkleinerung des Gitters muss darauf beruhen, dass im Gitter einige Calcium-Ionen gegen die kleineren Magnesium-Ionen ausgetauscht worden sind, und durch

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[74] Kemisk Maanedsblad, Kopenhagen, **21** (1940) 52. Vgl. auch A. Tovborg Jensen: 21 (1940) 49.

[75] Acta Odont. Scan. **15** (1957) 121.

[76] O. R. Trautz, E. Fassenden und M. Newton, Journ. dent. Res. **33** (1954) 687. Ann. New-York Acad. Sci. **60**, 696 (1955).

diese Verkleinerung scheint das Gitter stabilisiert worden zu sein. In einem Briefwechsel mit Tovborg Jensen hat Trautz mitgeteilt, dass vielleicht auch das Tricalciumphosphat im Zahnstein und in Blasensteinen Magnesium enthielt und verkürzte Kristallachsen besass. Tovborg Jensen hatte schon 1944[77] (nach einem genauen Studium der Debyeogramme) geschrieben, dass Frondel's Whitlockit von synthetischem alpha- und beta-Tricalciumphosphat verschieden war, und in einer neulich erschienenen Arbeit[78] haben Tovborg Jensen und S. R. Rowles nachgewiesen, dass auch das beta-Tricalciumphosphat in Zahnstein verkürzte Kristallachsen besitzt. Es war möglich, annähernd den Gehalt von Magnesium aus der Verkleinerung der Kristalldimensionen zu berechnen, wenn zum Vergleich beta-Tricalciumphosphate mit bekannten Gehalten von Magnesium benutzt wurden, die durch Zusammensintern der Bestandteile bei 1100° dargestellt worden waren. Es ergab sich, dass höchstens 9,5 Atomprozente Calcium im Gitter gegen Magnesium ausgetauscht werden konnten, und dass bis zu dieser Grenze die Gitterverkürzungen dem Magnesiumgehalt proportional waren.

In einer Arbeit zusammen mit Aase Møller hat Tovborg Jensen[62] gezeigt, dass eine Substitution von Calcium-Ionen mit Magnesium-Ionen dagegen nicht stattfindet, wenn man Hydroxylapatit-Kristalle in Anwesenheit von Magnesiumverbindungen durch Zusammensintern der Bestandteile bei 950° darstellt.

Nach den Resultaten dieser Versuchsreihen lag es für Tovborg Jensen nahe anzunehmen, dass der im Speichel und Harn wirkende Faktor, der die Ausscheidung von Whitlockit-Kristallen hervorrief, anwesende Magnesium-Ionen waren. Er meint, dass die Magnesium-Ionen nicht nur auf die Weise wirken können, dass das beta-Tricalciumphosphat-Gitter durch Umtausch von etwas Calcium mit Magnesium stabilisiert wird, sondern auch indem eventuell gebildete Hydroxylapatit-Keime nur langsam wachsen können, weil Magnesium-Ionen, die an ihrer Oberfläche adsorbiert werden, nicht in das Gitter aufgenommen werden können. Tovborg Jensen meint indessen, dass ausser Magnesium-Ionen noch ein anderer Faktor bei der Ausfällung von Whitlockit-Kristallen wirksam sein muss. Sonst ist nicht zu verstehen, dass Whitlockit-Kristalle in den normalen tierischen und menschlichen Kalk-Ausscheidungen (in Knochen, Dentin und Emaille) nie vorhanden sind, trotzdem Blutplasma Magnesium-reicher ist als Speichel (es enthält 6—7 mal mehr).

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[77] Medd. dansk geol. For. **10** (1944) 475.

[78] A. Tovborg Jensen und S. R. Rowles: Nature **179** (1957) 912. Ausführlicher in Acta Odont. Scan. **15** (1957) 121.

Auch andere zweiwertige Ionen, z. Beisp. Fe^{++}, können in das Whitlockit-Gitter aufgenommen werden und dadurch das Gitter stabilisieren. Es soll auch daran erinnert werden, dass A. Povloff und A. S. Posner[79], die reine Hydroxylapatit-Kristalle durch Autoklavierung von 2-Calciumphosphat mit Wasser bei 300° dargestellt haben, entdeckt haben, dass Verunreinigung mit Fe oder Cr eine Bildung von gut ausgebildeten Whitlockit-Kristallen im Endprodukt hervorruft.

8. Die angewandten analytischen Verfahren.

a. Phosphorsäure-Bestimmung.

Kolorimetrische Bestimmung. Die Bestimmung der Phosphorsäure geschah in der ersten Zeit kolorimetrisch durch Messung der blauen Farbe, die entsteht, wenn Phosphormolybdänsäure mit Stannochlorid reduziert wird. Die Bestimmungen wurden nach Atkins's[80] Modifikation ausgeführt. Die blaue Farbe wurde mit Pulfrich's Stufenphotometer gemessen unter Anwendung des Lichtfilters mit Schwerpunkt bei 7200 Å. Die Lösungen wurden bis zu einer Phosphatkonzentration von ca. 10^{-5} m verdünnt und in 3 cm Küvette gemessen. Zur Eichung wurden Lösungen von sekundärem Natriumphosphat (nach Sørensen) mit Phosphatkoncentrationen $0{,}4 \cdot 10^{-5}$, $0{,}8 \cdot 10^{-5}$ und $1{,}2 \cdot 10^{-5}$ m angewandt. Die erreichte Genauigkeit wird auf 2 $^0/_0$ geschätzt.

Bei den späteren und wichtigsten Versuchen wurde die Phosphatbestimmung durch Apatittitrierung nach Damsgaard-Sørensen[81] ausgeführt.

Die Apatittitrierung. Die Titrierungen wurden in 200 ml Erlenmeyer-Kolben in einem Kohlendioxyd-freien Luftstrom (etwa 500 ml/Minute) ausgeführt, mit 0,1 *n* HCl und 0,1 *n* NaOH (Kohlendioxyd-frei) und in einem Volumen von 100 ml. Die angewandten Mikrobüretten hatten ein Volumen von 2 oder 5 ml und waren in 0,01 ml geteilt. Die NaOH-Lösung war mit einem $Ba(OH)_2$-Rohr von der Atmosphäre abgesperrt, und die Auslaufspitze der NaOH-Bürette war mit einem dünnen Glasrohr verlängert, der in dem Titrierkolben hineingesteckt wurde, um die Aufnahme von Kohlendioxyd zu verhindern. 1 ml von einer Indikatorlösung mit 0,1 g Methylrot und 0,5 g

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[79] Science, **124** (1956) 583.

[80] W. R. G. Atkins, J. Agr. Science **14** (1924) 192. Siehe auch K. A. Bondorff und F. Steenbjerg: 256. Beretning fra Statens Forsøgsvirksomhed i Plantekultur, Tidsskrift for Planteavl **38** (1931) 273.

[81] Kemisk Maanedsblad **15** (1934) 73. Siehe auch A. Tovborg Jensen: Landbohøjskolens Aarsskrift 1935.

Phenolphthalein in 1 l Alkohol wurde zugesetzt und zu der Farbe titriert, die 1 ml der Indikatormischung in einer Sørensen-Mischung[82] von 20 ml »Salzsäure« und 80 ml »Citrat« (mit pH = 4,7) besitzt (der Primärpunkt, wo die Phosphorsäure als $H_2PO_4^-$ vorhanden ist). Die Standard-Lösung war in einer ähnlichen Kolbe wie die zu titrierende Lösung angebracht. Es ist das beste, zur Standard-Lösung einen Tropfen Xylol hinzuzusetzen, um das Wachstum von Mikroorganismen zu verhindern, die oft schnell (in einem Tage) Methylrot reduzieren und entfärben können. Es ist notwendig, beim Primärpunkt einige Minuten zu warten, um alles Carbonat zu Kohlendioxyd umgebildet zu bekommen, und alles Kohlendioxyd mit dem Luftstrom zu entfernen. Nachdem bis zu diesem »Primärpunkt« titriert war, wurde 10 ml 0,5 m $CaCl_2$-Lösung zugesetzt und 0,1 *n* NaOH zugetropft, bis die Lösung Phenolphthalein-rot geworden war. Danach wurde zum Kochen erhitzt und gekocht, bis die Lösung gelb wurde (oder sogar Methylrot-rot geworden war). Durch Zusatz von 0,1 *n* NaOH wurde auf die Farbe eingestellt, die die Indikatormischung in einer kalten Mischung von 90 ml Kohlendioxyd-freiem Wasser, 7 ml »Borat« und 3 ml »Salzsäure« besitzt (in 7 ml »Borat« + 3 ml »Salzsäure« (unverdünnt) ist nach Sørensen pH = 8,68). Man setzt damit fort, abwechselnd zu kochen und 0,1 m NaOH zuzusetzen, bis die rote Farbe bei Kochen in einer Minute nicht verschwindet. Die Phenolphthalein-Farbe wird bei Abkühlung unter 100° etwas mehr rot. Es ist deshalb wichtig, die Farbe zu beurteilen, sofort nachdem die Kolbe von der Flamme genommen ist. Zwei bis dreimaliger Zusatz von 0,1 *n* NaOH ist das gewöhnliche. Hiermit ist zum ersten Apatitpunkt titriert.

Danach ist es praktisch, aber nicht notwendig, in ähnlicher Weise zu einem zweiten Apatitpunkt zu titrieren, das heisst, bis zu der Farbe zu titrieren, die 1 ml Indikatorlösung in einer kalten Mischung von 90 ml Kohlendioxyd-freiem Wasser, 8,5 ml »Borat« und 1,5 ml »Salzsäure« besitzt (in 8,5 ml »Borat« + 1,5 ml »Salzsäure« (unverdünnt) ist nach Sørensen pH = 9,00). Während der Titrierungen verdampft etwas Wasser. Das Volumen wird aber normal nicht mehr als auf 100 ml vermindert (der Zusatz von 10 ml Calciumchlorid vergrösserte es von 100 ml auf 110 ml).

Die Berechnung des Phosphorsäure-Gehaltes wird durchgeführt, indem man vom NaOH-Verbrauch vom Primärpunkt bis zum 1. Apatitpunkt den Verbrauch von NaOH abzieht, den man findet, wenn man 100 ml reines Wasser vom Primärpunkt bis zum 1. Apatitpunkt titriert. Dieser Verbrauch soll etwa 0,13 ml 0,1 *n* NaOH betragen. Von dem in dieser Weise korrigierten Verbrauch von NaOH wird der Gehalt an Phosphorsäure berechnet,

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[82] Compt. rend., Laboratoire Carlsberg, Kopenhagen 8 (1910) 1.

indem man sich dessen bedient, dass $2^1/_3$ Mol NaOH einem Mol H_3PO_4 entspricht. Eine ähnliche Berechnung wird mit der Titrierung zum 2. Apatitpunkt ausgeführt. Hier soll der Verbrauch bei der Titrierung von 100 ml Wasser etwa 0,20 ml 0,1 *n* NaOH betragen. Die beiden Berechnungen müssen annähernd dasselbe Resultat ergeben, und man kann dann ihren Mittelwert als das endgültige Resultat betrachten. Die Resultate der Titrierungen erlauben auch den Neutralisationsgrad der Phosphorsäure in der Lösung zu berechnen.

Versuche von Augusta Unmack mit anderen Verfahren zu Bestimmung von Phosphorsäure in sehr verdünnten Lösungen. Es wäre für fortgesetzte Untersuchungen über die Calciumphosphate sehr wertvoll, ein schnelles und gutes Verfahren zur Bestimmung von Phosphorsäure in 0,001 m und noch verdünnteren Lösungen zu besitzen. Augusta Unmack[83] hat zu diesem Zweck einige Untersuchungen durchgeführt. Die argentometrische Titrierung (Ausfällung von Ag_3PO_4 mit $AgNO_3$ und Zurücktitrierung mit Thiocyanat-Lösung) konnte nach einigen kleinen Änderungen zur Titrierung von etwa 50 ml 0,001 m Phosphorsäure in Anwesenheit von Calcium mit einer Genauigkeit von etwa 1,5 $^0/_0$ angewandt werden. Das Verfahren ist aber beschwerlich und langsam. Etwas bessere Resultate ergab die azidimetrische Titrierung der bei Zusatz von $AgNO_3$ freigemachten Säure. Sie ergab in den Händen von A. Unmack eine Genauigkeit von etwa $^1/_2$ $^0/_0$ bei Anwendung von etwa 50 ml einer 0,001 m Phosphorsäure. Die Methode ist etwas schneller und genauer als die argentometrische. Die gewichtsanalytische Bestimmung von Phosphorsäure durch Fällung und Wägen von Ammoniumphosphormolybdat zeigte sich wenig geeignet.

b. Calcium-Bestimmung.

Oxalat-Fällung. In den älteren Versuchen wurde Calcium durch Fällung von Calciumoxalat in siedender Lösung mit einer bekannten Menge 0,002 *n* $Na_2C_2O_4$-Lösung bestimmt. Nach 4 Stunden wurde das ausgefällte Calciumoxalat abfiltriert, mit kochendem Wasser gewaschen und das Filtrat mit 0,02 *n* Permanganat titriert. Die Lösungen wurden gewöhnlich bis auf $^1/_4$ oder $^1/_{10}$ Volumen eingedampft, ehe das Calciumoxalat ausgefällt wurde. Wurden die Lösungen unklar durch Ausscheidung von Calciumphosphat bei der Eindampfung oder beim Kochen, wurde Essigsäure (2 normal) tropfenweise zugesetzt, bis die Ausscheidung wieder aufgelöst war. Die erreichte Genauigkeit wird auf etwa 2 $^0/_0$ geschätzt.

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[83] Kemisk Maanedsblad (1944) 133.

Apatit-Titrierung. Bei den späteren Versuchen wurde das genauere und auch schnellere Verfahren benutzt, den Calciumgehalt der Lösungen aus den bei den Apatit-Titrierungen gewonnenen Zahlen zu berechnen. Enthalten die Lösungen nur Calcium und Phosphat, kann man den Calciumgehalt aus der bei der Titrierung zum Primärpunkt benutzten Säuremenge berechnen, indem man dazu die gefundene Phosphorsäurenmenge ($^3/_7$ des Basenverbrauchs von Primärpunkt bis zum Apatitpunkt, korrigiert für den Blindverbrauch, bestimmt bei Titrierung vom Wasser) addiert.

c. pH-Bestimmung.

Als Mass für die saure Reaktion der Lösungen haben wir nicht den gewöhnlichen pH-Wert, sondern den negativen Logarithmus der Wasserstoffionenaktivität $-\log A_H = pA_H$ benutzt[84]. Die Bestimmungen von pA_H wurden, wenn nichts anders bemerkt wird, elektrometrisch mit einer Chinhydron-Elektrode ausgeführt, die gegen eine 3,5 *m* KCl oder 0,1 *m* KCl-Kalomelektrode gemessen wurde. Als Zwischenflüssigkeit wurde 3,5 *m* KCl benutzt und für Flüssigkeitspotentiale wurde nicht korrigiert. Die angewandte Kalomelelektrode wurde fast täglich gegen eine 0,01 *m* HCl, 0,09 *m* NaCl-Chinhydronelektrode kontrolliert. Man ging davon aus, dass pA_H in 0,01 *m* HCl, 0,09 *m* NaCl bei 18° gleich 2,057 und bei 37° gleich 2,042 ist ([84] S. 58 und 60). Bei 18° sind die pA_H-Werte 0,035 und bei 37° 0,019 grösser als Sørensen's konventionelle pH-Werte. Man konnte gewöhnlich die folgenden Formeln verwenden:

$$pA_H = (0{,}4501 - E_{3,5\,m})/0{,}0577 \quad \text{bei } 18°,$$
$$pA_H = (0{,}3670 - E_{0,1\,m})/0{,}0577 \quad \text{bei } 18° \text{ und}$$
$$pA_H = (0{,}3534 - E_{0,1\,m})/0{,}0615 \quad \text{bei } 37°.$$

$E_{3,5\,m}$ und $E_{0,1\,m}$ sind die gemessenen Potentiale gegen 3,5 *m* KCl, bzw. 0,1 *m* KCl-Kalomelektroden.

In Lösungen mit $pA_H > 8$ und bei den späteren und genauesten Messungen wurden Wasserstoffelektroden angewandt und gegen eine Wasserstoffelektrode in 0,01 *m* HCl, 0,09 *m* NaCl gemessen mit 3,5 *m* KCl eingeschaltet. pA_H wurde aus dem gemessenen Potential, E_{H_2}, nach folgenden Formeln berechnet:

$$pA_H = 2{,}057 + E_{H_2}/0{,}0577 \quad \text{bei } 18°,$$
$$pA_H = 2{,}042 + E_{H_2}/0{,}0615 \quad \text{bei } 37°.$$

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[84] Siehe N. Bjerrum und A. Unmack, Mat. Fys. Medd. Dan. Vid. Selsk. **9**, nr. 1 (1929) 82 und 9.

Da die Lösungen gewöhnlich einen sehr kleinen Puffergehalt besassen, wurde immer etwas von dem Calciumphosphatniederschlag im Elektrodengefäss mitgenommen, wenn es sich darum handelte, die Reaktion in einer Lösung zu bestimmen, die mit Calciumphosphat geschüttelt worden war. Trotz dieser Vorsichtsmassregel glauben wir jedoch, dass die pA_H-Bestimmungen in den pufferarmen und oft schlecht leitenden Lösungen nicht immer auf 0,01 Einheit richtig sind. Namentlich in den älteren Versuchen muss man mit einer Unsicherheit von mehreren Einheiten im zweiten Dezimale von pA_H rechnen.

d. Berechnung der Verteilung der Phosphorsäure auf ihre verschiedenen Formen (H_3PO_4, $H_2PO_4^-$, HPO_4^{--}, PO_4^{---}).

Die Verteilung der Phosphorsäure in den Lösungen auf ihre verschiedenen Formen ist bestimmt durch die folgenden Gleichungen:

$$\frac{A_H \cdot [H_2PO_4^-]}{[H_3PO_4]} = K'; \quad \frac{A_H \cdot [HPO_4^{--}]}{[H_2PO_4^-]} = K''; \quad \frac{A_H \cdot [PO_4^{---}]}{[HPO_4^{--}]} = K'''.$$

Hier sind K', K'' und K''' die unvollständigen Dissoziationskonstanten, und die Formeln in Klammern repräsentieren die molaren Konzentrationen der entsprechenden Stoffe.

Die benutzten Werte für die unvollständigen Dissoziationskonstanten wurden nach den folgenden Formeln berechnet (Bjerrum und Unmack[84] S. 126, 133, 142):

$$\begin{array}{lrl}
18^\circ & pK' = & 2{,}120 - 0{,}499\sqrt{\mu} - 0{,}34\,\mu \\
- & pK'' = & 7{,}227 - 1{,}497\sqrt{\mu} + 1{,}04\,\mu \\
- & pK''' = & 12{,}465 - 2{,}495\sqrt{\mu} + 2{,}25\,\mu \\
37^\circ & pK' = & 2{,}232 - 0{,}515\sqrt{\mu} - 0{,}54\,\mu \\
- & pK'' = & 7{,}165 - 1{,}545\sqrt{\mu} + 1{,}12\,\mu \\
- & pK''' = & 12{,}180 - 2{,}575\sqrt{\mu} + 2{,}63\,\mu
\end{array}$$

Hier ist μ die Ionenstärke der Lösung. Sie wurde berechnet, ohne die geringe Komplexbildung zwischen Calcium und Phosphorsäure zu berücksichtigen (sie beträgt gewöhnlich unter 10 %, wie in der folgenden Abhandlung näher ausgeführt wird).

Bei der Berechnung der Verteilung der Phosphorsäure kann man meistens von den Mengen von H_3PO_4 und PO_4^{---} absehen. Wenn pA_H zwischen

5 und 9 liegt, sind die Mengen dieser Formen praktisch gesprochen verschwindend klein. Man hat dann zur Berechnung von $[HPO_4^{--}]$ die folgende Formel:

$$[HPO_4^{--}] = [P] . K''/(A_H + K''),$$

wo [P] die molare Konzentration der Phosphorsäure bedeutet.

Um $p[HPO_4^{--}] = -\log [HPO_4^{--}]$ aus $p[P] = -\log [P]$ zu berechnen hat man $-\log (K''/(A_H + K''))$ zu addieren.

Ist $pA_H > pK''$, kann man dazu die folgende Formel verwenden:

$$-\log (K''/(A_H + K'')) = \text{der Additionslogarithmus zu } pA_H - pK''.$$

Die gewöhnlichen Tabellen enthalten die Werte der Additionslogarithmen zu allen positiven Zahlen. Ist $pA_H < pK''$, muss man die folgende Formel benutzen:

$-\log (K''/(A_H + K'')) = (pK'' - pA_H) +$ dem Additionslogarithmus zu $(pK'' - pA_H)$. Hat man $[HPO_4^{--}]$ berechnet, ist es leicht durch Subtraktion von [P] $[H_2PO_4^-]$ zu berechnen, und mit Benutzung der 1. und 3. Dissoziationskonstante kann man dann, wenn es gewünscht werden sollte, die kleinen Mengen von H_3PO_4 und PO_4^{---} berechnen.

9. Knochen- und Zahn-phosphate.

Wie früher geschildert, sind sich die Gelehrten noch nicht ganz darüber einig geworden, inwieweit die aus wässrigen Lösungen gewonnenen Ausfällungen von Calciumphosphaten, in welchen das Verhältnis CaO/P_2O_5 annähernd gleich 3 ist, als Hydroxylapatit aufzufassen sind mit einer Adsorptionsschicht von phosphorsäurereicheren Verbindungen oder als Tricalciumphosphatdihydrat mit einem Hydroxylapatit-Gitter, in welchem $Ca(OH)_2$ durch 2 oder $3\,H_2O$ substituiert ist. Eine ähnliche Divergenz existiert über die Struktur der mineralischen Substanz der Knochen und der Zähne. Ist diese Substanz Hydroxylapatit mit Calciumcarbonat ausserhalb des Gitters (an der Oberfläche oder als freie Calcit- oder Aragonit-Phase) oder ist das Calciumcarbonat in das Apatitgitter aufgenommen? Selbst über die Struktur des gut kristallisierten Minerals Francolit, $3\,Ca_3(PO_4)_2$, $CaCO_3$, hat man sich nicht einigen können. Ist das Carbonat ausserhalb des Gitters oder als Gitterbaustein aufgenommen? Betreffs dieser Streitfrage, die meine Untersuchungen nicht näher berühren, will ich mich damit begnügen auf die Vorträge und Diskussionen auf den Konferenzen über »Metabolic Interrelations with special reference to calcium« hinzuweisen, die von dem Josiah Macy Foundation in den Jahren 1950, 1951 und 1952 in New York abgehalten wurden[85]. Es soll jedoch darauf aufmerksam gemacht werden, dass Hendricks, der früher die Knochensubstanz als substituiertes Hydroxylapatit aufgefasst hat, sie jetzt als Hydroxylapatit mit adsorbierten Verunreinigungen auffasst. Er meint, dass das Atomgitter der Knochensubstanz mehr Apatit-ähnlich ist, als es mit den notwendigen Substitutionen vereinbar sei. Ich muss gestehen, dass auch mir die Substitutionen, die notwendig sind, um aus dem Hydroxylapatit-Gitter ein Gitter mit der Zusammensetzung der Knochensubstanz zu bekommen, sehr unwahrscheinlich vorkommen. Sie erinnern mich an den alten satirischen Privatbrief von einem Herrn S. C. H. Windler, den Liebig in seinen Annalen der Chemie und Pharmacie **33** (1840) 308 abgedruckt hat, und der nach E. v. Meyer's Geschichte der Chemie aus F. Wöhler's Feder stammen soll. In diesem Briefe teilt S. C. H. Windler mit, dass, nachdem es früher gelungen war, Wasserstoff und Sauerstoff durch Chlor zu substituieren, es ihm nun gelungen sei, auch Kohlenstoff durch Chlor zu substituieren, und in einer Fussnote schreibt er: Je viens d'apprendre qu'il y a déjà dans les Magasins à Londres des étoffes en chlore filé, très recherchés dans les hôpitaux et préferés à tous autres pour bonnet de nuits, caleçons etc.«

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[85] Siehe auch Posner, Fabry und Dallemagne, Biochim. et Biophys. Acta **15** (1954) 304.

CALCIUMORTHOPHOSPHATE II.

KOMPLEXBILDUNG IN LÖSUNGEN VON CALCIUM- UND PHOSPHAT-IONEN

VON

NIELS BJERRUM

Synopsis.

In dieser Abhandlung wird versucht, die Grösse der Komplexbildung zwischen Calcium- und Phosphat-Ionen aus pH-Messungen in ganz verdünnten Lösungen von Calciumphosphat zu berechnen. Es gelingt jedoch nur, eine angenäherte Bestimmung durchzuführen. Sie zeigt, dass bei Calcium- und bei Phosphat-Koncentrationen von der Grössenordnung 0,001 molar nur 0,8—7,1 % des Calciums komplex gebunden ist.

Setzt man Calciumchlorid zu einer Lösung von Natriumphosphat hinzu, so werden die Lösungen mehr sauer, selbst wenn die Lösungen so verdünnt sind, dass kein Niederschlag entsteht. Die Erklärung ist, dass Calcium-Ionen Hydrogen-Ionen von den Hydrogenphosphat-Ionen verdrängen unter Bildung von Calciumphosphat-Komplexen. Es werden hierbei als Komplexe sowohl wahre Komplexe wie Ionenassoziationsprodukte bezeichnet (vgl. Bjerrum, Dan. Mat.-fys. Medd. Kopenhagen 7 (1926) no. 9). Die Wirkung der Calcium-Ionen ist von ähnlicher Natur, nur schwächer, wie die Wirkung der Aluminium-Ionen auf eine Phosphatlösung, die von Bjerrum und Dahm[1] beschrieben ist. Wir wollen versuchen, aus dieser Wirkung die Grösse der Komplexbildung zwischen Calcium-Ionen und Phosphat-Ionen zu berechnen. Genau kann es nicht gemacht werden; unter einigen vereinfachenden Annahmen kann man aber eine angenäherte Berechnung durchführen.

Die Unterschiede zwischen den drei Dissoziationskonstanten der Orthophosphorsäure sind in der Hauptsache (abgesehen von gewissen statistischen Faktoren) eine elektrostatische Wirkung der abnehmenden elektrischen Ladung des Phosphat-Ions, wenn ein oder mehrere Protonen neben den betrachteten schon verhanden sind[2]. Wir wollen annehmen, dass die Aufnahme von positiv geladenen Calcium-Ionen in ähnlicher Weise wie die Aufnahme von Protonen die Säurestärke der an der PO_4-Gruppe gebundenen Protonen vergrössert.

Wir definieren den Neutralisationsgrad, N, der Phosphorsäure in einer Lösung als die Anzahl Basenäquivalente, die bei einer Darstellung der Lösung aus Phosphorsäure pro Mol Phosphorsäure zugesetzt werden muss. Wenn keine Komplexbildung vorhanden ist, wird die mittlere Anzahl von Protonen gebunden an eine PO_4-Gruppe gleich $3 - N - [H^+] + [HO^-]$ sein. Liegt der pH-Wert der Lösung zwischen 5 und 9, können wir gewöhnlich von den H^+- und HO^--Konzentrationen absehen, und wir wollen im folgenden annehmen, dass diese Vereinfachung erlaubt ist. Zwischen dem

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[1] Zeitschr. physik. Ch. Bodenstein Festband (1931) 627.

[2] N. Bjerrum: Zeitschr. physik. Ch. **106** (1923) 219.

Neutralisationsgrad N und der H^+-Konzentration besteht für $1 < N < 2$ folgende Zusammenhang (K_2 ist die 2. Dissoziationskonstante der Phosphorsäure):

$$(N-1)/(2-N) = K_2/[H^+].$$

Die beiden Seiten der Gleichung sind nämlich gleich $[HPO_4^{--}]/[H_2PO_4^-]$, wenn man von der Anwesenheit von H_3PO_4 und PO_4^{---} absehen kann, d. h. wenn N nicht zu nahe an 1 oder 2 liegt.

Sind in der Lösung Calcium-Ionen vorhanden, und bezeichnet $[Ca_k]$ die atomare Konzentration des komplex gebundenen Calciums und $[P]$ die Totalkonzentration der Phosphorsäure, dann kann man die Grösse $N_{app} = N - 2\,[Ca_k]/[P]$ als einen apparenten Neutralisationsgrad der Phosphorsäure in der Lösung auffassen. Diese Grösse ist die Mittelzahl der elektrischen Ladung auf den einzelnen Phosphatgruppen in der Lösung, und $3 - N_{app}$ gibt die Gesamtzahl der Protonen und der Calciumäquivalente an, die im Mittel an die einzelnen PO_4-Gruppen gebunden sind.

Wir nehmen nun an, dass komplex gebundene (bzw. assoziierte) Calciumäquivalente die Säurestärke der an PO_4-Gruppen gebundenen Protone in derselben Weise herabsetzen wie nebenbei gebundene Protone, und zwar so, dass ein Calcium-Ion in einem Monophosphato-Komplex als zwei Protone und in einem Diphosphato-Komplex auf jede der zwei Phosphato-Gruppen als ein einzelnes Proton und somit auch im ganzen als zwei Protone wirkt. Wir wollen also annehmen, dass der Komplex $CaHPO_4$ eine Säuredissoziationskonstante von ähnlicher Grösse wie die erste Dissoziationskonstante der Phosphorsäure (K_1) besitzt, und für die Diphosphato-Komplexe, $Ca(H_2PO_4)_2$, $Ca(H_2PO_4)(HPO_4)^-$ und $Ca(HPO_4)_2^{--}$, wollen wir annehmen, dass die einzelnen H_2PO_4-Gruppen ein ähnliche Säurestärke besitzen wie die Protone in H_3PO_4 (K_1) und die einzelnen HPO_4-Gruppen eine ähnliche Säurestärke wie die Protone in $H_2PO_4^-$ (K_2).

Diese Annahmen sind natürlich nur Annäherungen. Wir wissen nicht mit Sicherheit, dass die positiven Ladungen der gebundenen Calcium-Ionen genau so wirken wie die positiven Ladungen der gebundenen Protone. Es erfordert ja, dass die molekularen Abstände in beiden Fällen dieselben sind. Und was speziell die Diphosphato-Komplexe angeht, so haben wir die gegenseitige elektrostatische Wirkung der beiden Phosphato-Gruppen auf einander nicht berücksichtigt. Wir können indessen zur Zeit kaum bessere Annahmen machen, und ich glaube, dass die obigen Annahmen eine brauchbare Annäherung repräsentieren werden.

Um weiterzukommen, werden wir die Berechnungen unter zwei verschiedenen Annahmen durchführen: 1) dass nur Monophosphato-Komplexe gebildet werden, und 2) dass nur Diphosphato-Komplexe gebildet werden.

1. Annahme. Wenn es sich nur um Monophosphato-Komplexe handelt, so haben wir nur die Formen $CaHPO_4$ und $CaPO_4^-$ zu berücksichtigen. Da $CaHPO_4$, abgesehen von einem statistischen Faktor 3, annähernd dieselbe Säuredissoziationskonstante wie $H_3PO_4 (pK_1 = \text{ca } 2)$ besitzen muss, so wird bei den pH-Werten in unseren Lösungen ihre Konzentration klein sein, und wir brauchen nur mit der Form $CaPO_4^-$ zu rechnen[2a]. Für die Totalkonzentration des nicht komplexen Phosphats, $[P_{uk}]$, und die des komplexen Phosphats, $[P_k]$, gelten dann:

$$[P_k] = [Ca_k] \text{ und } [P_{uk}] = [P] - [Ca_k], \tag{1}$$

wo $[Ca_k]$ die atomare Konzentration des komplexen Calciums ist. Der Neutralisationsgrad, N_{uk}, des nicht komplexen Phosphats ist:

$$N_{uk} = (2+x)/(1+x), \tag{2}$$

wo $x = [H^+]/K_2$ ist. Es gilt nämlich:

$$(2-N_{uk})/(N_{uk}-1) = [H_+]/K_2 = x, \tag{3}$$

da beide Seiten der Gleichung gleich $[H_2PO_4^-]/[HPO_4^{--}]$ sind. Der apparente Neutralisationsgrad (N_{app} = Anzahl freier Ladungen pro PO_4) in $CaPO_4^-$ ist eins. Für den apparenten Neutralisationsgrad in der Lösung gilt deshalb:

$$N_{\text{app}} \cdot [P] = ([P]-[Ca_k])\,(2+x)/(1+x) + [Ca_k], \text{ also} \tag{4}$$

$$N_{\text{app}} = (2+x)/(1+x) - [Ca_h]/([P]\,(1+x)). \tag{5}$$

Der wahre Neutralisationsgrad der Lösung, berechnet als die pro Mol Phosphorsäure zugesetzten Äquivalente Base, bezeichnen wir mit N, und es gilt:

$$N - N_{\text{app}} = 2\,[Ca_k]/[P]. \tag{6}$$

Aus (5) und (6) folgt dann:

$$[Ca_k] = [N-(2+x)/(1+x)]\cdot[P]\cdot(1+x)/(1+2\,x). \tag{7}$$

2. Annahme. Wenn man dagegen annimmt, dass nur Diphosphato-Komplexe gebildet werden, so kommt man zu folgenden Resultaten. Das

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[2a] In dieser Beziehung ist es von Interesse, dass Daniel und Salmon (Journ. Chem. Soc. London 1957, 4210) konstatiert haben, dass das von ihnen dargestellte Phosphato-tetrammin-cobalt(III) dihydrat die Zusammensetzung $Co(NH_3)_4PO_4, 2\,H_2O$ besitzt und somit nicht HPO_4, sondern PO_4 als Ligand enthält.

Diphosphato-Komplex ist vorhanden in den Formen $Ca(HPO_4)_2^{--}$, $Ca(HPO_4)(PO_4)^{---}$ und $Ca(PO_4)_2^{4-}$, dagegen nicht als $Ca(H_2PO_4)_2$ oder $Ca(H_2PO_4)(HPO_4)^-$, da die Säuredissoziationskonstante der an Ca gebundenen H_2PO_4-Gruppen nach unseren Annahmen von ähnlicher Grösse sind wie die 1. Dissoziationskonstante der Phosphorsäure (pK_1 = ca 2). Wir nehmen nun an, dass die einzelnen HPO_4-Gruppen in diesen Komplexen sich in bezug auf ihre H^+-Abspaltung unabhängig voneinander verhalten. Wir können sie dann mit $caHPO_4^-$ und $caPO_4^-$ bezeichnen, wo ca ein halbes Ca-Atom bezeichnet.

Es gilt dann in der Lösung:

$$2\,[Ca_k] = [P_k] = [caHPO_4^-] + [caPO_4^{--}], \tag{8}$$

$$[P_{uk}] = [H_2PO_4^-] + [HPO_4^{--}]. \tag{9}$$

Da

$$[H_2PO_4^-]/[HPO_4^{--}] = [H^+]/K_2 = x \text{ und} \tag{10}$$

$$[caHPO_4^-]/[caPO_4^{--}] = [H^+]/K_2 = x \text{ ist,} \tag{11}$$

ergibt sich:

$$[H_2PO_4^-] + [caHPO_4^-] = [P] \cdot x/(1+x) \tag{12}$$

$$[HPO_4^{--}] + [caPO_4^{--}] = [P] \cdot 1/(1+x) \tag{13}$$

und somit:

$$N_{\mathrm{app}} = (2+x)/(1+x). \tag{14}$$

Nach (6) ist:

$$N - N_{\mathrm{app}} = 2\,[Ca_k]/[P] \tag{15}$$

und somit ist:

$$[Ca_k] = (N-(2+x)/(1+x)) \cdot [P]/2 \tag{16}$$

In Tabelle 1 sind die Resultate einiger pH-Bestimmungen bei 18°C in Lösungen, die durch Zusatz von genau abgemessenen Mengen 0,00917 *m* $Ca(OH)_2$ und 0,0096 *m* H_3PO_4 zu Wasser dargestellt worden waren, zusammengestellt. In den zwei ersten Kolonnen sind die molaren Totalkonzentrationen von Calcium, [Ca], und von Phosphorsäure, [P], aufgeführt. Dann folgt in der 3. Kolonne der aus der Zusammensetzung berechnete Neutralisationsgrad ($N = 2\,[Ca]/[P]$) und in der 4. der experimentell bestimmte pA_H-Wert. pA_H ist gleich $-\log A_H$, wo A_H ein Mass für die Aktivität der H^+-Ionen in der Lösung ist und zwar angegeben in der Skala definiert von BJERRUM und UNMACK[3].

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[3] Mat. Fys. Medd. Dan. Vid. Selsk. Kopenhagen **9**, nr. 1 (1929) 10 und 51ff.

TABELLE 1.

Berechnung des komplex gebundenen Calciums in Lösungen von Calciumphosphat (aus pA_H-Bestimmungen bei $t = 18°$).

$[Ca] \cdot 10^3$	$[P] \cdot 10^3$	N	pA_H	$\mu \cdot 10^3$	pK''	$\frac{2+x}{1+x}$	Nur Monophosphato-Komplexe anwesend		Nur Diphosphato-Komplexe anwesend	
							$[Ca_k] \cdot 10^3$	$\frac{[Ca_k]}{[Ca]}$	$[Ca_k] \cdot 10^3$	$\frac{[Ca_k]}{[Ca]}$
0,910	0,956	1,904	7,807	3,95	7,137	1,823	.065	.071	0,038	0,042
0,916	1,115	1,586	7,171	3,43	7,143	1,516	.054	.059	0,040	0,044
0,914	1,723	1,060	5.930	2.85	7.150	1,057	.027	.030	0,026	0,028
0,688	0,716	1,923	7,916	2,72	7,152	1,852	.043	.062	0,025	0,036
0,687	0,718	1,915	7,916*	2,72	7,152	1,851	.040	.059	0,023	0,034
0,693	0,721	1,923	7,968	2,64	7,153	1,867	.035	.051	0,020	0,029
0,688	0,865	1,590	7,169	2,58	7,154	1,508	.047	.068	0,035	0,051
0,689	0,960	1,437	6,940	2,41	7,155	1,379	.035	.051	0,028	0,040
0,688	0,965	1,426	7,001*	2,47	7,156	1,411	.009	.013	0,007	0,010
0,688	1,241	1,109	6,183	2,20	7,160	1,095	.010	.015	0,009	0,013
0,688	1,246	1,103	6,147	2,19	7,160	1,088	.009	.013	0,009	0,013
0,458	0,473	1,934	8,002*	1,81	7,165	1,872	.027	.059	0,015	0,032
0,458	0,476	1,926	7,968	1,82	7,165	1,863	.026	.057	0,015	0,033
0,455	0,623	1,460	6,992*	1,65	7,168	1,399	.024	.052	0,019	0,042
0,456	0,670	1,362	6,833	1,61	7,169	1,316	.018	.039	0,015	0,034
0,458	0,826	1,110	6,171	1,47	7,172	1,091	.008	.017	0,008	0,018
0,458	0,862	1,064	5,948*	1,43	7,172	1,056	.004	.009	0,004	0,008

Die meisten pA_H-Werte sind mit Chinhydron-Elektroden gemessen. Nur die mit einem Stern* gekennzeichneten Werte sind mit Wasserstoff-Elektroden gemessen. μ in der 5. Kolonne gibt die Ionenstärke an, berechnet ohne eine Komplexbildung zu berücksichtigen ($\mu = 2\,[Ca] + 2\,[HPO_4^{--}] + [H_2PO_4^-]/2 = [P]\,(5\,N - 2)/2$). pK'' in der 6. Kolonne ist die 2. unvollständige Dissoziationskonstante der Phosphorsäure bei 18° und bei der betreffenden Ionenstärke[4]: $pK'' = 2{,}227 - 1{,}497\sqrt{\mu} + 1{,}04\,\mu$. In der 7. Kolonne folgen die Werte von $(2+x)/(1+x)$, wo $\log x = pK'' - pA_H$, und in der 8. bis 11. Kolonne stehen endlich die Werte von $[Ca_k]$, der Konzentration des komplexen Calciums, und von $[Ca_k]/[Ca]$, dem Bruchteil des Calciums, der komplex gebunden ist, beide berechnet sowohl unter der Annahme von nur Monophos-

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[4] Nach Bjerrum und Unmack: Mat. Fys. Medd. Dan. Vid. Selsk. Kopenhagen **9**, nr. 1 (1929) 133.

phato-Komplexen, wie unter der Annahme von nur Diphosphato-Komplexen (Gleichungen (7) und (16)).

Bei den Berechnungen ist es wichtig, dass die benutzten Werte von pK'' und von pA_H miteinander korrespondieren. Benutzt man $p[H^+]$-Werte, muss man mit der sogenannten Konzentrations-Dissoziationskonstante K_2 rechnen, und benutzt man pA_H-Werte, muss man mit Bjerrum und Unmack's sogenannter unvollständiger Dissoziationskonstante K'' rechnen. Es ist natürlich auch wichtig, dass bei der elektrometrischen Bestimmung von pK'' dieselbe pA_H-Skala benutzt worden ist wie bei unseren elektrometrischen pA_H-Bestimmungen in dieser Arbeit.

Die Versuche sind in der Tabelle in drei Abteilungen aufgeteilt mit annähernd denselben Calcium-Konzentrationen und in jeder Abteilung nach steigender Phosphorsäure-Konzentration geordnet. Man ersieht aus der Tabelle, dass mit steigender Phosphorsäure-Konzentration der Bruchteil des Calciums, der komplex gebunden ist, im Allgemeinen etwas abnimmt. Dieses im ersten Augenblick etwas unerwartete Verhalten wird dadurch hervorgerufen, dass mit steigender Phosphat-Konzentration die Lösung auf Grund ihrer Darstellungsweise immer mehr sauer wird, und die Komplexbildung kann als eine Konkurrenz zwischen den Calcium-Ionen und den Wasserstoff-Ionen um die Phosphat-Ionen aufgefasst werden. Hätte man die Phosphat-Konzentration durch Zusatz nicht von Phosphorsäure, sondern von Natriumphosphat vergrössert, hätte man eine Abnahme des komplex gebundenen Calciums mit steigender Phosphat-Konzentration nicht beobachtet.

Die Menge der komplex gebundenen Calcium-Ionen liegt in allen Lösungen zwischen 0,8 und 5,1 $^0/_0$, wenn man nur mit Monophosphato-Komplexen rechnet, und zwischen 0,9 und 7,1 $^0/_0$, wenn man nur mit Diphosphato-Komplexen rechnet. Ist die Steigerung des Säuregrads der Lösungen durch Bildung von sowohl Mono- wie Diphosphato-Komplexen verursacht, dürfen wir annehmen, dass die Menge des komplexen Calciums innerhalb derselben Grenzen liegen wird (0,8 – 7,1 $^0/_0$).

Wir haben versucht, aus den Zahlen der Tabelle Komplexitäts-Konstanten zu berechnen; sie waren aber bei weitem nicht konstant. Wahrscheinlicherweise sind die gemachten Annahmen zu diesem Zweck nicht genügend genau.

Die gemachten Annahmen über die Säurestärke der Komplexe sind nicht so genau, dass es sich lohnen würde, eine grosse Rechenarbeit darauf zu verwenden, zu untersuchen, ob es möglich sein sollte, durch Annahme von gleichzeitiger Anwesenheit von Monophosphato- und von Diphosphato-Komplexen zu konstanten Komplexitäts-Konstanten zu kommen.

Es wäre vielleicht eine lohnende Arbeit, eine grössere Anzahl von genauen pH-Messungen in Calciumphosphatlösungen auszuführen und sie mit Leitfähigkeitsmessungen zu supplieren, um eine breitere Grundlage für Berechnungen über die Komplexbildung zwischen Calcium und Phosphat zu erhalten.

Da in Natriumphosphat-Lösungen vielleicht auch eine kleine Komplexbildung (bzw. Ionenassoziation) zwischen Natrium und Phosphat vorhanden sein kann, wäre es auch von Bedeutung, Natrium- und Kaliumphosphat-Lösungen zu vergleichen und die bei den Berechnungen angewandten pK''-Werte nur aus den Messungen in den wahrscheinlicherweise am wenigsten komplexen Kaliumphosphat-Lösungen zu berechnen.

Nachdem die hier beschriebenen Messungen und Berechnungen der Komplexbildung zwischen Calcium und Phosphat in den dreissiger Jahren ausgeführt worden waren und in einer Mitteilung auf der skandinavischen Naturforscherversammlung in Helsingfors 1936 als vorläufiges Resultat bekannt gegeben worden war, dass die Komplexbildung in verdünnten Lösungen von Calciumphosphaten gewöhnlich kleiner als 10 $^0/_0$ ist, haben GREENWALD und seine Mitarbeiter[5] 1940 Untersuchungen über die Dissoziation von Calciumphosphaten publiziert. Ausgehend davon, dass von verschiedener Seite eine unvollständige Dissoziation von Salzen zweiwertiger Kationen wahrscheinlich gemacht worden ist, haben sie Titrierungskurven von Phosphorsäure in Lösungen von KCl, NaCl und $CaCl_2$ bestimmt, und aus den grösseren H^+-Koncentrationen, die man erhält, wenn man in $CaCl_2$-Lösung titriert, haben sie die Unvollständigkeit der Dissoziation des Calciumphosphats berechnet. Sie nehmen an, dass die einzige komplexe Verbindung $CaHPO_4$ ist und berechnen für die Dissoziationskonstante, $K = (Ca^{++}] [HPO_4^{--}]/CaHPO_4$, folgende Werte bei gewöhnlicher Temperatur: $pK = 1{,}50$ bei $\mu = 0{,}2$, $pK = 2{,}20$ bei $\mu = 0{,}006$.

Ich habe versucht, nach meinem Rechnungsverfahren aus ihren Daten die unvollständige Dissoziation (d. h. die Ionenassoziation oder die Komplexbildung, wie ich sie nenne) des Calciumphosphats zu berechnen. Es ist aber schwer, die Berechnungen durchzuführen. Die Temperaturen sind meistens nur als gewöhnliche Temperatur angegeben. Es wird zwar mitgeteilt, dass eine Reihe der Messungen bei 25° ausgeführt sind; es wird aber nicht deutlich angegeben, um welche Reihe es sich handelt. Die Skala der pH-Werte ist auch nicht näher angegeben, und es ist nach den angeführten Daten nicht leicht, die NaCl-, bzw. die KCl-Reihe zu wählen, die mit der $CaCl_2$-Reihe zu vergleichen ist.

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[5] J. Biolog. Chem. **125** (1940) 65

Greenwald nimmt an, dass nur $CaHPO_4$ und nicht $CaPO_4^-$ gebildet wird, weil nur diese Annahme zu einer einigermassen unveränderlichen Dissoziationskonstante führt. Wie ich aber schon besprochen habe, ist diese Annahme meiner Ansicht nach sehr unwahrscheinlich, da $CaHPO_4$ eine recht starke Säure sein muss. Es muss aber anderseits zugegeben werden, dass man sagen kann, dass die von ihm berechneten einigermassen konstanten Dissoziationskonstanten für die Richtigkeit seiner Annahme sprechen.

Später hat Arnold[6] die erniedrigende Wirkung von Ca^{++}-Ionen auf den pH-Wert von Phosphat-Lösungen diskutiert. Er nimmt nur die Existenz eines Komplexes vom Typus $CaPO_4^-$ (oder $(CaPO_4^-)_m$) an. Er kommt zum Resultat, dass in Lösungen mit einem Ca/P-Verhältnis gleich 1,0 und mit $p[Ca]$ ($= -\log [Ca]$) in der Nähe von 3,4 20 bis 25 $^0/_0$ des Calciums komplex gebunden ist. Dies ist etwa viermal mehr als nach meinen Zahlen in der Tabelle 1.

1953 haben R. E. Gosselin und E. R. Coghlan[7] die Komplexbildung zwischen Calcium- und Orthophosphat-Ionen untersucht, indem sie die Verteilung des mit radioaktivem Calcium indizierten Calciums zwischen einem Kationen-Austauscher und einer wässrigen Lösung von Orthophosphat in 0,15 m NaCl bei pH= 7,4 und 37° C bestimmten. Aus ihren Resultaten berechnen sie die Zusammensetzung des Komplexes und finden, dass der Komplex Ca^{++} und PO_4^{--} im Verhältnis 1:1 enthält, und da Phosphorsäure in einer Lösung mit pH = 7,4 vorzugsweise als HPO_4^{--}-Ion vorhanden ist, nehmen sie weiter an, dass der Ligand im Komplex dieses Ion ist. Für die Dissoziation des Komplexes nach

$$CaHPO_4 \rightleftarrows Ca^{++} + HPO_4^{--}$$

berechnen sie nach Schubert[8] eine Dissoziationskonstante $K_c = 10^{-1,86}$ (bei 37° und pH = 7,4 in einer Lösung von 0,15 m NaCl). Nach diesem Wert ist bei $[HPO_4^{--}] = 10^{-3}$ etwa 13 $^0/_0$ des Calciums komplex gebunden vorhanden.

Man hat schon vor 60 Jahren gewusst, dass die Polymetaphosphate des Calciums komplex sind und hat diese Eigenschaft technisch zur Herabsetzung der Konzentration der Calcium-Ionen in Calcium-Ionen-haltigem Wasser benutzt. Die Polymetaphosphat-Ionen bilden mit Calcium-Ionen weit beständigere Komplexe als die Orthophosphat-Ionen. J. R. van Wazer und Doris A. Campanella[9] erklären diese starke komplexbildende Fähigkeit der Polymetaphosphat-Ionen dadurch, dass das Calcium-Ion an ein

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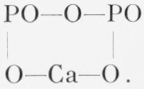
[6] Trans. Faraday Soc. **46** (1950) 1064.
[7] Archiv of Biochem. und Biophysics **45** (1953) 301.
[8] Journ. Biol. Chem. **185** (1950) 387.
[9] Journ. Amer. Chem. Soc. **72** (1950) 655.

Polymetaphosphat-Ion chelat-artig gebunden wird, indem es an zwei benachbarte Phosphor-Atome gebunden wird unter Bildung von 6-Ringen wie



Schlussbemerkung. Die Frage nach der Grösse der Komplexbildung zwischen Ca^{++}-und PO_4^{---}-Ionen kann noch nicht als gelöst betrachtet werden. Die Unsicherheit rührt namentlich davon her, dass die Annahme der Formel $CaHPO_4$ für den Komplex zu Komplexitätskonstanten führt, die mit der H^+-Koncentration weniger variieren (vgl. GREENWALD[5] und GOSSELIN[7]) als die Annahme der aus elektrostatischen Gründen wahrscheinlicheren Formel $CaPO_4^-$ (Seite 72 und 78). Die Frage verdient eine genauere Untersuchung. Wir können heute mit Sicherheit nur sagen, dass eine gewisse Komplexbildung vorhanden ist, die jedoch ziemlich geringfügig zu sein scheint.

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DANISH SCIENTIFIC INVESTIGATIONS IN ARGENTINA UNDER
THE AUSPICES OF FUNDACIÓN WILLIAMS, BUENOS AIRES

CONTRIBUTIONS TO THE MIDDLE CAMBRIAN PALEONTOLOGY AND STRATIGRAPHY OF ARGENTINA

BY

VALDEMAR POULSEN

København 1958
i kommission hos Ejnar Munksgaard

CONTENTS

Synopsis.

A new dolichometopid genus and two new alokistocarid species are established; a few previously established genera and species of stratigraphic significance are revised. It is shown that the *Glossopleura* zone probably constitutes the lowermost part of the Cambrian sequence in the provinces of Mendoza and San Juan. The *Glossopleura* zone in Mendoza comprises the horizons Crucense and Isidrense of Rusconi, and is characterized by genera such as *Mendospidella*, *Glossopleura*, *Alokistocare*, *Kistocare*, *Alokistocarella*. A close parallel is to be found in the Arrojos formation of Mexico.

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INTRODUCTION

The geological and paleontological research carried out in Argentina from October 1954 to March 1955 by professor CHR. POULSEN and the writer was made possible through the great financial support from Mr. THOMAS J. WILLIAMS K.D., director of the Williams Foundation, Buenos Aires. The writer is greatly indebted to THOMAS WILLIAMS and all members of his staff also for their constant efforts to make our stay a pleasant and unforgettable experience. He likewise wishes to express his gratitude to the Carlsberg Foundation and to Statens almindelige Videnskabsfond for financial support covering expenses in connection with the voyage and provision of scientific equipment respectively.

Thanks are also due to professor Dr. ARMANDO F. LEANZA of the Geological Institute of the University of Buenos Aires for allowing the writer to study his collections from Mendoza and to borrow specimens of a new alokistocarid species.

Finally the writer is indebted to professor CARLOS RUSCONI of the Natural History Museum of Mendoza for kind permission to see his collections and for guiding an excursion to the localities at Cerillo Martillo.

The Middle Cambrian deposits in Mendoza were discovered in 1945, and have mainly been treated by RUSCONI, who, as stated by himself, favoured a quick spreading of the knowledge of these finds in preliminary treatments. However praiseworthy, this involved a great number of erroneous assignments resulting in some paleontological and stratigraphical confusion.

The systematic descriptions and revisions given in the present paper are mainly based on material collected by professor CHR. POULSEN and the writer; two specimens of *Alokistocare elongatum* n. sp. were borrowed from the Geological Institute of the University of Buenos Aires with the kind permission of Dr. LEANZA. Under the heading *Incerti ordinis* are listed a few of a large number of incorrectly identified species, which are not represented in the collections of the present writer. Nevertheless they are considered here, as they, due to the erroneous assignment, give a false impression of the stratigraphic range of the Middle Cambrian deposits in Mendoza.

The terminology used for systematic descriptions is essentially the same as that proposed by HOWELL et al. (1947). The term "fixed cheeks" covers the entire non-axial area of the cranidium; a distinction is made between anterior region, palpebral region, and posterior region of fixed cheeks. The terms "width", "length", etc. are qualified by the abbreviations "sag." (sagittal) and "tr." (transverse), whenever the direction of measurement is ambiguous.

MIDDLE CAMBRIAN FAUNAL ZONES IN THE CORDILLERAN REGION.

GENERAL STATEMENT

The question of the number of faunal zones is rapidly becoming an important problem for writers dealing with Middle Cambrian stratigraphy. The problem is closely connected with the probable presence of different facies in corresponding time intervals; this was hinted at by RASETTI (1951, p. 80), when he suggested that the *Wenkchemnia-Stephenaspis* zone and the *Plagiura-Kochaspis* zone might represent different facies from one and the same time interval. This possibility was approved of by LOCHMAN (1953, p. 487). Assuming the above mentioned suggestion to be correct, future revisions of the stratigraphic sub-divisions should include the selection of trilobites, impartial to changes in facies, as zonal guide fossils.

The best known and most widely distributed of the Middle Cambrian faunas is that of the *Glossopleura* zone, a striking faunal feature of which is the great similarity in composition, when even widely separated localities are compared; many genera are universally distributed, and apart from that similarities may be found in very closely related genera, as in the case of *Clavaspidella-Athabaskia-Mendospidella*. Fortunately, many of the genera from this zone show an adequate impartiality toward different facies.

LOCHMAN, in discussing the *Wenkchemnia-Stephenaspis* zone (1953, p. 487), expresses the opinion that *Oryctocephalus* and *Oryctocephalites* appear to be characteristic of a more western, possibly deeper, part of the Cordilleran trough. In this connection the present writer would like to point out that *Oryctocephalus* is not always characteristic of a deeper environment, as the Argentine species are found in limestone containing an ordinary shallow water fauna.

SYSTEMATIC DESCRIPTIONS

Class **HYALOSPONGEA** Vosmaer, 1886.

Order **Lyssakida** Zittel, 1887.

Family **PROTOSPONGIIDAE** Hinde, 1887.

Genus **Protospongia** Salter, 1864.

?Protospongia sp.

1952 ?*Protospongia asperoensis* Rusconi, Rev. Mus. Hist. Nat. Mendoza, vol. VI., Entr. 1–4, p. 115, pl. II, fig. 7.

Discussion: There is no obvious reason for assigning the commonly occurring isolated spicules to species. Apparently only stauracts are known, and on this basis even a generic distinction is problematic. The spicules may just as well be referred to *Kiwetinokia* Walcott, 1920.

Horizon and locality: Lower part of *Glossopleura* zone, associated with *Chancelloria eros* Walcott, 1920, Co. Martillo.

Order **Heteractinida** Hinde, 1888.

Family **CHANCELLORIIDAE** de Laubenfels, 1955.

Genus **Chancelloria** Walcott, 1920.

Chancelloria eros Walcott, 1920.

1954 *Chancelloria cruceana* Rusconi, bol. paleont. Buenos Aires, no. 29, figs. 1 a–b.

Discussion: Rusconi's description and figures as well as specimens examined by the present writer show a great resemblance to *Chancelloria eros* Walcott, as also mentioned by Rusconi. The shape of the body of the sponge is not known, but the individual anahexaenes are identical to those of *C. eros* Walcott. Under these circumstances the author finds no justification for establishing a new species.

This point of view is in full accordance with the opinion of Lochman (1952, p. 112). Identical spicules are found in the basal part of the *Glossopleura* zone in Sonora, Mexico. For reasons similar to those set forth above Lochman prefers to refer the spicules to *C. eros* Walcott.

Horizon and locality: Lower part of *Glossopleura* zone, Co. Martillo.

Class **TRILOBITA**

Order **Zacanthoidida** Richter, 1932.

Family **ORYCTOCEPHALIDAE** Beecher, 1897.

Genus **Oryctocephalus** Walcott, 1886.

Oryctocephalus asperoensis Rusconi, 1952.

1952 *Oryctocephalus* (*Vinãkainella*) *asperoensis* Rusconi, Rev. Mus. Hist. Nat. Mendoza, vol. VI, p. 97, pl. I, fig. 14 and pl. III, figs. 9–14 and 18–19. Text figure 5.

1952 *Vinãkainella spinulosa* Rusconi, Rev. Mus. Hist. Nat. Mendoza, vol. VI, p. 100, pl. III, figs. 20–21. Text figure 6.

Discussion: The Middle Cambrian of Mendoza contains two species belonging to *Oryctocephalus: O. asperoensis* and *O. pentacantha* Rusconi. *O.* (*Vinãkainella*) *asperoensis* and *O.* (*Vinãkainella*) *spinulosa* undoubtedly represent different developmental stages of one and the same species.

Both species agree perfectly with the general conception of *Oryctocephalus,* and as Rusconi does not indicate any morphological differences that might favour a subgeneric distinction, the present writer suggests that the subgeneric name *Vinãkainella* be abandoned. Furthermore, the name *Vinãkainella* is an awkward choice, as it indicates a close relationship to *Kainella* Walcott, 1925, and *Pseudokainella* Harrington, 1938. A comparison will show that these genera differ decisively in all diagnostically important respects; moreover *Kainella* and *Pseudokainella* are confined to the Ordovician.

Horizon and locality: *Glossopleura* zone, Co. Martillo. Associated with *Kistocare mendozanum* (Rusconi).

Family **DOLICHOMETOPIDAE** Walcott, 1916.

Genus **Mendospidella** Rusconi, 1952.

Type species: *Clavaspidella digesta* Leanza, 1947.
(Designated by the present writer).

Mendospidella digesta (Leanza).

Plate I, figs. 1–3.

1947 *Clavaspidella digesta* Leanza, Rev. Mus. La Plata, Sec. Paleontol. tomo III, p. 228, pl. I, figs. 5, 7, 12 and 17.

1952 *Mendospidella quebradensis* Rusconi, Rev. Mus. Hist. Nat. Mendoza, vol. VI, p. 75, pl. I, figs. 3–5.

Apart from numerous adult specimens, which do not add to the knowledge of this species, the material contains a small number of apparently late meraspid cranidia, which are easily referred to *Mendospidella*, as they exhibit many of the characteristic features of the adult. Thus glabella and the glabellar furrows have obtained their final shape. The palpebral lobe is long, curved and extends from the anterolateral corner of glabella to a little short of posterior margin of cranidium. The cranidia measure from 0,5–1 mm in length and 0,8–1,3 mm in width.

Discussion: When Rusconi established the genus *Mendospidella* in 1952 no type species was chosen. Two new species were assigned to *Mendospidella*, and the present writer has designated the most common of these as type species.

Rusconi was of the opinion that the specimens referred to *Clavaspidella digesta* by Leanza, represented two distinct species, and one of these (Leanza 1947, pl. I, fig. 17) was included in *Mendospidella quebradensis*. However, an examination of numerous specimens has convinced the present writer that all of Leanza's figured specimens belong to one and the same species. Consequently the specific name *quebradensis* is a junior synonym of *digesta* and must be abandoned.

The establishment of the genus *Mendospidella* was fully justified, as pointed out by Rusconi. *Mendospidella* differs from *Clavaspidella* in having the pygidium provided with strongly impressed pleural furrows, and the cranidium of *Mendospidella* has short, oblique eye ridges, whereas those of *Clavaspidella* are long and at a right angle to the glabellar axis.

Furthermore it is generally assumed that the occurrence of *Clavaspidella* is restricted to Northwestern Greenland.

Horizon and locality: *Glossopleura* zone, Co. Martillo, Provincia de Mendoza, and about 2 miles west of Zonda, Provincia de San Juan.

Genus **Glossopleura** Poulsen, 1927.

Discussion: A study of Rusconi's collections and an examination of specimens collected by C. Poulsen and the present writer clearly showed that a number of species referred by Rusconi to *Asaphus* or *?Asaphus* belongs to *Glossopleura*. A brief review of these corrections was published by Rusconi in 1954 (Bol. Paleont. Buenos Aires, no. 29). It appears from the mentioned publication that Rusconi believes in the assignment of Upper Cambrian species to *Glossopleura*. This must be an erroneous conception, the genus *Glossopleura* being restricted to the Middle Cambrian.

Horizon and locality: *Glossopleura* zone, Co. Martillo. The present writer is of opinion that the following species from this locality can be safely referred to *Glossopleura*:

?Asaphus asperoensis Rusconi, 1952.
?Ogygopsis martillensis Rusconi, 1952.
?Asaphus inexsulcatus Rusconi, 1946.

Genus **Chilometopus** Rusconi, 1952.

Chilometopus parabolicus Rusconi, 1952.

Plate I, fig. 4.

Discussion: Supplementary material collected by the present writer allows of a few additions and corrections to the original description concerning the shape of glabella and the anterior portion of cephalon, the true nature of which, presumably owing to poor state of preservation, was not recognized by Rusconi.

Glabella is not ovate, as described by Rusconi, but practically cylindrical, slightly expanded anteriorly, truncate in front, and separated from the narrow anterior border by a narrow anterior border furrow. Anterior branches of facial suture follow a course parallel to the axial furrows. The original description of the other parts of the exoskeleton seems to be adequate.

It appears from the above correction that the relationship of *Chilometopus parabolicus* to *Chilometopus asperoensis* Rusconi (1952, p. 89) is more close than suggested by the original description.

It must be pointed out that Rusconi's restoration of *C. parabolicus* (text fig. 4) is incorrect and misleading, a fact which can easily be established by comparison of this figure with pl. III, figs. 5 and 23 in the same paper.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

Genus **Asperocare** n. g.

Type species: *Asperocare argentinum* n. sp.

This new genus is represented by eight cranidia, all belonging to one and the same species; a couple of these are directly attached to thoracic segments.

Diagnosis: Cranidium sub-trapezoidal. Glabella sub-cylindrical, somewhat contracted anteriorly, reaching anterior border furrow, with four pairs of glabellar furrows. Anterior region of fixed cheeks relatively wide; posterior region obliquely backward-directed, with acute lateral extremities. Palpebral lobes of medium length, moderately curved, situated somewhat posteriorly and fairly distant from glabella. Eye ridges prominent, oblique. Thorax of at least eleven segments, with narrow pleural region.

The relationship of this genus is discussed below in connection with description of the type species.

Asperocare argentinum n. sp.

Plate I, figs. 5–10, text fig. 1.

Cranidium sub-trapezoidal in outline. Glabella 1,5 times as long as wide, sub-cylindrical to slightly conical, truncately rounded in front, strongly convex transversally and sagittally, profile highest a little behind midpoint. Four pairs of glabellar furrows, of which the three anterior are separated from the axial furrow; first and second pairs short, indistinctly marked, converging towards the front of glabella; third pair short, moderately impressed, directed slightly backward; fourth pair fairly long, strongly oblique, directed backward. Axial furrows well-impressed, fairly wide. Occipital furrow narrow, well-impressed laterally. Occipital ring wide (tr.), rounded triangular, provided with a pointed node. Anterior border furrow shallow, narrow medially, having a forward turn around anterior end of glabella, joining pre-glabellar furrow. Anterior border slightly concave, upturned. Anterior margin emarginate with the exception of a faint forward turn in front of glabella. Anterior region of fixed cheeks relatively wide, a little expanded towards the front, slightly downsloping laterally and anterolaterally. Palpebral region half as wide as adjacent part of glabella, of low convexity, horizontal. Eye ridges prominent, directed slightly forward, joining glabella between first and second glabellar furrow. Palpebral lobes well-defined,

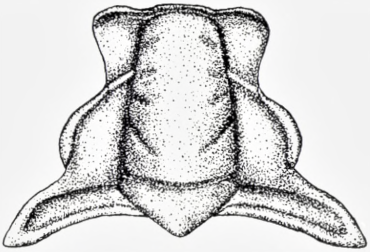

Fig. 1. *Asperocare argentinum* n. sp., cranidium (magnified).

upturned, of medium length, strongly curved posteriorly, delimited by a well-impressed furrow. Posterior region of fixed cheeks of approximately same width (tr.) as occipital ring, obliquely backward-directed, strongly sloping throughout, rapidly tapering to acute lateral extremities; posterior border furrow wide and well-impressed. Facial suture cutting anterior margin moderately out at side, curving out and back to anterior border furrow, then following a straight line back to the palpebral lobe, joining the latter a little behind anterior end; posterior branch swerving out and back to posterior margin.

Thorax of at least eleven segments, with wide axis and narrow pleural regions; axial rings carrying small nodes; pleurae slightly backward-curved, broadly furrowed proximally; pleural extremities poorly preserved, but the general shape of the pleurae seems to indicate terminations without spines.

Outer surface of test finely granulated.

The holotype cranidium has the following dimensions:

Length	4 mm
Width at posterior margin	6 -
Width between the eyes	4 -
Length of glabella..................	3 -
Width of glabella at base	2 -

Discussion: The relationships of *Asperocare* n. g. cannot be accounted for in detail, this genus being known only from cranidia and poorly preserved thoracic segments. It has many characters in common with *Chilometopus* Rusconi, 1952, which must be a close relative, but differs from the latter in having a conical glabella, wider anterior region of fixed cheeks, slightly more divergent anterior branches of facial suture, anterior border of quite different proportions, and acute lateral extremities of posterior cheek region.

Judging from the general features of cranidium, thorax and pygidium, *Chilometopus* may safely be placed in the Dolichometopidae; the anterior branches of facial suture in *Chilometopus* as well as in *Asperocare* n. g. are much less divergent than those of the Zacanthoididae, accordingly, the two genera in question are not referable to that family.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

Order **Ptychoparida** Richter, 1932.

Family **ALOKISTOCARIDAE** Resser, 1939.

Genus **Alokistocare** Lorenz, 1906.

Type species: *Conocephalites subcoronatus* Hall and Whitfield, 1877.

Middle Cambrian ptychoparoid trilobites with a more or less flat cranidium, long, usually concave anterior border, wide fixed cheeks, numerous thoracic segments, and a small pygidium may be referred to a number of genera. Rasetti (1951, p. 202) has emphasized some of the generic differences found in this group of trilobites.

In addition to this the present writer wishes to point out that *Amecephalus*, *Alokistocare* and *Amecephalina* are separable on basis of the nature of the anterior border alone. *Amecephalus* is distinguished by an essentially flat anterior border, of moderate width, and a moderately curving anterior margin. The strongly curved anterior margin and anterior border furrow as well as the narrow anterior border serve to separate *Amecephalina* from the other two genera. With regard to *Alokistocare* the present writer is of the opinion that the concave, upturned border, about half as broad as length (sag.) of pre-glabellar field, is an important feature; thus the species *Alokistocare modestum* Lochman (1952) must probably be referred to another genus on account of the convex, descending anterior border. This species seems to be more closely related to *Kistocare* rather than to *Alokistocare*.

Unfortunately the above mentioned features may be seriously affected by the state of preservation, therefore great care is expedient when dealing with this group of trilobites.

Alokistocare elongatum n. sp.

Plate I, figs. 11–12.

Known from three cranidia, two of which, originating from Provincia de San Juan, were borrowed from the Geological Institute of the University of Buenos Aires with the kind permission of Dr. Leanza. The third one was collected at Co. Martillo, Mendoza.

Cranidium sub-rectangular. Glabella tapered, moderately convex, somewhat truncated in front, less than half of cranidial length. Four pairs of glabellar furrows; fourth pair well-impressed, directed slightly backward; first, second and third pair are shallow, not well-preserved in any of the specimens. Axial furrows more impressed than pre-glabellar furrow. Occipital furrow shallow throughout. Occipital ring short (sag.) and simple. Pre-glabellar field as long (sag.) as glabella, with strong relief. An elongate, prominent boss covers the greater part of the frontal area; boss slightly expanded anteriorly, medially covering half of anterior border. Anterior border furrow narrow and shallow, slightly curved, becoming even more shallow when crossing pre-glabellar boss. Anterior border strongly concave, upturned, three-fifths (sag.) the length of pre-glabellar field. Anterior margin evenly curved. Palpebral region of fixed cheeks slightly convex, horizontal, as wide as adjacent portion of glabella. Palpebral lobe not preserved; apparently of size and position usual in the genus. Eye ridges straight, prominent, almost at a right angle to glabellar axis, joining glabella at anterior corner. Anterior region of fixed cheeks long (sag.), downsloping. Posterior region of fixed cheeks, not well-preserved in any of the specimens, seems to be slender, of moderate length (tr.). Posterior border furrow shallow, of same width as the occipital furrow. Facial suture cutting anterior margin moderately out at side, curving back to anterior border furrow, then running straight back to palpebral lobes following a course almost parallel to sagittal axis. Posterior branches of facial suture unknown.

Dimensions of holotype cranidium:

Length	7	mm
Width at posterior margin	8–10	-
Width between the eyes	6	-
Length of glabella	3	-
Width of glabella at base	3	-
Length of pre-glabellar field (sag.)	2,5	-
Width of anterior border (sag.)	1,5	-
Length of pre-glabellar boss	2	-

Discussion: *Alokistocare elongatum* n. sp. is readily recognized on basis of the frontal area alone, especially the pre-glabellar boss attracts attention. In some cases doubt has arisen as to the course of anterior border furrow in relation to a pre-glabellar boss. In *A. elongatum* n. sp. a shallow continuation of anterior border furrow is seen to cross the pre-glabellar boss. Even if effaced in most species this probably represents a general feature; consequently, a comparison of anterior border furrow to an eventual furrow in front of or back of the pre-glabellar boss should be avoided, whenever the boss crosses anterior border furrow.

Horizon and locality: *Glossopleura* zone, Quebrada de Juan Pobre in Sierra Chica de Zonda, San Juan, and Co. Martillo, Mendoza.

Alokistocare australe n. sp.

Plate I, figs. 13–15.

Known from two imperfect cranidia.

Cranidium somewhat wider than long. Glabella tapered, moderately convex, truncately rounded in front, half the length of cranidium. Traces of four pairs of glabellar furrows can be observed; the fourth pair seems to be longer and more deeply impressed than the other pairs. Axial furrows and pre-glabellar furrow well-impressed. Occipital furrow apparently shallow throughout. Occipital ring only preserved laterally, probably of shape usual in the genus. Pre-glabellar field half as long (sag.) as glabella, downsloping, provided with an elongate boss covering most of pre-glabellar field and part of anterior border. Pre-glabellar field, apart from the boss, distinguished by a fine network of inosculating lines. Anterior border furrow shallow, slightly curved. It is not possible to see a continuation of anterior border furrow across the pre-glabellar boss; however, this may be due to the poor state of preservation. Anterior border concave, slightly upturned, about half as broad (sag.) as length of pre-glabellar field. Palpebral region of fixed cheeks convex, horizontal, two-thirds the width of adjacent portion of glabella. Palpebral lobes not preserved; apparently of size and position usual in the genus. Eye ridges prominent, slightly curved, directed a little forward. Anterior region of fixed cheeks long (sag.), downsloping, showing a fine net of inosculating lines. Posterior region of fixed cheeks not well-preserved in any of the specimens, but seems to be slender, of moderate length (tr.). Posterior border furrow well-impressed. Facial suture cutting anterior margin far out at side, curving back to anterior border furrow, then approaching glabella when running back to the palpebral lobes, from here swerving out following a course almost parallel to posterior margin. The rear part of facial suture not known.

The holotype cranidium has following dimensions:

Length		8,5 mm
Width at base	about	12 -
Width between the eyes		9 -
Length of glabella		4 -
Width of glabella at base		4 -
Length of pre-glabellar field (sag.)		2 -
Width of anterior border (sag.)		1 -
Length of pre-glabellar boss	about	2 -

Discussion: This new species is easily distinguishable from *A. elongatum* n. sp. by the difference in the basic dimensions, thus the frontal area is much wider (tr.) in *A. australe* n. sp.; moreover, the shape of the preglabellar boss and the tapering of glabella are quite different in the two species.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

Genus **Kistocare** LOCHMAN, 1948.

Kistocare mendozanum (RUSCONI).

1945a *Plesioparabolina mendozana* RUSCONI, An. Soc. Cient. Argentina, CXXXIX, p. 216, text fig. 1.

1947 *Amecephalus mendozanus* (RUSCONI) LEANZA, Rev. Mus. La Plata, Sec. Paleont., vol. III, p. 232, pl. I, fig. 13.

1952 *Syspacephalus asperoensis* RUSCONI, Rev. Mus. Hist. Nat. Mendoza, vol. VI, p. 102, pl. V, figs. 4–5.

All of the numerous specimens collected by C. POULSEN and the present writer show the presence of a fourth pair of glabellar furrows; this pair, representing the anterior pair of glabellar furrows, is very faint, converging slightly forward. The three other pairs are in good agreement with the description given by RUSCONI (1952). A few, especially well-preserved specimens show a fine granulation on the outer surface of test.

Discussion: For several reasons the assignment to *Amecephalus* cannot be correct. Thus *Amecephalus* is not known to occur in the *Glossopleura* zone, and the proportions of the cranidium do not agree with those of the type species (*Ptychoparia piochensis* WALCOTT, 1886 (part.)), and with regard to the pygidium of the species in question the distinct segmentation and the relatively slender axis further emphasize the difference.

The species *Syspacephalus asperoensis* was based on obviously young individuals (cranidia about 2,5 mm in length); hence it is understandable that the identity with the previously established species *Amecephalus mendozanus* (RUSCONI) (= *Plesioparabolina mendozana* RUSCONI) was not recognized by RUSCONI. In this connection it must be noted that, unfortunately, the figure given by LEANZA in 1947 was not particularly enlightening.

Reference of the species to *Syspacephalus* RESSER (1936) must be left out of consideration, as it differs decisively in two important respects: The palpebral lobes are situated almost on posterior one-third line of glabella, and the anterior branches of the facial suture are clearly divergent; finally the present writer believes that *Syspacephalus* is restricted to the Lower

Cambrian and the Lower Middle Cambrian. It is true that Rasetti mentions the occurrence of *Syspacephalus* in the *Albertella* zone at Mount Stephen (Rasetti 1951, *Syspacephalus tardus*, p. 247). This species apparently only differs little from the type species, *Agraulos charops* Walcott, 1917, but it must be noticed that its stratigraphic position has not been established with certainty.

A comparison with *Kistocare* Lochman, 1948, shows that the Argentine species very well matches the generic diagnosis. The plausibility of referring the species to *Kistocare* is supported by the stratigraphic position (apparently *Kistocare* is found only in the *Glossopleura* zone) and by the association with other, closely related members of Alokistocaridae.

Horizon and locality: *Glossopleura* zone, Co. Martillo, and two miles west of Zonda, Provincia de San Juan.

Genus **Alokistocarella** Resser, 1938.

Alokistocarella mexicana Lochman, 1952.

Plate I, figs. 16–19.

The material contains two cranidia, which agree perfectly with the original description. Due to poor state of preservation one of the cranidia fails to show the granulation, whereas the external surface of the other is covered with medium-sized granules except furrows and bulge on the anterior border. The Argentine specimens differ only in the somewhat higher convexity of the cranidia, so possibly the specimens described by Lochman have been object to a certain amount of flattening. Evidently, an important feature in this species, as also demonstrated by the Argentine specimens, is the slight downsloping of anterior border.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

Genus **Amecephalina** Poulsen, 1927.

Amecephalina argentina (Kayser).

A single, somewhat fragmentary and distorted, cranidium, originating from Co. Martillo, may be safely included in this species in spite of the poor state of preservation. Reference to *Amecephalina* was made by Harr. & Leanza in 1943.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

Genus **Eteraspis** Resser, 1935.

Eteraspis orbignyana (Kayser).

A few small cranidia, representing young holaspid stages, are referred to this species. The cranidia agree perfectly with the description and figures given by Harrington and Leanza (1943).

Discussion: This genus shows some similarity to *Alokistocarella* and *Kistocare,* and a reference to the Alokistocaridae may be plausible, the ptychoparoid element of the *Glossopleura* zone in Argentina being represented almost exclusively by members of this family.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

INCERTI ORDINIS

I.

"Clavaspidella asperoensis" Rusconi, 1952, Rev. Mus. Hist. Nat. Mendoza, vol. VI, p. 108, pl. II, fig. 2.

Discussion: For reasons as mentioned in connection with *Mendospidella digesta* (Leanza) p. 7 this species is not referable to *Clavaspidella.*

Horizon and locality: *Glossopleura* zone, Co. Martillo.

II.

"? *Glossopleura pedemontana*" Rusconi, 1955, Rev. Mus. Hist. Nat. Mendoza, vol. VIII, p. 18, pl. I, fig. 15.

Discussion: The pygidium differs from that of *Glossopleura* in having a pleural platform, which gradually merges into a narrow and indistinctly defined border, and in the lack of a post-axial ridge, and finally in the peculiar course of the interpleural grooves, which are narrow and shallow proximally, expanded and deeply impressed distally.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

III.

"? *Fieldaspis minuta*" Rusconi, 1955, Rev. Mus. Hist. Nat. Mendoza, vol. VIII, p. 17, pl. II, fig. 5.

Discussion: The pygidium figured and described by Rusconi can hardly be assigned to *Fieldaspis* Rasetti (1951) in spite of some similarity, especially to *Fieldaspis bilobata* Rasetti (1951, p. 161). The Argentine species differs from *Fieldaspis* in some important respects. Thus the basic shape of the pleural platform varies somewhat, not being transversely elongate in a notable degree. The axis tapers considerably to terminate in a remarkably pointed terminal segment, moreover the border seems to be comparatively narrow. Finally the presence of *Fieldaspis*, which apparently is restricted to the *Plagiura-Kochaspis* zone, is not to be expected in the Middle Cambrian of Mendoza, all the more so because the available evidence indicates that deposits belonging to the *Glossopleura* zone constitute the lowermost part of the Cambrian sequence in Argentina.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

IV.

"*Amecephalus cormoranus*" Rusconi, 1955, Bol. Paleont. Buenos Aires, no. 32 and Rev. Mus. Hist. Nat. Mendoza, vol. VIII, p. 23, pl. I, fig. 7.

Discussion: Rusconi based this species on pygidia, which unfortunately fail to show any convincing resemblance to *Amecephalus* Walcott, 1924 (type species *Ptychoparia piochensis* Walcott, 1886, (part.)). On the contrary some notable differences may be pointed out. The pygidium of *Amecephalus* is characterized by the effaced segmentation of the pleural platform, the width of the axis (half of pygidial width) and the small number of axial segments (three to four). The pygidium of the Argentine species is distinguished by a slender axis, a distinctly segmented pleural platform, six axial segments, and moreover by being much wider than that of the type species. Finally, *Amecephalus* is nowhere known to occur in the *Glossopleura* zone.

Horizon and locality: *Glossopleura* zone, Co. Martillo.

THE MIDDLE CAMBRIAN FAUNA OF SAN JUAN

Harrington and Leanza (1943, p. 217) listed the following species from two localities in San Juan:

At QUEBRADA DE LA LAJA: *Amecephalina argentina* (Kayser), *Ehmania* (?) *lajensis* (Kayser), *Ehmania* (?) *hypselogena* Harr. & Leanza, *Billingsella* (?) sp. indet.

At QUEBRADA DE JUAN POBRE: *Eteraspis orbignyana* (Kayser), *Eteraspis prosorysa* Harr. & Leanza.

An addition to the fauna at Quebrada de Juan Pobre is *Alokistocare elongatum* n. sp. (associated with *Billingsella* (?) and *Eteraspis*).

From a new locality by the roadside, about two miles west-northwest of Zonda (N) (Zonda (N) about eight miles west-northwest of San Juan), a fauna, collected by the present writer, contains the following species: *Zacanthoides ferula* LEANZA, *Mendospidella digesta* (LEANZA), *Kistocare mendozanum* (RUSCONI), *Amecephalina argentina* (KAYSER).

Thus the fauna now comprises following species:

Alokistocare elongatum n. sp.
Amecephalina argentina (KAYSER)
Ehmania (?) *lajensis* (KAYSER)
— *hypselogena* HARR. & LEANZA
Eteraspis orbignyana (KAYSER)
— *prosorysa* HARR. & LEANZA
Kistocare mendozanum (RUSC.)
Mendospidella digesta (LEANZA)
Zacanthoides ferula LEANZA
Billingsella sp. indet.

STRATIGRAPHY

The presence of a Middle Cambrian fauna in San Juan was first recognized by HARRINGTON and LEANZA in 1943. Their study of collections from Sierra Chica de Zonda in addition to a revision of older collections, described by KAYSER in 1876, resulted in a comparison to the Maryville formation of Tennessee, Georgia, and Alabama.

The Middle Cambrian deposits in the province of Mendoza were originally referred to Ordovician or Lower Silurian by RUSCONI in 1945. Later in 1945 he proposed a Cambrian age after having made new collections.

However, the first well-founded reference of these deposits to Middle Cambrian was made by LEANZA in 1947.

In the recent years Cambrian faunas, younger than that found at Co. Martillo, were discovered and described by RUSCONI (1950–1955). These younger faunas will not be considered in the present paper.

It appears from a consideration of all the known Argentine Middle Cambrian trilobites that genera diagnostic of levels lower than the *Glosso-*

pleura zone have never been found. It is true that some species have been referred to genera such as *Amecephalus, Fieldaspis,* and *Syspacephalus*; however, it soon became evident that in all instances the generic references were erroneous.

In related regions transgressions reached a maximum in Upper Middle Cambrian; thus it seems reasonable to assume that not until that time did the transgression penetrate as far south as Argentina.

MIDDLE CAMBRIAN OF MENDOZA

In 1955 (Rev. Mus. Hist. Nat. Mendoza, vol. VIII) Rusconi presented following sub-divisions of the Middle Cambrian of Mendoza:

Isidreana formation	Horizon Villavicense (Cerillo El Solitario)	
	Horizon Isidrense	Cerillo Martillo
	Horizon Crucense	

Horizon Crucense: Localities at base of, and in the vicinity of Co. Martillo. Rusconi is of opinion that this horizon belongs to Upper Lower Cambrian or Lower Middle Cambrian; however, well-founded species such as *Mendospidella digesta* (Leanza), *M. asperoensis* Rusc. (*Mendospidella* undoubtedly substituting the closely related *Athabaskia* from the North American and Mexican Cordilleran region), *Kistocare mendozanum* (Rusc.), *Glossopleura asperoensis* (Rusc.), *Gl. inexsulcata* (Rusc.), and *Gl. martillensis* (Rusc.) unquestionably indicate an age corresponding to the *Glossopleura* zone.

In the type section of the Arrojos formation in Sonora, Mexico, a layer containing *Chancelloria eros* Walcott appears above the lowermost *Glossopleura* beds; as the same species occurs in the basal layers of the Middle Cambrian section at Co. Martillo, the lower part of the *Glossopleura* zone here may possibly be absent.

Horizon Isidrense: Localities west of Estancia San Isidro and at Co. Martillo. Well-founded species from this horizon are such as *Kistocare mendozanum* (Rusc.), *Kootenia incerta* (Rusc.), *Zacanthoides ferula* Leanza, *Glossopleura inexsulcata* (Rusc.), *Alokistocarella mexicana* Lochman, all except the last one also known from horizon Crucense. From horizon Isidrense Rusconi lists a number of genera definitely younger than the normal *Glosso-*

pleura fauna; this younger element, probably originating from overlying beds, seems to be of Upper Cambrian age.

It will appear that all evidence justifies the incorporation of the two mentioned horizons in the *Glossopleura* zone; the present writer prefers the use of the term *Glossopleura* zone, as it facilitates comparisons with other regions.

A distinction between faunules within this zone is not possible until a thorough revision of previously established species has been made, as genera and species listed by Rusconi comprise forms from widely separated stratigraphical levels (Middle Cambrian-Ordovician) as well as from definitely separate faunal realms.

MIDDLE CAMBRIAN OF SAN JUAN

Of the ten species listed from San Juan six are known from the *Glossopleura* zone in the Co. Martillo region, and of these species *Kistocare mendozanum* (Rusc.) and *Mendospidella digesta* (Leanza) must be regarded as diagnostic of the *Glossopleura* zone. Consequently it is safe to include the deposits at Quebrada de La Laja, Quebrada de Juan Pobre, and the new locality two miles west of Zonda (N) in this zone.

CONCLUSIVE REMARKS ON THE GLOSSOPLEURA ZONE IN ARGENTINA

As pointed out above, a thorough revision of previously established genera and species will be necessary in order to enable a detailed correlation with other regions. However, the occurrence of genera such as *Glossopleura*, *Mendospidella* (substituting *Athabaskia*), *Alokistocare*, *Kistocare*, *Alokistocarella*, *Zacanthoides*, and *Kootenia* indicates that part of the Argentine Middle Cambrian forms a close parallel to the upper half of the Arrojos formation of Mexico; of special interest is the Argentine occurrence of *Alokistocarella mexicana* Lochman.

The youngest Middle Cambrian deposits in Mendoza are found at Cerillo El Solitario, Canota (Horizon Villavicense of Rusconi). The fauna from this locality apparently cannot be compared to that of the Tren dolomite in Mexico, therefore it is probable that the connection between Mexico and Argentina was completely interrupted towards the end of *Glossopleura* time. The fauna at Canota seems to have affinities mainly to North American faunas east of the Cordilleran trough.

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Plate I.

Mendospidella digesta (Leanza). — Page 6.

Figs. 1–3. Three meraspid cranidia; figs. 1–2, somewhat early meraspid stage, × 25. Fig. 3, late meraspid stage, × 25.

Chilometopus parabolicus Rusconi. — Page 8.

Fig. 4. Cranidium attached to thoracic segments, × 3.

Asperocare argentinum n. g. et n. sp. — Page 9.

Figs. 5–10. Figs. 5–7, cranidium (holotype), dorsal, lateral, and frontal view, × 4. Fig. 8, cranidium (paratype), × 3. Fig. 9, cranidium with attached thoracic segments (paratype), × 3. Fig. 10, cranidium (paratype), × 3.

Alokistocare elongatum n. sp. — Page 11.

Figs. 11–12. Two cranidia. Fig. 11, paratype, × 3. Fig. 12, holotype, × 3.

Alokistocare australe n. sp. — Page 13.

Figs. 13–15. Cranidium (holotype), dorsal, frontal, and lateral view, × 3.

Alokistocarella mexicana Lochman. — Page 15.

Figs. 16–19. Figs. 16–18, cranidium, dorsal, frontal, and lateral view, × 3. Fig. 19, approximately dorsal view of a cranidium showing the granulation, × 8.

Færdig fra trykkeriet den 29. maj 1958.

PLATE 1


1


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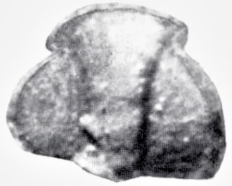
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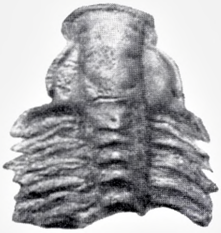
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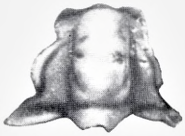
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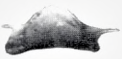
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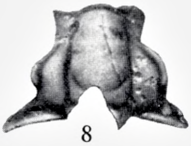
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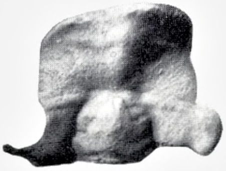
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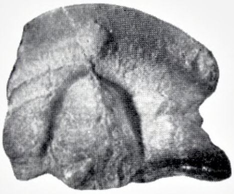
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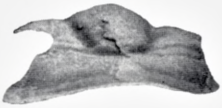
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TABLE OF LIGAND FIELD INTEGRALS

BY

C. J. BALLHAUSEN AND E. M. ANCMON

København 1958
i kommission hos Ejnar Munksgaard

Synopsis.

Numerical values of integrals occurring in ligand field calculations are tabulated as functions of the "effective" charges of the wave functions and of the bond lenghts. The integrals fall into three classes: 1: The electronic interaction integral $G^n_{a,b} = \int R(a) \frac{r^n_<}{r^{n+1}_>} R(b) r^2 \, dr$ with $\alpha)$ $a = b = 3d$, $n = 0$, 2 and 4, $\beta)$ $a = 3d$, $b = 4p$, $n = 1$ and 3, $\gamma)$ $a = 3d$, $b = 4s$, $n = 2$ and $\delta)$ $a = b = 4s$, $n = 0$. 2: The first derivatives $B^n_{a,b} = \frac{d}{dr_0} G^n_{a,b}$ with respect to the bond length r_0. Tabulated are $\alpha)$ $a = b = 3d$, $n = 0, 2$ and 4, and $\beta)$ $a = 3d$, $b = 4p$, $n = 1$ and 3. 3: The second derivatives $C^n_{a,b} = \frac{d^2}{dr_0^2} G^n_{a,b}$. Tabulated are $\alpha)$ $a = b = 3d$, $n = 0, 2$ and 4. All the integrals are evaluated using hydrogenlike wavefunctions.

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§ I. Introduction.

In calculations using the ligand field theory very little numerical work is required in order to evaluate the angular parts of the various matrix elements, especially if the tables given by Condon and Shortley1) are utilized. The remaining part of the problem, that is the calculation of the radial integrals, is certainly not difficult, but only tedious when hydrogenlike wave functions2) are used. Thus in order to facilitate ligand field calculations the following radial integrals were calculated by use of an I. B. M. 650 magnetic drum data-processing machine. Hydrogenlike wave functions were used in all the calculations.

§ 2. Table I.

Table I gives values of the integrals

$$G^n_{3d,\,3d} = \int R(3\,d)\,\frac{r^n_<}{r^{n+1}_>}\,R(3\,d)\,r^2\,dr$$

$$= \int_0^{r_0} R^2(3\,d)\,\frac{r^{n+2}}{r_0^{n+1}}\,dr + \int_{r_0}^{\infty} R^2(3\,d)\,\frac{r_0^n}{r^{n-1}}\,dr$$

with n = 0, 2 and 4.

$R\,(3\,d)$ is the usual hydrogenlike $3\,d$ wave function2) having the "effective" charge Z_{3d}, and r_0 is the bond distance, that is the distance from the metal ion to the ligand. These integrals are the basic ones, used in ligand field theory to calculate the splitting of the d-levels in fields of various symmetries.3, 4, 5, 6, 7)

The same table further tabulates the integrals defined as $\frac{d}{dr_0}\,G^n_{3d,\,3d} = B^n_{3d,\,3d}$ and $\frac{d}{dr_0}\,B^n_{3d,\,3d} = C^n_{3d,\,3d}$. The $B^n_{3d,\,3d}$ integrals are used to obtain the splitting of the $3\,d$-orbitals,6, 7) if a dipole model is assumed for the complex, and are further useful in calculations of the Jahn-Teller effect.[8, 9, 10] The $C^n_{3d,\,3d}$ integrals occur likewise in Jahn-Teller calculations.[10]

By use of the integrals[11] $A_n(\alpha) = \int_1^\infty e^{-\alpha t}\, t^n\, dt$ we obtain as our master formulae:

$$G^n_{3d,\,3d} = \frac{Z_{3d}}{1080\, a_0}\left[\frac{(n+6)\,!}{y^{n+1}} - y^6\left(A_{6+n}(y) - A_{5-n}(y)\right)\right]$$

$$B^n_{3d,\,3d} = \frac{Z^2_{3d}}{1620\, a_0^2}\left[-\frac{(n+6)\,!\,(n+1)}{y^{n+2}} - 6\,y^5\left(A_{6+n}(y) - A_{5-n}(y)\right)\right.$$
$$\left. - y^6\left(A_{6-n}(y) - A_{7+n}(y)\right)\right]$$

and

$$C^n_{3d,\,3d} = \frac{Z^3_{3d}}{2430\, a_0^3}\left[\frac{(n+6)\,!\,(n+1)\,(n+2)}{y^{n+3}} - 30 y^4\left(A_{6+n}(y) - A_{5-n}(y)\right)\right.$$
$$\left. + 12 y^5\left(A_{7+n}(y) - (A_{6-n}(y)\right) - y^6\, A_{8+n}(y) - A_{7-n}(y))\right].$$

Here $y = \frac{2 r_0 Z_{3d}}{3 a_0}$, a_0 being the Bohr-radii and Z_{3d} the "effective" charge on the $3d$ wave function. Values of these functions are given in Table I for $Z_{3d} = 3.65$ to 7.85 and $r = \frac{r_0}{a_0}$ going from 3.40 to 4.20.

The factor $\frac{1}{a_0}$ in $G^n_{3d,\,3d}$, $\frac{1}{a_0^2}$ in $B^n_{3d,\,3d}$ and $\frac{1}{a_0^3}$ in $C^n_{3d,\,3d}$ have been ommitted from the tables.

§ 3. Table II.

This Table records values of the integral $G^2_{3d,\,4s} = \int R(3d)\frac{r^2_<}{r^3_>} R(4s)\, r^2\, dr$. We have for the master formula:

$$G^2_{3d,\,4s} = \frac{1}{24\cdot 81\cdot\sqrt{30}}\;\frac{(Z_{4s}\cdot Z_{3d})^{3/2} Z^2_{3d}}{a_0}\left[24\, r^4\left(\frac{6\,!}{b^7} - A^6(b)\right)\right.$$
$$- 18\, Z_{4s}\, r^5\left(\frac{7\,!}{b^8} - A_7(b)\right) + 3\, Z^2_{4s}\, r^6\left(\frac{8\,!}{b^9} - A_8(b)\right) - \frac{1}{8} Z^3_{4s}\, r^7\left(\frac{9\,!}{b^{10}} - A_9(b)\right)$$
$$\left. + 24\, r^4 A_1(b) - 18\, Z_{4s}\, r^5 A_2(b) + 3\, Z^2_{4s}\, r^6 A_3(b) - \frac{1}{8} Z^3_{4s}\, r^7 A_4(b)\right]$$

$$b = \frac{4\, Z_{3\,d} + 3\, Z_{4\,s}}{12\, a_0}\, r_0$$

Z_{4s} and Z_{3d} are the "effective charges" of the radial wave function. In Table II Z_{4s} goes from 2.5 to 5.0, Z_{3d} from 3.65 to 7.85 and $r = \frac{r_0}{a_0}$ from 3.40 to 4.20. The factor $\frac{1}{a_0}$ has been left out. These integrals are used [12] for calculating the interaction between $4s$ and $3d$.

§ 4. Table III.

Here we tabulate the integrals $G^1_{3d,\,4p}$, $G^3_{3d,\,4p}$ $B^1_{3d,\,4p}$ and $B^3_{3d,\,4p}$. The master formulae are:

$$G^1_{3d,\,4p} = \frac{Zd\,(Zd\,Zp)^{5/2}}{19440\sqrt{2}\,a_0\,X^2\,b^5}\left[20\,C_6\,(X) - 5\left(\frac{Zp}{b}\right)C_7\,(X) + \frac{1}{4}\cdot\left(\frac{Zp}{b}\right)^2 C_8\,(X)\right]$$
$$+ \frac{Zd\,(Zd\,Zp)^{5/2}\,X}{19440\sqrt{2}\,a_0\,b^5}\left[20\,\bar{A}_3 - 5\left(\frac{Zp}{b}\right)\bar{A}_4\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 \bar{A}_5\,(X)\right]$$

$$G^3_{3d,\,4p} = \frac{Zd\,(Zd\,Zp)^{5/2}}{19440\sqrt{2}\,a_0\,X^4\,b^5}\left[20\,C_8\,(X) - 5\left(\frac{Zp}{b}\right)C_9\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 C_{10}(X)\right]$$
$$+ \frac{Zd\,(Zd\,Zp)^{5/2}\,X^3}{19440\sqrt{2}\,a_0\,b^5}\left[20\,\bar{A}_1\,(X) - 5\left(\frac{Zp}{b}\right)\bar{A}_2\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 \bar{A}_3\,(X)\right]$$

$$B^1_{3d,\,4p} = -\frac{Zd\,(Zd\,Zp)^{5/2}}{9720\sqrt{2}\,a_0^2\,X^3\,b^4}\left[20\,C_6\,(X) - 5\left(\frac{Zp}{b}\right)C_7\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 C_8\,(X)\right]$$
$$+ \frac{Zd\,(Zd\,Zp)^{5/2}}{19440\sqrt{2}\,a_0^2\,b^4}\left[20\,\bar{A}_3\,(X) - 5\left(\frac{Zp}{b}\right)\bar{A}_4\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 \bar{A}_5\,(X)\right]$$

$$B^3_{3d,\,4p} = -\frac{Zd\,(Zd\,Zp)^{5/2}}{4860\sqrt{2}\,a_0^2\,b^4\,X^5}\left[20\,C_8\,(X) - 5\left(\frac{Zp}{b}\right)C_9\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 C_{10}\,(X)\right]$$
$$+ \frac{Zd\,(Zd\,Zp)^{5/2}\,X^2}{6480\sqrt{2}\,a_0^2\,b_4}\left[20\,\bar{A}_1 - 5\left(\frac{Zp}{b}\right)\bar{A}_2\,(X) + \frac{1}{4}\left(\frac{Zp}{b}\right)^2 \bar{A}_3\,(X)\right]$$

$$\text{with } b = \frac{4\,Z\,d + 3\,Z\,p}{12} \text{ and } X = \frac{r_0\,b}{a_0}$$

$$\text{and } \bar{A}_l\,(X) = X^{l+1}\,A_l\,(X)$$
$$C_l\,(X) = l\,! - \bar{A}_l\,(X)$$

Zd and Zp are the "effective" charges on the wave functions. The integrals are used to calculated interactions between the two wave functions in a suitable ligand field, and are of special value in calculations of band intensities.[13]

In Table III $Zp = 3.0 \rightarrow 4.25$, $Zd = 3.65 \rightarrow 7.85$ and $r = 3.4 \rightarrow 4.2$. The factors $\frac{1}{a_0}$ for the G integrals and $\frac{1}{a_0^2}$ for the B integrals have been left out.

§ 5. Table IV.

This table tabulates $G^0_{4s,\,4s} = \int R(4s)\frac{1}{r_>}R(4s)r^2dr$. The master formula is:

$$G^0_{4s,\,4s} = \frac{Z_s}{2304\cdot x\cdot a_0}\Big[C_8(X) - 24\,C_7(X) + 216\,C_6(X) - 912\,C_5(X) + 1872\,C_4(X) - 1728\,C_3(X) + 576\,C_2(X)\Big]$$
$$+ \frac{Z_s}{2304\,a_0}\Big[\bar{A}_7(X) - 24\,\bar{A}_6(X) + 216\,\bar{A}_5(X) - 912\,\bar{A}_4(X) + 1872\,\bar{A}_3(X) - 1728\,\bar{A}_2(X) + 576\,\bar{A}_1(X)\Big].$$

Here C_l and $\bar{A}_l$ are the same functions previously defined, and $X = \frac{Z_s}{2\,a_0}r_0$ with Z_s the "effective" charge of the $4s$ wave function. The factor $\frac{1}{a_0}$ has been left out in the table. The range is $Z_s = 2.5 \rightarrow 5.0$ and $r = 3.20 \rightarrow 4.20$.

In ligand field calculations this table is used to calculate the displacement of the $4s$ level.[12]

§ 6 The Tabulation.

In all the tables the power of ten with which to multiply the tabulated number is given as an upper subscript. This power is the same *down* a column until it changes. E. G. $1.579362^{-3} = 1.579362\cdot 10^{-3}$ to be multiplied further by the suitable power of a_0 as specified in the explanations to the various tables.

Since the numbers in the tables are taken directly from the output of the IBM 650, the last two figures may be in doubt due to round off error during the computation.

§ 7 Acknowledgments.

We wish to thank Dr. Marion C. Gray and Dr. Andrew D. Liehr for many helpful discussions. Further thanks are due to Mrs. W. S. Cadmus, Mrs. E. Jenkins, Mrs. L. Doran, Mrs. E. Hart, Mrs. R. Schuler and Mrs. C. Gartland for the excellent job they did in preparing the manuscript of the tables. One of us (C. J. B.) further wants to thank Bell Telephone Laboratories, Inc. Murray Hill, New Jersey, where this work was performed, for their hospitality.

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Table I. $G^{n}_{3d,\,3d}$, $B^{n}_{3d,\,3d}$ and $C^{n}_{3d,\,3d}$ $n = 0, 2, 4$

$Z_{3d} = 3.65 \rightarrow 7.85 \quad r = 3.40 \rightarrow 4.20.$

r = 3.40

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.7934351^{-1} 1.2650043^{-2}	1.5605660^{-1} -2.3833079^{-2}	1.0459682^{-1} -2.2744288^{-3}	-6.2185011^{-2}	-6.5866407^{-2}	-5.4615218^{-2}
4.00	2.8471121^{-1} 2.0121271^{-2}	1.4780920^{-1} -1.8484781^{-3}	9.5323033^{-2} 1.7157523	-6.9137073	-7.6023160	-6.3184111
4.30	2.8783085^{-1} 2.6137916^{-2}	1.3882109^{-1} 1.6076041^{-2}	8.5873660 3.2255888	-7.3793972	-8.0997174	-6.6501070
4.60	2.8997183^{-1} 3.1491204^{-2}	1.2900832^{-1} 3.1609698^{-2}	7.6015456 4.4476832	-7.7383170	-8.2994356	-6.6668864
4.95	2.9160612^{-1} 3.6720488^{-2}	1.1737370^{-1} 4.5761434^{-2}	6.4847644 5.4344947	-8.0448595	-8.2372019	-6.3871942
5.25	2.9250291^{-1} 4.0311999^{-2}	1.0772814^{-1} 5.4330975^{-2}	5.6010675 5.9081395	-8.2315310	-8.0017899	-5.9765314
5.60	2.9316554^{-1} 4.3548623^{-2}	9.7206247 6.0535551	4.6835034 6.0865622	-8.3829021	-7.5918411	-5.3888725
5.90	2.9351836^{-1} 4.5621999^{-2}	8.8952826 6.3133581	4.0009848 5.9885829	-8.4708819	-7.1747853	-4.8492708
6.25	2.9377221^{-1} 4.7383361^{-2}	8.0267818 6.3731906	3.3222532 5.6707556	-8.5393968	-6.6573251	-4.2269849
6.55	2.9390408^{-1} 4.8453919^{-2}	7.3614055 6.2733039	2.8327094 5.2888195	-8.5777761	-6.2129166	-3.7249818
6.90	2.9399691^{-1} 4.9322982^{-2}	6.6710069 6.0404777	2.3557761 4.7795821	-8.6067119	-5.7134592	-3.1927807
7.20	2.9404413^{-1} 4.9829843^{-2}	6.1461033 5.7799049	2.0163148 4.3270659	-8.6224413	-5.3110150	-2.7879887
7.85	2.9409309^{-1} 5.0450535^{-2}	5.1896959 5.1380657	1.4547823 3.3991605	-8.6401143	-4.5367089	-2.0715129

TABLE I. (cont.).

r = 3.50

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.7319013^{-1} 1.3712567^{-2}	1.4947958^{-1} -1.5711581^{-2}	9.9133823^{-2} 3.4167520^{-3}	-6.0864826^{-2}	-6.5586388^{-2}	-5.4550317^{-2}
4.00	2.7789913^{-1} 2.0667431^{-2}	1.4030734^{-1} 4.9416613^{-3}	8.9097967^{-2} 2.1408748	-6.7095424	-7.3948989	-6.1246458
4.30	2.8058222^{-1} 2.6113976^{-2}	1.3089233^{-1} 2.1059906^{-2}	7.9389320 3.4659411	-7.1179303	-7.7540514	-6.3146006
4.60	2.8238999^{-1} 3.0844432^{-2}	1.2093819^{-1} 3.4480689^{-2}	6.9571900 4.4795217	-7.4264685	-7.8401489	-6.2197154
4.95	2.8374263^{-1} 3.5351561^{-2}	1.0941578^{-1} 4.6129663^{-2}	5.8729041 5.2298924	-7.6843928	-7.6814146	-5.8534131
5.25	2.8446973^{-1} 3.8372315^{-2}	1.0003324^{-1} 5.2744416^{-2}	5.0323389 5.5292846	-7.8380691	-7.3934802	-5.4043652
5.60	2.8499615^{-1} 4.1031083^{-2}	8.9937919 5.7052103	4.1741565 5.5523868	-7.9600433	-6.9527748	-4.8069474
5.90	2.8527065^{-1} 4.2694615^{-2}	8.2105067 5.8404504	3.5449479 5.3655052	-8.0294051	-6.5302964	-4.2818399
6.25	2.8546414^{-1} 4.4075827^{-2}	7.3932401 5.7984865	2.9267517 4.9916794	-8.0822788	-6.0243465	-3.6943786
6.55	2.8556254^{-1} 4.4896166^{-2}	6.7713166 5.6444070	2.4854676 4.5959527	-8.1112545	-5.6002798	-3.2314110
6.90	2.8563038^{-1} 4.5547299^{-2}	6.1293175 5.3797128	2.0592251 4.1007441	-8.1326380	-5.1319613	-2.7495480
7.20	2.8566417^{-1} 4.5918503^{-2}	5.6431522 5.1125318	1.7580279 3.6783080	-8.1440106	-4.7595795	-2.3885568
7.85	2.8569821^{-1} 4.6359495^{-2}	4.7607747 4.4983819	1.2636610 2.8451416	-8.1564229	-4.0525706	-1.7601368

r = 3.60

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.6717369^{-1} 1.4540833^{-2}	1.4295541^{-1} -8.7264319^{-3}	9.3704208^{-2} 8.2002084^{-3}	-5.9450303^{-2}	-6.4823740^{-2}	-5.3962145^{-2}
4.00	2.7129352^{-1} 2.0967009^{-2}	1.3303082^{-1} 1.0424426^{-2}	8.3086107^{-2} 2.4606399	-6.5011803	-7.1532089	-5.8937484
4.30	2.7359452^{-1} 2.5864419^{-2}	1.2331898^{-1} 2.4740648^{-2}	7.3250695 3.6040415	-6.8578692	-7.3903788	-5.9603249
4.60	2.7511642^{-1} 3.0018369^{-2}	1.1332811^{-1} 3.6179246^{-2}	6.3575566 4.4251433	-7.1220255	-7.3805704	-5.7738518
4.95	2.7623258^{-1} 3.3880185^{-2}	1.0200432^{-1} 4.5595205^{-2}	5.3132974 4.9692313	-7.3381687	-7.1451910	-5.3430787
5.25	2.7682025^{-1} 3.6406533^{-2}	9.2929720 5.0542600	4.5188817 5.1250073	-7.4641704	-6.8194925	-4.8715162
5.60	2.7723715^{-1} 3.8578741^{-2}	8.3284699 5.3303836	3.7203441 5.0285242	-7.5620615	-6.3616262	-4.2780444
5.90	2.7745001^{-1} 3.9906376^{-2}	7.5873454 5.3692289	3.1425986 4.7799803	-7.6165242	-5.9420830	-3.7749124
6.25	2.7759699^{-1} 4.0983887^{-2}	6.8198304 5.2536957	2.5812185 4.3755780	-7.6571611	-5.4538317	-3.2265463
6.55	2.7767017^{-1} 4.1609305^{-2}	6.2391776 5.0647190	2.1842503 3.9817016	-7.6789493	-5.0528243	-2.8031681
6.90	2.7771959^{-1} 4.2094739^{-2}	5.6424148 4.7848107	1.8037568 3.5118603	-7.6946883	-4.6164596	-2.3696319
7.20	2.7774368^{-1} 4.2365256^{-2}	5.1920150 4.5206870	1.5366029 3.1240759	-7.7028774	-4.2733446	-2.0491761
7.85	2.7776729^{-1} 4.2677110^{-2}	4.3771610 3.9436851	1.1010686 2.3837699	-7.7115617	-3.6290904	-1.4993983

TABLE I. (cont.).

r = 3.70

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.6130247^{-1} 1.5158818^{-2}	1.3652818^{-1} -2.7893300^{-3}	8.8355891^{-2} 1.2140228	-5.7963665^{-2}	-6.3660316^{-2}	-5.2938376^{-2}
4.00	2.6489741^{-1} 2.1056459^{-2}	1.2600936^{-1} 1.4758869^{-2}	7.7319544 2.6884565	-6.2909021	-6.8861575	-5.6355823
4.30	2.6686531^{-1} 2.5433026^{-2}	1.1611476^{-1} 2.7324082^{-2}	6.7471782 3.6578304	-6.6012469	-7.0170645	-5.5965991
4.60	2.6814293^{-1} 2.9059691^{-2}	1.0617481^{-1} 3.6937193^{-2}	5.8021198 4.3047555	-6.8265417	-6.9276058	-5.3368827
4.95	2.6906128^{-1} 3.2350530^{-2}	9.5117389 4.4391196	4.8033525 4.6722145	-7.0069825	-6.6329583	-4.8607749
5.25	2.6953484^{-1} 3.4452306^{-2}	8.6382129 4.7937604	4.0566678 4.7122211	-7.1098989	-6.2818330	-4.3796423
5.60	2.6986401^{-1} 3.6218011^{-2}	7.7198951 4.9459441	3.3168355 4.5267283	-7.1881628	-5.8176065	-3.8005036
5.90	2.7002857^{-1} 3.7272336^{-2}	7.0203117 4.9119291	2.7880859 4.2385427	-7.2307636	-5.4072132	-3.3243709
6.25	2.7013986^{-1} 3.8108873^{-2}	6.3005561 4.7453753	2.2794943 3.8228761	-7.2618766	-4.9407988	-2.8171462
6.55	2.7019411^{-1} 3.8583427^{-2}	5.7587889 4.5361842	1.9229119 3.4417714	-7.2781976	-4.5642347	-2.4325911
6.90	2.7023000^{-1} 3.8943640^{-2}	5.2040727 4.2530238	1.5834747 3.0041355	-7.2897382	-4.1595635	-2.0444704
7.20	2.7024713^{-1} 3.9139877^{-2}	4.7865757 3.9983570	1.3464879 2.6527142	-7.2956125	-3.8443629	-1.7609799
7.85	2.7026345^{-1} 3.9359440^{-2}	4.0332133 3.4633080	9.6237867^{-3} 2.0001550^{-2}	-7.3016663	-3.2579671	-1.2807935

r = 3.80

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.5558269^{-1} 1.5590173^{-2}	1.3023421^{-1} 2.1928733^{-3}	8.3128347^{-2} 1.5309326	-5.6424760^{-2}	-6.2170575^{-2}	-5.1559801^{-2}
4.00	2.5871172^{-1} 2.0969382^{-2}	1.1926439^{-1} 1.8096287^{-2}	7.1821167 2.8373065	-6.0806394	-6.6014261	-5.3586870
4.30	2.6039034^{-1} 2.4858338^{-2}	1.0928577^{-1} 2.8995630^{-2}	6.2058110 3.6435218	-6.3496860	-6.6409577	-5.2310287
4.60	2.6145998^{-1} 2.8007737^{-2}	9.9468923 3.6954233	5.2896917 4.1356384	-6.5411421	-6.4865278	-4.9145226
4.95	2.6221347^{-1} 3.0797793^{-2}	8.8729432 4.2708606	4.3401127 4.3546227	-6.6912344	-6.1476028	-4.4093179
5.25	2.6259399^{-1} 3.2537797^{-2}	8.0353700 4.5095015	3.6415800 4.3035527	-6.7749910	-5.7811977	-3.9289306
5.60	2.6285313^{-1} 3.3966276^{-2}	7.1634329 4.5641520	2.9586179 4.0546545	-6.8373369	-5.3190121	-3.3717045
5.90	2.6297997^{-1} 3.4799687^{-2}	6.5042393 4.4766125	2.4759975 3.7442254	-6.8705388	-4.9222280	-2.9256305
6.25	2.6306401^{-1} 3.5446216^{-2}	5.8299236 4.2767312	2.0160505 3.3315078	-6.8942758	-4.4801883	-2.4599252
6.55	2.6310411^{-1} 3.5804696^{-2}	5.3245703 4.0582567	1.6960491 2.9703851	-6.9064570	-4.1284687	-2.1125287
6.90	2.6313008^{-1} 3.6070824^{-2}	4.8087752 3.7801619	1.3932939 2.5684639	-6.9148879	-3.7544964	-1.7664035
7.20	2.6314221^{-1} 3.6212559^{-2}	4.4214718 3.5389260	1.1829596 2.2531532	-6.9190864	-3.4655251	-1.5162410
7.85	2.6315346^{-1} 3.6366495^{-2}	3.7240622 3.0474460	8.4374395^{-3} 1.6814097^{-2}	-6.9232909	-2.9320366	-1.0972071

TABLE I. (cont.).

r = 3.90

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.5001868^{-1} 1.5857694^{-2}	1.2410271^{-1} 6.3145805^{-3}	7.8053316^{-2} 1.7784129	-5.4851095^{-2}	-6.0421358^{-2}	-4.9899669^{-2}
4.00	2.5273558^{-1} 2.0736245^{-2}	1.1281021^{-1} 2.0577731^{-2}	6.6605970 2.9194354	-5.8720010	-6.3055475	-5.0703432
4.30	2.5416384^{-1} 2.4173795^{-2}	1.0283193^{-1} 2.9919845^{-2}	5.7008313 3.5754844	-6.1044462	-6.2675594	-4.8696852
4.60	2.5505704^{-1} 2.6895163^{-2}	9.3196486 3.6399971	4.8185903 3.9322895	-6.2665888	-6.0612268	-4.5108940
4.95	2.5567363^{-1} 2.9249464^{-2}	8.2812665 4.0701459	3.9204124 4.0288034	-6.3910113	-5.6907761	-3.9901216
5.25	2.5597857^{-1} 3.0683383^{-2}	7.4807483 4.2141688	3.2695387 3.9080915	-6.4589418	-5.3173021	-3.5184886
5.60	2.5618202^{-1} 3.1833928^{-2}	6.6546548 4.1936240	2.6409764 3.6168008	-6.5084384	-4.8635365	-2.9884290
5.90	2.5627951^{-1} 3.2489855^{-2}	6.0343272 4.0681882	2.2013915 3.2975315	-6.5342263	-4.4834057	-2.5739365
6.25	2.5634279^{-1} 3.2987411^{-2}	5.4029371 3.8486067	1.7859693 2.8978336	-6.5522730	-4.0670469	-2.1489208
6.55	2.5637234^{-1} 3.3257074^{-2}	4.9315239 3.6287838	1.4989412 2.5610522	-6.5613334	-3.7398706	-1.8364459
6.90	2.5639108^{-1} 3.3452887^{-2}	4.4516508 3.3612933	1.2288504 2.1959678	-6.5674721	-3.3951311	-1.5286725
7.20	2.5639965^{-1} 3.3554845^{-2}	4.0920100 3.1357065	1.0420142 1.9152375	-6.5704627	-3.1305366	-1.3082956
7.85	2.5640738^{-1} 3.3662356^{-2}	3.4455054 2.6873055	7.4196833^{-3} 1.4165498^{-2}	-6.5733736	-2.6451424	-9.4271713^{-3}

r = 4.00

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.4461312^{-1} 1.5983000^{-2}	1.1815660^{-1} 9.6688336^{-3}	7.3155608^{-2} 1.9642437	-5.3257963^{-2}	-5.8471998^{-2}	-4.8023526^{-2}
4.00	2.4696671^{-1} 2.0384348^{-2}	1.0665516^{-1} 2.2332497^{-2}	6.1682252 2.9461271	-5.6663094	-6.0040005	-4.7766479
4.30	2.4817900^{-1} 2.3408089^{-2}	9.6748280 3.0240766	5.2315723 3.4662382	-5.8664796	-5.9012036	-4.5173023
4.60	2.4892301^{-1} 2.5748719^{-2}	8.7340273 3.5416645	4.3867930 3.7066622	-6.0033506	-5.6544486	-4.1288037
4.95	2.4942631^{-1} 2.7726542^{-2}	7.7338135 3.8492097	3.5410013 3.7041780	-6.1061597	-5.2631679	-3.6035149
5.25	2.4967005^{-1} 2.8903156^{-2}	6.9707176 3.9172604	2.9365945 3.5320748	-6.1610754	-4.8891481	-3.1466618
5.60	2.4982936^{-1} 2.9825993^{-2}	6.1893788 3.8401324	2.3595334 3.2152808	-6.2002438	-4.4484999	-2.6471319
5.90	2.4990409^{-1} 3.0340133^{-2}	5.6061467 3.6892332	1.9597995 2.8972194	-6.2202080	-4.0869473	-2.2645770
6.25	2.4995159^{-1} 3.0721516^{-2}	5.0150886 3.4602459	1.5849108 2.5173157	-6.2338840	-3.6966623	-1.8785858
6.55	2.4997330^{-1} 3.0923568^{-2}	4.5751972 3.2446580	1.3274900 2.2071066	-6.2406012	-3.3932406	-1.5984716
6.90	2.4998680^{-1} 3.1067087^{-2}	4.1284089 2.9912294	1.0864123 1.8783305	-6.2450566	-3.0759866	-1.3253819
7.20	2.4999285^{-1} 3.1140150^{-2}	3.7940882 2.7822642	9.2026500^{-3} 1.6298771^{-2}	-6.2471798	-2.8338628	-1.1314429
7.85	2.4999814^{-1} 3.1214963^{-2}	3.1939095 2.3751287	6.5439541^{-3} 1.1963151^{-2}	-6.2491890	-2.3920052	-8.1241141^{-3}

TABLE I. (cont.).

r = 4.10

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.3936729^{-1} 1.5986260^{-2}	1.1241323^{-1} 1.2345265^{-2}	6.8453874^{-2} 2.0960633	-5.1658561^{-2}	-5.6374575^{-2}	-4.5989181^{-2}
4.00	2.4140163^{-1} 1.9937836^{-2}	1.0080259^{-1} 2.3477439^{-2}	5.7052781 2.9275989	-5.4646294	-5.7013154	-4.4826247
4.30	2.4242823^{-1} 2.2585515^{-2}	9.1026059 3.0082900	4.7969518 3.3265081	-5.6364738	-5.5452124	-4.1774511
4.60	2.4304649^{-1} 2.4589968^{-2}	8.1880810 3.4121972	3.9920530 3.4684326	-5.7516553	-5.2679963	-3.7699794
4.95	2.4345630^{-1} 2.6244630^{-2}	7.2276599 3.6176074	3.1986387 3.3877167	-5.8363433	-4.8647300	-3.2490117
5.25	2.4365062^{-1} 2.7206226^{-2}	6.5017760 3.6257044	2.6389907 3.1794799	-5.8806006	-4.4952432	-2.8112906
5.60	2.4377505^{-1} 2.7943526^{-2}	5.7637020 3.5072753	2.1102729 2.8504703	-5.9114997	-4.0710321	-2.3441478
5.90	2.4383219^{-1} 2.8344979^{-2}	5.2156499 3.3406429	1.7472161 2.5408975	-5.9269080	-3.7291142	-1.9930253
6.25	2.4386778^{-1} 2.8636221^{-2}	4.6623269 3.1098488	1.4090661 2.1850016	-5.9372410	-3.3646272	-1.6438509
6.55	2.4388369^{-1} 2.8787056^{-2}	4.2516350 2.9022697	1.1781511 1.9020502	-5.9422055	-3.0838550	-1.3933955
6.90	2.4389337^{-1} 2.8891858^{-2}	3.8352756 2.6648345	9.6279680^{-3} 1.6079684^{-2}	-5.9454287	-2.7921986	-1.1514315
7.20	2.4389762^{-1} 2.8944023^{-2}	3.5241224 2.4726092	8.1485160^{-3} 1.3890812^{-2}	-5.9469315	-2.5706643	-9.8083597^{-3}
7.85	2.4390124^{-1} 2.8995900^{-2}	2.9661303 2.1041558	5.7881616^{-3} 1.0129679^{-2}	-5.9483138	-2.1681059	-7.0222589

r = 4.20

Zd	$G^{0}_{3d,3d}$ $C^{0}_{3d,3d}$	$G^{2}_{3d,3d}$ $C^{2}_{3d,3d}$	$G^{4}_{3d,3d}$ $C^{4}_{3d,3d}$	$B^{0}_{3d,3d}$	$B^{2}_{3d,3d}$	$B^{4}_{3d,3d}$
3.65	2.3428124^{-1} 1.5886062^{-2}	1.0688511^{-1} 1.4428691^{-2}	6.3961356^{-2} 2.1811934	-5.0064155^{-2}	-5.4174301^{-2}	-4.3846954^{-2}
4.00	2.3603584^{-1} 1.9417824^{-2}	9.5251681 2.4116828	5.2715752 2.8729558	-5.2677976	-5.4011703	-4.1923300
4.30	2.3690326^{-1} 2.1726380^{-2}	8.5653580 2.9552631	4.3955779 3.1653386	-5.4148911	-5.2020490	-3.8527136
4.60	2.3741585^{-1} 2.3435979^{-2}	7.6797158 3.2612102	3.6319924 3.2252680	-5.5115352	-4.9029082	-3.4352800
4.95	2.3774877^{-1} 2.4814897^{-2}	6.7599143 3.3826610	2.8901643 3.0843788	-5.5810928	-4.4948647	-2.9255323
5.25	2.3790334^{-1} 2.5597794^{-2}	6.0705881 3.3443759	2.3732032 2.8525345	-5.6166557	-4.1337688	-2.5099093
5.60	2.3800029^{-1} 2.6184692^{-2}	5.3740172 3.1970193	1.8895477 2.5215179	-5.6409606	-3.7282085	-2.0758414
5.90	2.3804387^{-1} 2.6497022^{-2}	4.8591561 3.0221358	1.5600761 2.2254819	-5.6528175	-3.4063183	-1.7550334
6.25	2.3807045^{-1} 2.6718633^{-2}	4.3410210 2.7949913	1.2551070 1.8958594	-5.6606008	-3.0668805	-1.4401468
6.55	2.3808209^{-1} 2.6830836^{-2}	3.9573273 2.5978205	1.0478678 1.6397667	-5.6642593	-2.8074610	-1.2166367
6.90	2.3808902^{-1} 2.6907106^{-2}	3.5689343 2.3772189	8.5529480^{-3} 1.3781069^{-2}	-5.6665845	-2.5394751	-1.0024392
7.20	2.3809200^{-1} 2.6944225^{-2}	3.2789806 2.2012875	7.2336034^{-3} 1.1859216^{-2}	-5.6676454	-2.3367244	-8.5237322^{-3}
7.85	2.3809447^{-1} 2.6980082^{-2}	2.7594432 1.8685471	5.1339206^{-3} 8.6008320	-5.6685936	-1.9695788	-6.0880359

TABLE II. $G^2_{3d,\,4s}$ $Z_{3d} = 3.65 \rightarrow 7.85$

$r = 3.40 \rightarrow 4.20.$

$G^2_{3d,4s}$

$r = 3.40$

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	2.8236570^{-2}	4.6623955^{-2}	4.7730543^{-2}	3.3147247^{-2}	7.8207401^{-3}	-2.2722074^{-2}
4.00	2.3140754	4.2791826	4.7046683	3.6395632	1.4851669^{-2}	-1.2650428
4.30	1.8712124	3.8690211	4.5078120	3.7565517	1.9370026	-5.1566985^{-3}
4.60	1.4467943	3.4211036	4.2212532	3.7509961	2.2571823	1.1455436
4.95	9.9391264^{-3}	2.8869969	3.8151113	3.6243397	2.4834167	6.9807547
5.25	6.5091625	2.4417060	3.4345461	3.4405936	2.5709096	1.0758544^{-2}
5.60	3.0768787	1.9550459	2.9802381	3.1682062	2.5739864	1.3895808
5.90	6.1960420^{-4}	1.5749484	2.5983262	2.9049650	2.5110971	1.5647848
6.25	-1.7155328^{-3}	1.1800903	2.1753043	2.5824472	2.3823427	1.6790522
6.55	-3.3023902	8.8442028^{-3}	1.8391411	2.3047285	2.2390662	1.7145811
6.90	-4.7283905	5.8809274	1.4826407	1.9898389	2.0481772	1.6997260
7.20	-5.6351943	3.7329670	1.2092557	1.7336897	1.8737131	1.6504249
7.85	-6.8031325	1.7462468^{-4}	7.1742929^{-3}	1.2369404	1.4911184	1.4689699

TABLE II. (cont.).

$G^{2}_{3d,4s}$

4 = 3.50

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	2.9538936^{-2}	4.5874993^{-2}	4.4812702^{-2}	2.8616711^{-2}	2.5710436^{-3}	-2.7757030^{-2}
4.00	2.4358193	4.2054848	4.4268704	3.2116071	9.9235700	-1.7338878
4.30	1.9861453	3.7985447	4.2453074	3.3537315	1.4745594^{-2}	-9.5373864^{-3}
4.60	1.5557587	3.3558023	3.9765261	3.3755105	1.8264267	-2.9286232
4.95	1.0971258	2.8298540	3.5933329	3.2823871	2.0901416	3.2539114
5.25	7.5014125^{-3}	2.3929180	3.2336196	3.1279559	2.2094795	7.3165743
5.60	4.0315668	1.9170074	2.8041607	2.8895771	2.2487349	1.0769295^{-2}
5.90	1.5474400	1.5464827	2.4434084	2.6547508	2.2156526	1.2776536
6.25	-8.1500283^{-4}	1.1627074	2.0442790	2.3640077	2.1199414	1.4199378
6.55	-2.4236754^{-3}	8.7613775^{-3}	1.7275589	2.1120127	2.0033393	1.4779958
6.90	-3.8748368	5.8965043	1.3921668	1.8251027	1.8415273	1.4877569
7.20	-4.8038836	3.8246814	1.1353695	1.5910528	1.6901519	1.4581675
7.85	-6.0242473	4.0158649^{-4}	6.7437233^{-3}	1.1360745	1.3518201	1.3152017

$G^{2}_{3d,4s}$

r = 3.60

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.0504347^{-2}	4.4804276^{-2}	4.1732325^{-2}	2.4171540^{-2}	-2.3254998^{-3}	-3.2209296^{-2}
4.00	2.5252763	4.1026110	4.1363003	2.7950387	5.3614712	-2.1451306
4.30	2.0704551	3.7016743	3.9728912	2.9641050	1.0489088^{-2}	-1.3358615
4.60	1.6360215	3.2669184	3.7243890	3.0145006	1.4319372	-6.4679078^{-3}
4.95	1.1739912	2.7522468	3.3666591	2.9557600	1.7317835	2.6521139^{-5}
5.25	8.2505789^{-3}	2.3261085	3.0295225	2.8308577	1.8813292	4.3405224^{-3}
5.60	4.7659422	1.8634257	2.6264451	2.6262416	1.9544858	8.0673708
5.90	2.2734346	1.5042984	2.2877577	2.4192818	1.9490464	1.0294531^{-2}
6.25	-9.6697863^{-5}	1.1333857	1.9132165	2.1593595	1.8837437	1.1957200
6.55	-1.7118810^{-3}	8.5716959^{-3}	1.6162200	1.9320740	1.7915265	1.2730081
6.90	-3.1721615	5.8171375	1.3020393	1.6718305	1.6561282	1.3037542
7.20	-4.1111822	3.8295396	1.0617401	1.4587008	1.5256584	1.2909798
7.85	-5.3613984	5.5443765^{-4}	6.3104450^{-3}	1.0429130	1.2272135	1.1809586

TABLE II. (cont.).

$G^{2}_{3d,4s}$

r = 3.70

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.1157186^{-2}	4.3462808^{-2}	3.8553453^{-2}	1.9869809^{-2}	-6.8340587^{-3}	-3.6079341^{-2}
4.00	2.5852670	3.9757626	3.8390426	2.3949366	1.1910887	-2.4997226
4.30	2.1271825	3.5835600	3.6961964	2.5921339	6.6185560	-1.6637470
4.60	1.6907200	3.1594206	3.4700796	2.6717747	1.0748068^{-2}	-9.4953047^{-3}
4.95	1.2277035	2.6588451	3.1397248	2.6475098	1.4087392	-2.7292122
5.25	8.7881842^{-3}	2.2456107	2.8263674	2.5517776	1.5863756	1.7995777
5.60	5.3106142	1.7982557	2.4506029	2.3800764	1.6906915	5.7579193
5.90	2.8267400	1.4520023	2.1344483	2.1999800	1.7104465	8.1688316
6.25	4.6687829^{-4}	1.0953493	1.7846689	1.9694945	1.6726606	1.0031298^{-2}
6.55	-1.1412424^{-3}	8.3041658^{-3}	1.5073480	1.7656301	1.6024025	1.0964495
6.90	-2.5966974	5.6682873	1.2140988	1.5304807	1.4907144	1.1447241
7.20	-3.5351277	3.7703957	9.8994666^{-3}	1.3369211	1.3789558	1.1460624
7.85	-4.7962213	6.5123456^{-4}	5.8860347	9.5752734^{-3}	1.1161270	1.0638984

$G^{2}_{3d,4s}$

r = 3.80

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.1523802^{-2}	4.1899598^{-2}	3.5332477^{-2}	1.5757726^{-2}	-1.0934152^{-2}	-3.9379445^{-2}
4.00	2.6186982	3.8297944	3.5403476	2.0152140	-2.5754134^{-3}	-2.7998009
4.30	2.1593486	3.4489045	3.4200542	2.2410971	3.1393196	-1.9400854
4.60	1.7229579	3.0377862	3.2179001	2.3499915	7.5499252	-1.2041875
4.95	1.2613372	2.5537509	2.9162471	2.3596517	1.1203965^{-2}	-5.0476867^{-3}
5.25	9.1440397^{-3}	2.1552105	2.6273880	2.2922028	1.3236319	-3.4218817^{-4}
5.60	5.6937607	1.7248700	2.2793480	2.1520805	1.4560702	3.8042850^{-3}
5.90	3.2340819	1.3926383	1.9857646	1.9975122	1.4983883	6.3639655
6.25	9.0024450^{-4}	1.0512512	1.6605273	1.7947607	1.4851419	8.3879485
6.55	-6.8892120	7.9824495^{-3}	1.4025131	1.6128242	1.4343929	9.4511488
6.90	-2.1276087^{-3}	5.4706472	1.1296377	1.4010306	1.3437377	1.0077283^{-2}
7.20	-3.0566278	3.6656854	9.2108124^{-3}	1.2255927	1.2485617	1.0206979
7.85	-4.3129519	7.0634961^{-4}	5.4782021	8.7970865^{-3}	1.0172971	9.6181504^{-3}

TABLE II. (cont.).

$G^2_{3d,4s}$

$r = 3.90$

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.1632200^{-2}	4.0160845^{-2}	3.2118756^{-2}	1.1870680^{-2}	-1.4616069^{-2}	-4.2132143^{-2}
4.00	2.6285412	3.6691720	3.2446642	1.6587235	-5.9363825^{-3}	-3.0482752
4.30	2.1700118	3.3019584	3.1484653	1.9132541	4.7491096^{-5}	-2.1682301
4.60	1.7357409	2.9059702	2.9713578	2.0508544	4.7162772^{-3}	-1.4143920
4.95	1.2777844	2.4405553	2.6991583	2.0932988	8.6545872	-6.9666725^{-3}
5.25	9.3458894^{-3}	2.0581345	2.4350637	2.0528682	1.0915583^{-2}	-2.1225484
5.60	5.9412900	1.6461099	2.1146894	1.9425849	1.2488894	2.1697297
5.90	3.5194416	1.3287188	1.8433689	1.8119432	1.3110913	4.8443600
6.25	1.2253819	1.0032722	1.5421168	1.6350270	1.3193856	6.9940235
6.55	-3.3494101^{-4}	7.6257837^{-3}	1.3027957	1.4733921	1.2857548	8.1594745
6.90	-1.7468757^{-3}	5.2406994	1.0495037	1.2831236	1.2135473	8.8997863
7.20	-2.6592634	3.5298563	8.5583853^{-3}	1.1243251	1.1329308	9.1236240
7.85	-3.8982215	7.3097379^{-4}	5.0918397	8.0907815^{-3}	9.2944303^{-3}	8.7269919

$G^2_{3d,4s}$

$r = 4.00$

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.1510592^{-2}	3.8289028^{-2}	2.8954053^{-2}	8.2348245^{-3}	-1.7879827^{-2}	-4.4366680^{-2}
4.00	2.6177450	3.4979755	2.9556809	1.3274056^{-2}	-8.8983483^{-3}	-3.2486266
4.30	2.1620875	3.1465152	2.8846143	1.6100034	-2.6682369	-2.3519496
4.60	1.7319348	2.7674467	2.7331781	1.7752793	2.2321515	-1.5840611
4.95	1.2797689	2.3223267	2.4906869	1.8488972	6.4217681	-8.5257811^{-3}
5.25	9.4191752^{-3}	1.9571315	2.2512173	1.8338734	8.8821959	-3.5801120
5.60	6.0764675	1.5643320	1.9580273	1.7514179	1.0671708^{-2}	8.1775982^{-4}
5.90	3.7042095	1.2622997	1.7083817	1.6429316	1.1465643	3.5757889^{-3}
6.25	1.4614574	9.5315892^{-3}	1.4302710	1.4898114	1.1734942	5.8181330
6.55	-6.1760506^{-5}	7.2492880	1.2088615	1.3467873	1.1546764	7.0606621
6.90	-1.4390353^{-3}	4.9914016	9.7420561^{-3}	1.1761897	1.0984860	7.8892456
7.20	-2.3290361	3.3743207	7.9462811	1.0325582	1.0305438	8.1875495
7.85	-3.5407756	7.3386348^{-4}	4.7296978	7.4515522^{-3}	8.5136064^{-3}	7.9477334

Table II. (cont.).

$G^{2}_{3d,4s}$

r = 4.10

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.1187191^{-2}	3.6323183^{-2}	2.5872990^{-2}	4.8673516^{-3}	-2.0733519^{-2}	-4.6117920^{-2}
4.00	2.5891312	3.3197917	2.6763505	1.0223731^{-2}	-1.1475104	-3.4047166
4.30	2.1383746	2.9858737	2.6310105	1.3319681	-5.0254093^{-3}	-2.4952656
4.60	1.7141879	2.6251730	2.5054255	1.5234953	7.7615476^{-5}	-1.7172720
4.95	1.2697471	2.2016407	2.2924146	1.6263009	4.4833954^{-3}	-9.7645393^{-3}
5.25	9.3866680^{-3}	1.8544280	2.0770987	1.6348372	7.1143116	-4.7527914
5.60	6.1198558	1.4814366	1.8102974	1.5779956	9.0873023	-2.8693158^{-4}
5.90	3.8070089	1.1950178	1.5814965	1.4897971	1.0027152^{-2}	2.5258173^{-3}
6.25	1.6249981	9.0228528^{-3}	1.3254794	1.3583670	1.0454939	4.8310784
6.55	1.4541166^{-4}	6.8647762	1.1210590	1.2322649	1.0393415	6.1283261
6.90	-1.1909401^{-3}	4.7327298	9.0397903^{-3}	1.0795140	9.9690592^{-3}	7.0223559
7.20	-2.0541597	3.2077344	7.3762489	9.4961953^{-3}	9.3991747	7.3780384
7.85	-3.2312039	7.2165126^{-4}	4.3929350	6.8740320	7.8191384	7.2645926

$G^{2}_{3d,4s}$

r = 4.20

Z3d\Z4s	2.5	3.0	3.5	4.0	4.5	5.0
3.65	3.0689241^{-2}	3.4297856^{-2}	2.2904017^{-2}	1.7782986^{-3}	-2.3191307^{-2}	-4.7424297^{-2}
4.00	2.5454056	3.1377813	2.4089744	7.4404047	-1.3685643	-3.5206537
4.30	2.1014240	2.8228675	2.3895185	1.0791853^{-2}	-7.0453551^{-3}	-2.6023362
4.60	1.6849330	2.4816615	2.2895685	1.2951839	-1.7703703	-1.8180844
4.95	1.2499420	2.0806150	2.1054215	1.4249219	2.8163171	-1.0721595
5.25	9.2686649^{-3}	1.7518604	1.9134785	1.4550224	5.5884170	-5.6768631^{-3}
5.60	6.0893715	1.3989209	1.6720029	1.4214691	7.7133712	-1.1773385
5.90	3.8440577	1.1281559	1.4630561	1.3516412	8.7744766	1.6642578
6.25	1.7300797	8.5171037^{-3}	1.2279378	1.2398108	9.3348418	4.0061477
6.55	2.9921753^{-4}	6.4812858	1.0394951	1.1289726	9.3800711	5.3386789
6.90	-9.9157018	4.4721799	8.3887332^{-3}	9.9230406^{-3}	9.0727617	6.2784493
7.20	-1.8247588^{-3}	3.0366076	6.8484919	8.7478432	8.5968875	6.6768974
7.85	-2.9617116	6.9935457^{-4}	4.0816089	6.3526916	7.2005887	6.6638646

TABLE III. $G^{n}_{3d,\,4p}$ and $B^{n}_{3d,\,4p}$ $n = 1, 3$

$Z_{3d} = 3.65 \longrightarrow 7.85$ $Z_{4p} = 3.00 \longrightarrow 4.25$

$r = 3.40 \longrightarrow 4.20.$

$G^{1}_{3d,4p}$

$r = 3.40$

$Z_{3d} \backslash Z_{4p}$	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-5.5826319^{-2}	-5.3556282^{-2}	-4.7018024^{-2}	-3.6898631^{-2}	-2.3958286^{-2}	-8.9582621^{-3}
4.00	-5.3921596	-5.4217042	-5.0383860	-4.2947659	-3.2540377	-1.9828871^{-2}
4.30	-5.0664186	-5.2808202	-5.1057808	-4.5804562	-3.7565744	-2.6916349
4.60	-4.6414699	-5.0065638	-5.0125570	-4.6862804	-4.0683469	-3.2068025
4.95	-4.0724151	-4.5718326	-4.7524544	-4.6285807	-4.2288957	-3.5907773
5.25	-3.5566696	-4.1389167	-4.4385970	-4.4609935	-4.2257404	-3.7617683
5.60	-2.9538004	-3.6001479	-4.0058690	-4.1677217	-4.0963020	-3.8117544
5.90	-2.4540121	-3.1318605	-3.6034695	-3.8598926	-3.9052799	-3.7532612
6.25	-1.9052413	-2.5977446	-3.1213273	-3.4620096	-3.6178862	-3.5961373
6.55	-1.4713957	-2.1614163	-2.7116483	-3.1050116	-3.3355122	-3.4057883
6.90	-1.0123103	-1.6860776	-2.2504673	-2.6859525	-2.9829287	-3.1397324
7.20	-6.6025740^{-3}	-1.3115460	-1.8764366	-2.3341510	-2.6728026	-2.8878458
7.85	-2.4821979^{-4}	-6.1030747^{-3}	-1.1499735	-1.6222606	-2.0124515	-2.3117701

TABLE III. (cont.).

$G^1_{3d,4p}$
$r = 3.50$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-5.3929537^{-2}	-5.0865387^{-2}	-4.3668076^{-2}	-3.3059143^{-2}	-1.9816739^{-2}	-4.7068457^{-3}
4.00	-5.2117105	-5.1646869	-4.7177736	-3.9267905	-2.8566932	-1.5746335^{-2}
4.30	-4.8968436	-5.0374872	-4.8010062	-4.2296597	-3.3768773	-2.3006428
4.60	-4.4851194	-4.7794797	-4.7262435	-4.3551983	-3.7085968	-2.8349927
4.95	-3.9338249	-4.3661862	-4.4901829	-4.3228811	-3.8945507	-3.2431120
5.25	-3.4346662	-3.9530935	-4.1983782	-4.1784275	-3.9144002	-3.4358216
5.60	-2.8520051	-3.4383654	-3.7922876	-3.9130043	-3.8125918	-3.5118430
5.90	-2.3697142	-2.9908630	-3.4129174	-3.6292539	-3.6454805	-3.4758974
6.25	-1.8409969	-2.4806249	-2.9572761	-3.2591432	-3.3857372	-3.3449660
6.55	-1.4236691	-2.0640550	-2.5696095	-2.9253117	-3.1265439	-3.1766999
6.90	-9.8272727^{-3}	-1.6105760	-2.1329269	-2.5321850	-2.8000706	-2.9357101
7.20	-6.4507706	-1.2535498	-1.7786618	-2.2014512	-2.5113188	-2.7045333
7.85	-3.6790485^{-4}	-5.8586206^{-3}	-1.0905841	-1.5309819	-1.8935305	-2.1702751

$G^1_{3d,4p}$
$r = 3.60$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-5.1890513^{-2}	-4.8104761^{-2}	-4.0334141^{-2}	-2.9328534^{-2}	-1.5878536^{-2}	-7.4938641^{-4}
4.00	-5.0190270	-4.9026651	-4.4005226	-3.5711158	-2.4806210	1.1961613^{-2}
4.30	-4.7167493	-4.7907176	-4.5008669	-3.8920138	-3.0187836	-1.9392020
4.60	-4.3198466	-4.5503302	-4.4455607	-4.0377697	-3.3703850	-2.4920591
4.95	-3.7879209	-4.1597517	-4.2343236	-4.0310099	-3.5812207	-2.9230956
5.25	-3.3064847	-3.7672989	-3.9649364	-3.9095117	-3.6233323	-3.1361948
5.60	-2.7450461	-3.2772008	-3.5855551	-3.6714121	-3.5479962	-3.2364568
5.90	-2.2808774	-2.8507544	-3.2290320	-3.4110628	-3.4036060	-3.2213939
6.25	-1.7726825	-2.3644397	-2.7994317	-3.0677364	-3.1699973	-3.1146299
6.55	-1.3720757	-1.9674769	-2.4332293	-2.7560990	-2.9326015	-2.9666907
6.90	-9.4934645^{-3}	-1.5355177	-2.0202625	-2.3876705	-2.6305755	-2.7487251
7.20	-6.2603840	-1.1956062	-1.6850198	-2.0769115	-2.3617807	-2.5365443
7.85	-4.4518102^{-4}	-5.6043072^{-3}	-1.0336078	-1.4454844	-1.7835766	-2.0406229

TABLE III. (cont.).

$G^1_{3d,4p}$
r = 3.70

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.9747401^{-2}	-4.5313505^{-2}	-3.7053443^{-2}	-2.5739223^{-2}	-1.2168617^{-2}	2.8988671^{-3}
4.00	-4.8178447	-4.6393463	-4.0900421	-3.2305751	-2.1278212	-8.4846158
4.30	-4.5296873	-4.5439643	-4.2084352	-3.5699604	-2.6838786	-1.6078572^{-2}
4.60	-4.1489765	-4.3222677	-4.1732313	-3.7360495	-3.0548893	-2.1781577
4.95	-3.6377373	-3.9553208	-3.9871843	-3.7545722	-3.2896813	-2.6305012
5.25	-3.1748886	-3.5839891	-3.7402276	-3.6555176	-3.3529737	-2.8623829
5.60	-2.6353771	-3.1187893	-3.3872797	-3.4438716	-3.3026480	-2.9848640
5.90	-2.1897010	-2.7133803	-3.0531405	-3.2059974	-3.1795962	-2.9888722
6.25	-1.7022247	-2.2507498	-2.6488631	-2.8882366	-2.9704192	-2.9041451
6.55	-1.3183478	-1.8730439	-2.3033799	-2.5976604	-2.7533277	-2.7747187
6.90	-9.1368560^{-3}	-1.4620649	-1.9131782	-2.2525729	-2.4740248	-2.5777368
7.20	-6.0450450	-1.1387358	-1.5960982	-1.9606190	-2.2237309	-2.3828724
7.85	-4.9122868^{-4}	-5.3482051^{-3}	-9.7947815^{-3}	-1.3657826	-1.6821563	-1.9219255

$G^1_{3d,4p}$
r = 3.80

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.7534660^{-2}	-4.2525875^{-2}	-3.3856949^{-2}	-2.2316583^{-2}	-8.7041313^{-3}	6.2303138^{-3}
4.00	-4.6114353	-4.3778871	-3.7890821	-2.9072721	-1.7995568^{-2}	-5.3179137
4.30	-4.3387509	-4.3001134	-3.9261316	-3.2652292	-2.3730247	-1.3064890^{-2}
4.60	-3.9753612	-4.0978759	-3.9113237	-3.4514007	-2.7626234	-1.8928401
4.95	-3.4858181	-3.7551126	-3.7504593	-3.4945667	-3.0200670	-2.3645667
5.25	-3.0421566	-3.4051024	-3.5256484	-3.4171507	-3.1032382	-2.6134379
5.60	-2.5249891	-2.9647460	-3.1985372	-3.2308120	-3.0762225	-2.7559499
5.90	-2.0979433	-2.5801234	-2.8861061	-3.0143001	-2.9729847	-2.7771474
6.25	-1.6311448	-2.1407016	-2.5062150	-2.7207058	-2.7864298	-2.7122849
6.55	-1.2638230	-1.7817302	-2.1805716	-2.4499690	-2.5881053	-2.5995847
6.90	-8.7691429^{-3}	-1.3910403	-1.8120570	-2.1267855	-2.3297725	-2.4215815
7.20	-5.8152523	-1.0836578	-1.5122064	-1.8524280	-2.0965486	-2.2424132
7.85	-5.1464554^{-4}	-5.0960466^{-3}	-9.2842415^{-3}	-1.2917294	-1.5887317	-1.8132663

TABLE III. (cont.).

$G^1_{3d,4p}$

r = 3.90

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.5283013^{-2}	-3.9771085^{-2}	-3.0769875^{-2}	-1.9079235^{-2}	-5.4957742^{-3}	9.2440085^{-3}
4.00	-4.4026870	-4.1209284	-3.4998072	-2.6026777	-1.4964500^{-2}	-2.4581596
4.30	-4.1465831	-4.0615133	-3.6557931	-2.9789470	-2.0865003	-1.0344353^{-2}
4.60	-3.8013992	-3.8792119	-3.6613586	-3.1846268	-2.4935581	-1.6351826
4.95	-3.3342650	-3.5608547	-3.5253123	-3.2514615	-2.7720788	-2.1241496
5.25	-2.9101445	-3.2320947	-3.3221069	-3.1946567	-2.8736174	-2.3880814
5.60	-2.4154653	-2.8162490	-3.0199861	-3.0322551	-2.8680774	-2.5483647
5.90	-2.0069874	-2.4519659	-2.7284080	-2.8358560	-2.7830422	-2.5848415
6.25	-1.5606175	-2.0350878	-2.3718073	-2.5649346	-2.6172536	-2.5377091
6.55	-1.2095340	-1.6942004	-2.0650230	-2.3127479	-2.4361523	-2.4399859
6.90	-8.3992340^{-3}	-1.3229869	-1.7170402	-2.0100036	-2.1970674	-2.2790525
7.20	-5.5789858	-1.0308419	-1.4334432	-1.7520345	-1.9795124	-2.1140486
7.85	-5.2203974^{-4}	-4.8516646^{-3}	-8.8051987^{-3}	-1.2230659	-1.5027135	-1.7137338

$G^1_{3d,4p}$

r = 4.00

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.3019493^{-2}	-3.7073815^{-2}	-2.7812072^{-2}	-1.6040376^{-2}	-2.5482877^{-3}	1.1944401^{-2}
4.00	-4.1940555	-3.8706152	-3.2238329	-2.3176992	-1.2185778^{-2}	1.0296168^{-4}
4.30	-3.9554202	-3.8300351	-3.3987313	-2.7117146	-1.8240941	-7.9060577^{-3}
4.60	-3.6290650	-3.6678634	-3.4243546	-2.9360614	-2.2472453	-1.4039010^{-2}
4.95	-3.1847692	-3.3738268	-3.3124733	-3.0253235	-2.5450406	-1.9078251
5.25	-2.7803109	-3.0660139	-3.1301144	-2.9879109	-2.6633183	-2.1848317
5.60	-2.3080286	-2.6741220	-2.8519381	-2.8479368	-2.6773168	-2.3606075
5.90	-1.9178774	-2.3295652	-2.5802204	-2.6703137	-2.6088508	-2.4104929
6.25	-1.4915226	-1.9344187	-2.2457091	-2.4205048	-2.4619784	-2.3790169
6.55	-1.1562429	-1.6108641	-1.9567393	-2.1855648	-2.2965839	-2.2946104
6.90	-8.0337162^{-3}	-1.2582419	-1.6280917	-1.9017982	-2.0750827	-2.1489388
7.20	-5.3421216	-9.8058044^{-3}	-1.3597616	-1.6590313	-1.8718605	-1.9966752
7.85	-5.1834776^{-4}	-4.6175185	-8.3573367^{-3}	-1.1594741	-1.4235021	-1.6224579

Table III. (cont.).

$G^{1}_{3d,4p}$

$r = 4.10$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.0767493^{-2}	-3.4454106^{-2}	-2.4998464^{-2}	-1.3208054^{-2}	1.3844558^{-4}	1.4340306^{-2}
4.00	-3.9876342	-3.6286726	-2.9623168	-2.0527950	-9.6558286^{-3}	2.3774660^{-3}
4.30	-3.7671039	-3.6071149	-3.1558094	-2.4637056	-1.5852040	-5.7360614
4.60	-3.4599747	-3.4650127	-3.2009308	-2.7056463	-2.0228941	-1.1974705^{-2}
4.95	-3.0386677	-3.1949344	-3.1123001	-2.8158820	-2.3380194	-1.7139882
5.25	-2.6537935	-2.9075706	-2.9498502	-2.7965233	-2.4713380	-2.0020748
5.60	-2.2036092	-2.5388841	-2.6944223	-2.6773609	-2.5029072	-2.1911109
5.90	-1.8313968	-2.2133155	-2.4414951	-2.5171318	-2.4493839	-2.2525968
6.25	-1.4245034	-1.8389728	-2.1277952	-2.2868579	-2.3196122	-2.2348102
6.55	-1.1044984	-1.5319465	-1.8555641	-2.0678723	-2.1684648	-2.1621590
6.90	-7.6772825^{-3}	-1.1969736	-1.5450461	-1.8016566	-1.9629626	-2.0300783
7.20	-5.1088946	-9.3302083^{-3}	-1.2910049	-1.5729497	-1.7728202	-1.8892415
7.85	-5.0725418^{-4}	-4.3950433	-7.9396457^{-3}	-1.1006061	-1.3505055	-1.5386224

$G^{1}_{3d,4p}$

$r = 4.20$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-3.8546836^{-2}	-3.1928281^{-2}	-2.2339754^{-2}	-1.0585924^{-2}	2.5685170^{-3}	1.6444087^{-2}
4.00	-3.7851472	-3.3963914	-2.7159881	-1.8080061	-7.3675941	4.3801872^{-3}
4.30	-3.5831309	-3.3938178	-2.9275217	-2.2347422	-1.3689400^{-2}	-3.8181519
4.60	-3.2953816	-3.2714869	-2.9913553	-2.4930197	-1.8194751	-1.0142002^{-2}
4.95	-2.8969888	-3.0247771	-2.9248654	-2.6226309	-2.1499068	-1.5409417
5.25	-2.5314336	-2.7571991	-2.7812648	-2.6198954	-2.2965282	-1.8381523
5.60	-2.1028723	-2.4108183	-2.5472810	-2.5198784	-2.3437207	-2.0382948
5.90	-1.7480949	-2.1034049	-2.3119975	-2.3756508	-2.3035446	-2.1096612
6.25	-1.3600033	-1.7488670	-2.0178089	-2.1633574	-2.1891444	-2.1037272
6.55	-1.0546809	-1.4575137	-1.7612406	-1.9590653	-2.0508636	-2.0413907
6.90	-7.3332085^{-3}	-1.1392312	-1.4676555	-1.7090292	-1.8598706	-1.9213657
7.20	-4.8822784	-8.8820693^{-3}	-1.2269496	-1.4933032	-1.6816432	-1.7907564
7.85	-4.9144726^{-4}	-4.1849012	-7.5506732^{-3}	-1.0461004	-1.2831551	-1.4614835

TABLE III. (cont.).

$G^3_{3d,4p}$

$r = 3.40$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.8332420^{-2}	-4.5606067^{-2}	-3.9194342^{-2}	-2.9710292^{-2}	-1.7850979^{-2}	-4.3265659^{-3}
4.00	-4.6076452	-4.4623977	-3.9672722	-3.1733705	-2.1414909	-9.3537525
4.30	-4.3243947	-4.2739635	-3.8963332	-3.2339462	-2.3395498	-1.2699453^{-2}
4.60	-3.9891515	-4.0183759	-3.7468405	-3.2088432	-2.4492327	-1.5176568
4.95	-3.5642876	-3.6671247	-3.5023226	-3.0956770	-2.4833931	-1.7070110
5.25	-3.1924781	-3.3428684	-3.2543451	-2.9463809	-2.4484898	-1.7957185
5.60	-2.7687721	-2.9586033	-2.9419862	-2.7321824	-2.3518527	-1.8292035
5.90	-2.4247263	-2.6366167	-2.6682095	-2.5284074	-2.2348264	-1.8105176
6.25	-2.0536721	-2.2800868	-2.3542012	-2.2808185	-2.0726463	-1.7475184
6.55	-1.7650862	-1.9962614	-2.0967401	-2.0685883	-1.9210413	-1.6681476
6.90	-1.4642772	-1.6941412	-1.8156523	-1.8284448	-1.7384790	-1.5561175
7.20	-1.2368355	-1.4611675	-1.5939057	-1.6331521	-1.5826325	-1.4501173
7.85	-8.3361466^{-3}	-1.0370991	-1.1783754	-1.2535274	-1.2629381	-1.2102292

$G^3_{3d,4p}$

$r = 3.50$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.6061200^{-2}	-4.2346736^{-2}	-3.5099511^{-2}	-2.4983398^{-2}	-1.2724854^{-2}	9.5557002^{-4}
4.00	-4.3795213	-4.1431323	-3.5722427	-2.7224635	-1.6571203	-4.4075374^{-3}
4.30	-4.0999366	-3.9651619	-3.5183475	-2.8059640	-1.8829751	-8.0677039
4.60	-3.7720785	-3.7236522	-3.3891540	-2.8064798	-2.0223787	-1.0869375^{-2}
4.95	-3.3596896	-3.3923306	-3.1712232	-2.7252730	-2.0922993	-1.3141403
5.25	-3.0010729	-3.0872641	-2.9475646	-2.6042100	-2.0881094	-1.4345337
5.60	-2.5946877	-2.7268013	-2.6643465	-2.4229887	-2.0265844	-1.5035087
5.90	-2.2664100	-2.4256893	-2.4155078	-2.2468998	-1.9385561	-1.5136602
6.25	-1.9140502	-2,0933089	-2.1298551	-2.0303758	-1.8085096	-1.4822344
6.55	-1.6412407	-1.8295244	-1.8956500	-1.8433722	-1.6827769	-1.4280578
6.90	-1.3580728	-1.5495788	-1.6400966	-1.6307519	-1.5282834	-1.3432141
7.20	-1.1448231	-1.3343334	-1.4386682	-1.4572795	-1.3946184	-1.2586329
7.85	-7.6873759^{-3}	-9.4407095^{-3}	-1.0618094	-1.1191382	-1.1170644	-1.0594267

TABLE III. (cont.).

$G^{3}_{3d\ 4p}$

r = 3.60

Z3d Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.3577366^{-2}	-3.8971874^{-2}	-3.1007959^{-2}	-2.0391330^{-2}	-7.8692592^{-3}	5.8355524^{-3}
4.00	-4.1345578	-3.8169469	-3.1820139	-2.2890251	-1.2030235^{-2}	1.1424178^{-4}
4.30	-3.8623416	-3.6530693	-3.1484073	-2.3980568	-1.4584205	-3.8677760^{-3}
4.60	-3.5452915	-3.4288109	-3.0421516	-2.4260316	-1.6284141	-6.9920254
4.95	-3.1488649	-3.1204625	-2.8530794	-2.3780487	-1.7341862	-9.6308284
5.25	-2.8059357	-2.8365947	-2.6550340	-2.2856246	-1.7601215	-1.1135419^{-2}
5.60	-2.4191938	-2.5016181	-2.4017781	-2.1371862	-1.7324168	-1.2156059
5.90	-2.1081894	-2.2223121	-2.1780771	-1.9881618	-1.6718957	-1.2522573
6.25	-1.7757789	-1.9146596	-1.9205443	-1.8015683	-1.5719515	-1.2495010
6.55	-1.5194433	-1.6710495	-1.7090730	-1.6385766	-1.4701852	-1.2179805
6.90	-1.2543755	-1.4131026	-1.4781714	-1.4518745	-1.3414546	-1.1573760
7.20	-1.0554688	-1.2152250	-1.2961505	-1.2987603	-1.2279881	-1.0917736
7.85	-7.0631236^{-3}	-8.5756905^{-3}	-9.5573776^{-3}	-9.9887673^{-3}	-9.8844451^{-3}	-9.2836229^{-3}

$G^{3}_{3d,4p}$

r = 3.70

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-4.0938517^{-2}	-3.5542582^{-2}	-2.6979443^{-2}	-1.5987923^{-2}	-3.3274845^{-3}	1.0284213^{-2}
4.00	-3.8783414	-3.4895411	-2.8019271	-1.8775973	-7.8252552	4.1934395^{-3}
4.30	-3.6168946	-3.3429018	-2.7912173	-2.0139881	-1.0683351^{-2}	-1.0859631^{-4}
4.60	-3.3136696	-3.3138514	-2.7098444	-2.0704904	-1.2689889	-3.5451885^{-3}
4.95	-2.9361528	-2.8554773	-2.5510916	-2.0561354	-1.4098287	-6.5308723
5.25	-2.6109148	-2.5942265	-2.3793027	-1.9920838	-1.4646644	-8.3142507
5.60	-2.2455612	-2.2857692	-2.1561454	-1.8755615	-1.4688841	-9.6368001
5.90	-1.9528716	-2.0286918	-1.9572742	-1.7525042	-1.4339777	-1.0241884^{-2}
6.25	-1.6411610	-1.7458193	-1.7271227	-1.5942723	-1.3617483	-1.0469731
6.55	-1.4016247	-1.5221366	-1.5375104	-1.4537821	-1.2818408	-1.0354637
6.90	-1.1547333	-1.2856498	-1.3300628	-1.2911493	-1.1764217	-9.9613980^{-3}
7.20	-9.7004496^{-3}	-1.1045237	-1.1663275	-1.1567857	-1.0811145	-9.4711280
7.85	-6.4716423	-7.7789544^{-3}	-8.5985802^{-3}	-8.9180271^{-3}	-8.7548770^{-3}	-8.1482184

TABLE III. (cont.).

$G^{3}_{3d,4p}$

$r = 3.80$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-3.8197186^{-2}	-3.2112429^{-2}	-2.3064012^{-2}	-1.1815411^{-2}	8.6975626^{-4}	1.4285449^{-2}
4.00	-3.6158449	-3.1657677	-2.4362919	-1.4915463	-3.9772860^{-3}	7.8244487^{-3}
4.30	-3.3681928	-3.0389892	-2.4504238	-1.6563678	-7.1401847	3.2122587
4.60	-3.0813685	-2.8565102	-2.3952024	-1.7417494	-9.4465366	-5.1950326^{-4}
4.95	-2.7251404	-2.6004481	-2.2675075	-1.7606555	-1.1190595^{-2}	-3.8255769^{-3}
5.25	-2.4191083	-2.3626814	-2.1220313	-1.7241532	-1.2010638	-5.8617133
5.60	-2.0763506	-2.0811854	-1.9285221	-1.6381450	-1.2348483	-7.4537815
5.90	-1.8025871	-1.8463168	-1.7537477	-1.5395840	-1.2233811	-8.2693066
6.25	-1.5118928	-1.5878434	-1.5498353	-1.4078123	-1.1762627	-8.7203867
6.55	-1.2891506	-1.3835299	-1.3809477	-1.2881271	-1.1160060	-8.7790008
6.90	-1.0602012	-1.1676744	-1.1955248	-1.1475657	-1.0314063	-8.5696531
7.20	-8.8938368^{-3}	-1.0024970	-1.0488216	-1.0302827	-9.5223030^{-3}	-8.2221832
7.85	-5.9178497	-7.0505865^{-3}	-7.7364900^{-3}	-7.9683792^{-3}	-7.7657756	-7.1668549

$G^{3}_{3d,4p}$

$r = 3.90$

Z3d Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-3.5400641^{-2}	-2.8727532^{-2}	-1.9302599^{-2}	-7.9055321^{-3}	4.7029167^{-3}	1.7834428^{-2}
4.00	-3.3514058	-2.8496696	-2.0884664	-1.1332050^{-2}	-4.9656385^{-4}	1.1011906
4.30	-3.1201488	-2.7448155	-2.1287353	-1.3268176	-3.9577930^{-3}	6.1063245^{-3}
4.60	-2.8518341	-2.5857171	-2.1003172	-1.4407741	-6.5509343	2.1022609
4.95	-2.5187176	-2.3576630	-2.0037244	-1.4919337	-8.6096446	-1.4929482
5.25	-2.2329433	-2.1437365	-1.8841247	-1.4816900	-9.6801030	-3.7528495
5.60	-1.9134908	-1.8891339	-1.7193230	-1.4243653	-1.0286936^{-2}	-5.5802534
5.90	-1.6588871	-1.6760843	-1.5675792	-1.3485665	-1.0383188	-6.5774667
6.25	-1.3891513	-1.4412719	-1.3884721	-1.2411528	-1.0136046	-7.2198198
6.55	-1.1829316	-1.2555339	-1.2389857	-1.1404589	-9.7076268^{-3}	-7.4265699
6.90	-9.7143197^{-3}	-1.0592707	-1.0740153	-1.0199147	-9.0453050	-7.3735965
7.20	-8.1397380	-9.0910986^{-3}	-9.4301366^{-3}	-9.1803545^{-3}	-8.3953478	-7.1474821
7.85	-5.4041787	-6.3886645	-6.9644863	-7.1285478	-6.9013812	-6.3197583

TABLE III. (cont.).

$G^3_{3d,4p}$

r = 4.00

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-3.2590447^{-2}	-2.5426687^{-2}	-1.5727322^{-2}	-4.2804641^{-3}	8.1624417^{-3}	2.0935735^{-2}
4.00	-3.0887418	-2.5445233	-1.7609404	-8.0398800	2.6156586	1.3768566
4.30	-2.8760374	-2.4631053	-1.8280260	-1.0261151^{-2}	-1.1312075	8.5921659^{-3}
4.60	-2.6278679	-2.3283272	-1.8264835	-1.1677813	-3.9930263	4.3428863
4.95	-2.3191473	-2.1287220	-1.7604631	-1.2496354	-6.3407967	4.9332794^{-4}
5.25	-2.0542564	-1.9385607	-1.6658807	-1.2640032	-7.6377656	-1.9599202^{-3}
5.60	-1.7583707	-1.7103386	-1.5284579	-1.2332268	-8.4848599	-3.9877150
5.90	-1.5228428	-1.5184128	-1.3984260	-1.1782852	-8.7677371	-5.1381971
6.25	-1.2736875	-1.3062487	-1.2424768	-1.0930006	-8.7175274	-5.9409450
6.55	-1.0835067	-1.1381144	-1.1109547	-1.0094482	-8.4414193	-6.2715981
6.90	-8.8877661^{-3}	-9.6026313^{-3}	-9.6478855^{-3}	-9.0687401^{-3}	-7.9391952	-6.3494419
7.20	-7.4403571	-8.2410624	-8.4813429	-8.1876216	-7.4126092	-6.2250212
7.85	-4.9312570	-5.7898955	-6.2752675	-6.3872993	-6.1468492	-5.5889724

$G^3_{3d,4p}$

r = 4.10

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-2.9802586^{-2}	-2.2241697^{-2}	-1.2362370^{-2}	-9.5407650^{-4}	1.1246945^{-2}	2.3601659^{-2}
4.00	-2.8309649	-2.2529015	-1.4554364	-5.0451935^{-3}	5.3654221^{-3}	1.6113789
4.30	-2.6385181	-2.1959069	-1.5494422	-7.5433433	1.3508646	1.0693449
4.60	-2.4116727	-2.0858768	-1.5743467	-9.2237144	-1.7574093	6.2291776^{-3}
4.95	-2.1281389	-1.9146410	-1.5378722	-1.0329329^{-2}	-4.3654807	2.1618714
5.25	-1.8843682	-1.7477851	-1.4671115	-1.0699996	-5.8633029	-4.5363608^{-4}
5.60	-1.6119321	-1.5450827	-1.3554449	-1.0634363	-6.9211145	-2.6473865^{-3}
5.90	-1.3951198	-1.3733470	-1.2456304	-1.0273431	-7.3663660	-3.9236765
6.25	-1.1659138	-1.1826137	-1.1110602	-9.6192344^{-3}	-7.4865261	-4.8576876
6.55	-9.9112380^{-3}	-1.0309947	-9.9600855^{-3}	-8.9367606	-7.3418269	-5.2897648
6.90	-8.1233698	-8.7028274^{-3}	-8.6697785	-8.0708273	-6.9775796	-5.4750832
7.20	-6.7959368	-7.4707731	-7.6333414	-7.3117883	-6.5573023	-5.4346506
7.85	-4.4983505	-5.2501802	-5.6612936	-5.7338212	-5.4884892	-4.9583889

Table III. (cont.).

$G^3_{3d,4p}$

$r = 4.20$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-2.7067702^{-2}	-1.9197983^{-2}	-9.2248931^{-3}	2.0670699^{-3}	1.3961968^{-2}	2.5850602^{-2}
4.00	-2.5806357	-1.9767277	-1.1729942^{-2}	-2.3479688	7.7646398^{-3}	1.8071412
4.30	-2.4096990	-1.9446449	-1.2935360	-5.1097581	3.5044942	1.2437425
4.60	-2.2049340	-1.8593441	-1.3440152	-7.0366399	1.7489667^{-4}	7.7902344^{-3}
4.95	-1.9469095	-1.7159521	-1.3356564	-8.4062956	-2.6625105^{-3}	3.5426372
5.25	-1.7241654	-1.5716314	-1.2872607	-8.9829942	-4.3347982	7.9556319^{-4}
5.60	-1.4747323	-1.3932991	-1.1995153	-9.1349812	-5.5737625	-1.5308744^{-3}
5.90	-1.2760546	-1.2406431	-1.1083100	-8.9421996	-6.1576884	-2.9071288
6.25	-1.0659779	-1.0699855	-9.9328143^{-3}	-8.4642555	-6.4229486	-3.9453972
6.55	-9.0580802^{-3}	-9.3371629^{-3}	-8.9319134	-7.9170376	-6.3900724	-4.4584738
6.90	-7.4204520	-7.8883530	-7.7965550	-7.1919961	-6.1433224	-4.7302881
7.20	-6.2052660	-6.7752284	-6.8772922	-6.5404166	-5.8137947	-4.7581478
7.85	-4.1038753	-4.7649552	-5.1150977	-5.1580051	-4.9138761	-4.4137619

$G^3_{3d,4p}$

$r = 4.30$

Z3d\Z4p	3.00	3.25	3.50	3.75	4.00	4.25
3.65	-2.4411217^{-2}	-1.6314773^{-2}	-6.3256273^{-3}	4.7828139^{-3}	1.6318715^{-2}	2.7705399^{-2}
4.00	-2.3397893	-1.7173634	-9.1409413	5.7438302^{-5}	9.8297414^{-3}	1.9668701
4.30	-2.1911886	-1.7102241	-1.0603299^{-2}	-2.9508880^{-3}	5.3492652	1.3853347
4.60	-2.0088583	-1.6492402	-1.1351582	-5.1041843	1.8254946	9.0562406^{-3}
4.95	-1.7762721	-1.5327836	-1.1531708	-6.7126230	-1.2093070	4.6655940
5.25	-1.5741681	-1.4099767	-1.1254983	-7.4733927	-3.0295936	1.8166529
5.60	-1.3470310	-1.2546534	-1.0597050	-7.8181395	-4.4208866	-6.1111160^{-4}
5.90	-1.1657333	-1.1198482	-9.8544890^{-3}	-7.7733844	-5.1209030	-2.0633953^{-3}
6.25	-9.7382110^{-3}	-9.6782520^{-3}	-8.8811100	-7.4500417	-5.5075731	-3.1814184
6.55	-8.2741601	-8.4571165	-8.0150173	-7.0211960	-5.5684395	-3.7571568
6.90	-6.7770208	-7.1534710	-7.0187736	-6.4193886	-5.4206116	-4.0969243
7.20	-5.6661214	-6.1488864	-6.2044055	-5.8617859	-5.1678732	-4.1793376
7.85	-3.7456566	-4.3295158	-4.6295570	-4.6505483	-4.4119251	-3.9426708

Table III. (cont.).

$B^{1}_{3d,4p}$

r = 3.40

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	1.8121212^{-2}	2.6417281^{-2}	3.3439305^{-2}	3.8813768^{-2}	4.2328404^{-2}	4.3911644^{-2}
4.00	1.7299676	2.5313688	3.2098784	3.7299234	4.0710369	4.2260203
4.30	1.6302100	2.4031431	3.0589034	3.5636430	3.8976621	4.0537255
4.60	1.5065166	2.2484542	2.8804326	3.3703658	3.6993321	3.8600033
4.95	1.3379620	2.0417083	2.6453981	3.1189741	3.4443494	3.6140231
5.25	1.1786294	1.8485530	2.4278197	2.8880281	3.2117474	3.3912636
5.60	9.8273733^{-3}	1.6125125	2.1631936	2.6082099	2.9308152	3.1230198
5.90	8.1175908	1.4068991	1.9330150	2.3650270	2.6867287	2.8898866
6.25	6.1450504	1.1693546	1.6667581	2.0832780	2.4033218	2.6183780
6.55	4.5115178	9.7183537^{-3}	1.4446158	1.8473958	2.1650919	2.3890055
6.90	2.7080112	7.5235621	1.1964756	1.5825577	1.8961259	2.1283125
7.20	1.2701763	5.7587830	9.9557981^{-3}	1.3667602	1.6754644	1.9127539
7.85	-1.4537313	2.3609015	6.0386439	9.4112275^{-3}	1.2351067	1.4769185

$B^{1}_{3d,4p}$

r = 3.50

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	1.9745438^{-2}	2.7327253^{-2}	3.3486657^{-2}	3.7910780^{-2}	4.0446687^{-2}	4.1076984^{-2}
4.00	1.8721945	2.6018410	3.1955589	3.6235914	3.8711131	3.9359900
4.30	1.7546671	2.4567650	3.0302890	3.4469136	3.6922383	3.7637420
4.60	1.6140670	2.2869602	2.8400920	3.2465737	3.4923956	3.5745609
4.95	1.4279553	2.0655595	2.5950507	2.9911366	3.2401786	3.3385462
5.25	1.2559493	1.8627119	2.3720948	2.7600797	3.0132809	3.1274865
5.60	1.0482835	1.6187516	2.1047187	2.4835726	2.7421742	2.8756197
5.90	8.6974776^{-3}	1.4090561	1.8748731	2.2457166	2.5086410	2.6581644
6.25	6.6638421	1.1695333	1.6116396	1.9724767	2.2393363	2.4061267
6.55	4.9981929	9.7232681^{-3}	1.3939069	1.7453742	2.0142360	2.1939555
6.90	3.1766449	7.5506661	1.1525028	1.4919651	1.7612640	1.9534338
7.20	1.7366027	5.8169250	9.5833899^{-3}	1.2865805	1.5545215	1.7549337
7.85	-9.6371942^{-4}	2.5097349	5.8276923	8.8406802^{-3}	1.1437609	1.3543163

TABLE III. (cont.).

$B^{1}_{3d,4p}$

$r = 3.60$

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.0971160^{-2}	2.7820489^{-2}	3.3130052^{-2}	3.6647070^{-2}	3.8275360^{-2}	3.8047143^{-2}
4.00	1.9751706	2.6324246	3.1437744	3.4851496	3.6470363	3.6318838
4.30	1.8413125	2.4728767	2.9674153	3.3019496	3.4670021	3.4642738
4.60	1.6858565	2.2908388	2.7690557	3.0985765	3.2699101	3.2838880
4.95	1.4850723	2.0584815	2.5182868	2.8436795	3.0250579	3.0621906
5.25	1.3030788	1.8491876	2.2935202	2.6161580	2.8073596	2.8659395
5.60	1.0868126	1.6009482	2.0272483	2.3467484	2.5495242	2.6333098
5.90	9.0334632^{-3}	1.3900784	1.8006910	2.1169961	2.3289295	2.4333542
6.25	6.9671870	1.1516127	1.5434538	1.8549402	2.0758847	2.2022394
6.55	5.2913629	9.5698091^{-3}	1.3322666	1.6384356	1.8652568	2.0080073
6.90	3.4743144	7.4417541	1.0996153	1.3980657	1.6293215	1.7880118
7.20	2.0486503	5.7549113	9.1354263^{-3}	1.2040879	1.4370154	1.6065226
7.85	-6.0025182^{-4}	2.5633717	5.5605650	8.2585133^{-3}	1.0560362	1.2402224

$B^{1}_{3d,4p}$

$r = 3.70$

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.1833677^{-2}	2.7947138^{-2}	3.2432854^{-2}	3.5096389^{-2}	3.5894893^{-2}	3.4905208^{-2}
4.00	2.0431087	2.6287151	3.0612760	3.3221814	3.4068237	3.3217253
4.30	1.8947749	2.4573712	2.8771781	3.1362787	3.2297059	3.1628573
4.60	1.7267890	2.2661114	2.6741599	2.9336500	3.0391746	2.9948940
4.95	1.5143623	2.0264525	2.4216809	2.6833991	2.8056236	2.7910067
5.25	1.3250590	1.8137678	2.1983195	2.4625511	2.5999478	2.6118883
5.60	1.1032264	1.5645805	1.9365068	2.2033548	2.3580238	2.4004589
5.90	9.1725558^{-3}	1.3550899	1.7157057	1.9838872	2.1520785	2.2190906
6.25	7.0990941	1.1202669	1.4668624	1.7350056	1.9166944	2.0095709
6.55	5.4322047	9.3007559^{-3}	1.2638617	1.5303615	1.7212895	1.8334193
6.90	3.6386092	7.2350123	1.0414422	1.3040517	1.5028339	1.6337245
7.20	2.2408664	5.6071555	8.6439129^{-3}	1.1220239	1.3250293	1.4687841
7.85	-3.3485572^{-4}	2.5490459	5.2614830	7.6842701^{-3}	9.7327308^{-3}	1.1352467

TABLE III. (cont.).

$B^{1}_{3d,4p}$

r = 3.80

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.2369982^{-2}	2.7756862^{-2}	3.1455180^{-2}	3.3326471^{-2}	3.3376729^{-2}	3.1722500^{-2}
4.00	2.0802322	2.5960769	2.9543083	3.1414730	3.1574093	3.0121993
4.30	1.9195792	2.4157690	2.7657977	2.9564798	2.9868897	2.8656018
4.60	1.7415356	2.2182943	2.5614490	2.7580110	2.8062058	2.7130066
4.95	1.5205071	1.9748112	2.3109167	2.5159707	2.5871588	2.5295637
5.25	1.3264649	1.7615424	2.0917712	2.3043871	2.3956879	2.3691709
5.60	1.1018813	1.5143484	1.8372304	2.0578581	2.1715523	2.1800861
5.90	9.1557914^{-3}	1.3084193	1.6241796	1.8502941	1.9813496	2.0177620
6.25	7.0972945	1.0793701	1.3855708	1.6159521	1.7643748	1.8298583
6.55	5.4554087	8.9509684^{-3}	1.1919522	1.4239498	1.5844565	1.6714694
6.90	3.7007709	6.9610602	9.8076251^{-3}	1.2122202	1.3834281	1.4913955
7.20	2.3416407	5.4009124	8.1329897	1.0423137	1.2198484	1.3422385
7.85	-1.4464374^{-4}	2.4878436	4.9482017	7.1310560^{-3}	8.9620814^{-3}	1.0394761

$B^{1}_{3d,4p}$

r = 3.90

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.2617594^{-2}	2.7297653^{-2}	3.0253140^{-2}	3.1398136^{-2}	3.0783192^{-2}	2.8558933^{-2}
4.00	2.0906805	2.5395536	2.8285374	2.9489671	2.9046604	2.7087189
4.30	1.9200312	2.3531378	2.6388047	2.7681949	2.7439471	2.5773082
4.60	1.7344462	2.1523417	2.4361821	2.5768775	2.5758268	2.4423405
4.95	1.5077629	1.9082523	2.1908149	2.3460158	2.3737782	2.2811655
5.25	1.3113819	1.6968936	1.9782618	2.1457527	2.1980645	2.1404209
5.60	1.0865824	1.4542155	1.7332718	1.9137090	1.9929166	1.9741208
5.90	9.0184904^{-3}	1.2536557	1.5295046	1.7191558	1.8190129	1.8307644
6.25	6.9936465	1.0320727	1.3024638	1.5001803	1.6206484	1.6639885
6.55	5.3899118	8.5483934^{-3}	1.1190250	1.3211859	1.4560802	1.5226786
6.90	3.6864278	6.6439780	9.1965228^{-3}	1.1241473	1.2720491	1.3612265
7.20	2.3740015	5.1573263	7.6203698	9.6624229^{-3}	1.1221526	1.2268809
7.85	-1.1391341^{-5}	2.3957741	4.6333447	6.6070700	8.2514360^{-3}	9.5264056^{-3}

TABLE III. (cont.).

$B^1_{3d,4p}$

r = 4.00

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.2613609^{-2}	2.6615037^{-2}	2.8878004^{-2}	2.9365454^{-2}	2.8167449^{-2}	2.5463564^{-2}
4.00	2.0784122	2.4637863	2.6890087	2.7497842	2.6534357	2.4155573
4.30	1.9001587	2.2740516	2.5010208	2.5761640	2.5052173	2.3016054
4.60	1.7094945	2.0726374	2.3028449	2.3945296	2.3518064	2.1858665
4.95	1.4799333	1.8308276	2.0653923	2.1772213	2.1685563	2.0480417
5.25	1.2833893	1.6235359	1.8613662	1.9898103	2.0095908	1.9272872
5.60	1.0606008	1.3874754	1.6276923	1.7735026	1.8240211	1.7836171
5.90	8.7904662^{-3}	1.1937236	1.4343180	1.5926161	1.6665249	1.6587329
6.25	6.8146250	9.8089442^{-3}	1.2197314	1.3893672	1.4865297	1.5121954
6.55	5.2594142	8.1149849	1.0469268	1.2234111	1.3368654	1.3870252
6.90	3.6163012	6.3024198	8.5961582^{-3}	1.0408479	1.1691179	1.2429716
7.20	2.3563490	4.8925747	7.1186595	8.9460078^{-3}	1.0321813	1.1223410
7.85	7.9208330^{-5}	2.2848163	4.3255896	6.1169342	7.6008172^{-3}	8.7424858^{-3}

$B^1_{3d,4p}$

r = 4.10

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.2393807^{-2}	2.5751272^{-2}	2.7375910^{-2}	2.7275294^{-2}	2.5574049^{-2}	2.2475512^{-2}
4.00	2.0471426	2.3729960	2.5401477	2.5482586	2.4076550	2.1359492
4.30	1.8636609	2.1825663	2.3565752	2.3842931	2.2740890	2.0411127
4.60	1.6702676	1.9829927	2.1652023	2.2143952	2.1369717	1.9455923
4.95	1.4403656	1.7459808	1.9379251	2.0124379	1.9736899	1.8315381
5.25	1.2455874	1.5445666	1.7439368	1.8389394	1.8319650	1.7306216
5.60	1.0267125	1.3168108	1.5228635	1.6391024	1.6660536	1.6089507
5.90	8.4966482^{-3}	1.1309654	1.3406216	1.4721528	1.5247053	1.5017145
6.25	6.5819537	9.2780612^{-3}	1.1389807	1.2846085	1.3624862	1.3742405
6.55	5.0830770	7.6677075	9.7697967^{-3}	1.1314531	1.2270498	1.2640960
6.90	3.5068918	5.9504846	8.0169986	9.6290283^{-3}	1.0746741	1.1360908
7.20	2.3032060	4.6187264	6.6364140	8.2780942	9.4985929^{-3}	1.0280160
7.85	1.3829274^{-4}	2.1637585	4.0306247	5.6626820	7.0082147	8.0367950^{-3}

TABLE III. (cont.).

$B^{1}_{3d,4p}$

$r = 4.20$

Z3d Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.1992130^{-2}	2.4745145^{-2}	2.5787764^{-2}	2.5167772^{-2}	2.3039373^{-2}	1.9624801^{-2}
4.00	2.0003032	2.2709326	2.3857668	2.3479658	2.1703953	1.8722278
4.30	1.8138845	2.0822322	2.2089502	2.1957237	2.0531167	1.7975807
4.60	1.6199331	1.8866705	2.0263461	2.0391471	1.9333528	1.7227182
4.95	1.3919664	1.6565951	1.8110343	1.8538054	1.7906435	1.6322943
5.25	1.2006130	1.4625257	1.6281968	1.6948478	1.6662165	1.5506610
5.60	9.8723137^{-3}	1.2443707	1.4205810	1.5117759	1.5196257	1.4499826
5.90	8.1574969	1.0672193	1.2498740	1.3587124	1.3938705	1.3593308
6.25	6.3131556	8.7432540^{-3}	1.0613500	1.1865494	1.2485838	1.2495554
6.55	4.8761832	7.2192941	9.1009208^{-3}	1.0457512	1.1265404	1.1532216
6.90	3.3711899	5.5986039	7.4659388	8.9057140^{-3}	9.8849667^{-3}	1.0398534
7.20	2.2258898	4.3445806	6.1790963	7.6602099	8.7490113	9.4316343^{-3}
7.85	1.7442772^{-4}	2.0388921	3.7519085	5.2445123	6.4703410	7.4025731

$B^{3}_{3d,4p}$

$r = 3.40$

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.1445857^{-2}	3.1794198^{-2}	4.0740825^{-2}	4.7734434^{-2}	5.2435370^{-2}	5.4697745^{-2}
4.00	2.1769891	3.1369107	3.9537619	4.5781783	4.9804853	5.1488997
4.30	2.1595670	3.0519021	3.8016801	4.3644893	4.7142163	4.8412983
4.60	2.1039947	2.9287939	3.6141186	4.1202590	4.4243989	4.5188529
4.95	1.9984159	2.7469459	3.3623735	3.8100216	4.0704145	4.1376344
5.25	1.8806023	2.5671382	3.1279345	3.5321437	3.7627356	3.8149078
5.60	1.7209382	2.3398365	2.8431618	3.2039735	3.4076004	3.4501662
5.90	1.5724294	2.1375975	2.5967452	2.9258509	3.1118801	3.1514874
6.25	1.3935169	1.9009280	2.3139193	2.6113804	2.7818630	2.8223595
6.55	1.2406526	1.7026391	2.0801580	2.3542618	2.5145919	2.5582861
6.90	1.0679790	1.4814741	1.8217695	2.0721040	2.2231598	2.2721286
7.20	9.2786216^{-3}	1.3034160	1.6149192	1.8472474	1.9918193	2.0458114
7.85	6.5727136	9.6101224^{-3}	1.2183790	1.4171552	1.5500575	1.6141435

TABLE III. (cont.).

$B^{3}_{3d,4p}$

r = 3.50

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.3875140^{-2}	3.3278713^{-2}	4.1039638^{-2}	4.6694161^{-2}	4.9992043^{-2}	5.0871237^{-2}
4.00	2.3752695	3.2374380	3.9360748	4.4303323	4.6990220	4.7381658
4.30	2.3196438	3.1139170	3.7483707	4.1867326	4.4108643	4.4183829
4.60	2.2280665	2.9563708	3.5310312	3.9200157	4.1078447	4.0933734
4.95	2.0850060	2.7406970	3.2524443	3.5925841	3.7482418	3.7192298
5.25	1.9397801	2.5377514	3.0016432	3.3070474	3.4428654	3.4093823
5.60	1.7539820	2.2901637	2.7049138	2.9770454	3.0970798	3.0655144
5.90	1.5879709	2.0758579	2.4536144	2.7023898	2.8137700	2.7882079
6.25	1.3938745	1.8305418	2.1702875	2.3965619	2.5018845	2.4864890
6.55	1.2319454	1.6287692	1.9396832	2.1497995	2.2522514	2.2469768
6.90	1.0525538	1.4072101	1.6881309	1.8820880	1.9827647	1.9897129
7.20	9.0936763^{-3}	1.2312501	1.4890880	1.6708847	1.7706938	1.7877303
7.85	6.3820112	8.9844283^{-3}	1.1129275	1.2718449	1.3698827	1.4055970

$B^{3}_{3d,4p}$

r = 3.60

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.5705480^{-2}	3.4116293^{-2}	4.0691874^{-2}	4.5056936^{-2}	4.7048017^{-2}	4.6680502^{-2}
4.00	2.5146959	3.2767429	3.8596090	4.2308806	4.3774430	4.3023938
4.30	2.4234364	3.1192169	3.6425647	3.9651574	4.0762940	3.9800003
4.60	2.2995626	2.9326609	3.4023452	3.6839361	3.7687197	3.6612839
4.95	2.1242750	2.6900999	3.1051336	3.3483342	3.4127842	3.3032395
5.25	1.9565532	2.4700636	2.8447754	3.0622561	3.1166973	3.0126939
5.60	1.7504545	2.2089935	2.5434028	2.7377443	2.7870995	2.6956001
5.90	1.5717746	1.9880185	2.2927838	2.4718894	2.5209090	2.4434218
6.25	1.3677416	1.7396843	2.0145332	2.1797912	2.2313765	2.1721180
6.55	1.2007953	1.5386105	1.7910571	1.9468217	2.0019900	1.9587223
6.90	1.0188273	1.3207691	1.5500686	1.6965743	1.7564703	1.7311535
7.20	8.7561295^{-3}	1.1498053	1.3613208	1.5008664	1.5646643	1.5535122
7.85	6.0893494	8.3109962^{-3}	1.0090332	1.1349603	1.2051781	1.2193896

TABLE III. (cont.).

$B^3_{3d,4p}$

r = 3.70

Z3d\Z4p	3,0	3.25	3.50	3.75	4.00	4.25
3.65	2.6984103^{-2}	3.4380364^{-2}	3.9795297^{-2}	4.2941128^{-2}	4.3736100^{-2}	4.2266237^{-2}
4.00	2.6013043	3.2633050	3.7349783	3.9920893	4.0290073	3.8551335
4.30	2.4778340	3.0768980	3.4951887	3.7119446	3.7232559	3.5387644
4.60	2.3259332	2.8670517	3.2389221	3.4237585	3.4189457	3.2339659
4.95	2.1240008	2.6044948	2.9308458	3.0881244	3.0746613	2.8993801
5.25	1.9387226	2.3731227	2.6670983	2.8076574	2.7935870	2.6330481
5.60	1.7179251	2.1047994	2.3674646	2.4946991	2.4854846	2.3468940
5.90	1.5310566	1.8819194	2.1222017	2.2418620	2.2398354	2.1221928
6.25	1.3217796	1.6353625	1.8535259	1.9673079	1.9754511	1.8828276
6.55	1.1533336	1.4384298	1.6402356	1.7505275	1.7678159	1.6959822
6.90	9.7226815^{-3}	1.2275690	1.4125407	1.5196656	1.5471572	1.4978328
7.20	8.3149940	1.0637990	1.2357848	1.3404569	1.3757864	1.3437702
7.85	5.7323146	7.6237436^{-3}	9.0943030^{-3}	1.0083328	1.0566566	1.0549648

$B^3_{3d,4p}$

r = 3.80

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.7763338^{-2}	3.4145998^{-2}	3.8444840^{-2}	4.0456773^{-2}	4,0175875^{-2}	3.7750493^{-2}
4.00	2.6413797	3.2054385	3.5721451	3.7250265	3.6652628	3.4076961
4.30	2.4897023	2.9956059	3.3161976	3.4377926	3.3625522	3.1048897
4.60	2.3143750	2.7682114	3.0503995	3.1495257	3.0682979	2.8203202
4.95	2.0914481	2.4922672	2.7385753	2.8209502	2.7422853	2.5148791
5.25	1.8933842	2.2548569	2.4768512	2.5512288	2.4806967	2.2762511
5.60	1.6631051	1.9848021	2.1843423	2.2546438	2.1979449	2.0236254
5.90	1.4720702	1.7640955	1.9482149	2.0179746	1.9750867	1.8275373
6.25	1.2616352	1.5232745	1.6925731	1.7636048	1.7374137	1.6204011
6.55	1.0946413	1.3332056	1.4916968	1.5645127	1.5521182	1.4596612
6.90	9.1731279^{-3}	1.1317915	1.2791317	1.3540238	1.3563060	1.2898191
7.20	7.8092575	9.7679046^{-3}	1.1153946^{-}	1.1916437	1.2048994	1.1580238
7.85	5.3396273	6.9469164	8.1587268^{-3}	8.9284354^{-3}	9.2418823^{-3}	9.1108213^{-3}

Table III. (cont.).

$B^{3}_{3d,4p}$

r = 3.90

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.8098536^{-2}	3.3487490^{-2}	3.6730412^{-2}	3.7704361^{-2}	3.6472447^{-2}	3.3236730^{-2}
4.00	2.6412109	3.1110624	3.3802346	3.4394800	3.2960266	2.9693215
4.30	2.4657035	2.8833504	3.1144853	3.1519019	3.0030896	2.6863907
4.60	2.2716602	2.6439736	2.8451923	2.8696221	2.7245921	2.4270110
4.95	2.0332418	2.3607802	2.5359015	2.5540942	2.4220786	2.1548269
5.25	1.8268640	2.1220569	2.2808081	2.2992191	2.1832470	1.9460797
5.60	1.5918157	1.8550289	1.9998043	2.0226269	1.9283968	1.7282141
5.90	1.4001261	1.6398752	1.7757335	1.8043124	1.7295650	1.5608587
6.25	1.1919856	1.4079304	1.5356475	1.5717591	1.5191315	1.3852612
6.55	1.0288503	1.2267880	1.3486705	1.3910804	1.3560133	1.2495154
6.99	8.5747516^{-3}	1.0365783	1.1523152	1.2012026	1.1843368	1.1062696
7.20	7.2692565	8.9138217^{-3}	1.0020651	1.0554480	1.0519629	9.9506336^{-3}
7.85	4.9327130	6.2971419	7.2935975^{-3}	7.8869489^{-3}	8.0707444^{-3}	7.8609364

$B^{3}_{3d,4p}$

r = 4.00

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.8045734^{-2}	3.2476507^{-2}	3.4735239^{-2}	3.4773632^{-2}	3.2716198^{-2}	2.8810270^{-2}
4.00	2.6069200	2.9875662	3.1674385	3.1438967	2.9294402	2.5472900
4.30	2.4121214	2.7474014	2.8978261	2.8620114	2.6520080	2.2892884
4.60	2.2040133	2.5012733	2.6304427	2.5909019	2.3938562	2.0587751
4.95	1.9553109	2.2163674	2.3290975	2.2932593	2.1187330	1.8224841
5.25	1.7446904	1.9804429	2.0844127	2.0563524	1.9048477	1.6446750
5.60	1.5090136	1.7204018	1.8183249	1.8022806	1.6792839	1.4616387
5.90	1.3196579	1.5134971	1.6084423	1.6036618	1.5048465	1.3223243
6.25	1.1166305	1.2928146	1.3855874	1.3936791	1.3213548	1.1768262
6.55	9.5924612^{-3}	1.1220642	1.2133652	1.2315205	1.1796857	1.0644798
6,90	7.9548920	9.4420376^{-3}	1.0336729	1.0618974	1.0309163	9.4573028^{-3}
7.20	6.7179973	8.0939470	8.9693407^{-3}	9.3216595^{-3}	9.1631914^{-3}	8.5321690
7.85	4.5271202	5.6850802	6.5033987	6.9561600	7.0426820	6.7816030

TABLE III. (cont.).

B^3
3d,4p
r = 4.10

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.7660162^{-2}	3.1180573^{-2}	3.2534850^{-2}	3.1743096^{-2}	2.8983254^{-2}	2.4539564^{-2}
4.00	2.5443301	2.8416963	2.9409714	2.8454330	2.5720873	2.1471023
4.30	2.3347737	2.5942416	2.6728774	2.5744683	2.3148441	1.9178731
4.60	2.1170444	2.3461355	2.4121172	2.3187955	2.0805268	1.7186849
4.95	1.8628591	2.0643726	2.1232096	2.0427736	1.8354625	1.5196413
5.25	1.6516043	1.8347024	1.8919081	1.8260409	1.6477384	1.3728502
5.60	1.4188474	1.5848463	1.6432484	1.5960483	1.4518714	1.2237928
5.90	1.2342821	1.3882501	1.4489799	1.4177305	1.3015044	1.1111973
6.25	1.0385929	1.1805299	1.2443093	1.2303672	1.1439958	9.9382234^{-3}
6.55	8.8838180^{-3}	1.0211225	1.0871727	1.0863402	1.0226252	9.0296364
6.90	7.3341244	8.5623490^{-3}	9.2409298^{-3}	9.3616975^{-3}	8.9518815^{-3}	8.0638283
7.20	6.1724627	7.3202528	8.0055080	8.2157805	7.9691400	7.3057281
7.85	4.1336510	5.1169109	5.7886430	6.1302555	6.1453044	5.8538825

B^3
3d,4p
r = 4.20

Z3d\Z4p	3.0	3.25	3.50	3.75	4.00	4.25
3.65	2.6995030^{-2}	2.9662253^{-2}	3.0196800^{-2}	2.8680331^{-2}	2.5336166^{-2}	2.0477317^{-2}
4.00	2.4588578	2.6795016	2.7070529	2.5500177	2.2291154	1.7727257
4.30	2.2389377	2.4295232	2.4452432	2.2943379	1.9957125	1.5749375
4.60	2.0157407	2.1836887	2.1950736	2.0574623	1.7877043	1.4084487
4.95	1.7603642	1.9092123	1.9221961	1.8057652	1.5742454	1.2468859
5.25	1.5515991	1.6886141	1.7064947	1.6105901	1.4130699	1.1304038
5.60	1.3247070	1.4514069	1.4769633	1.4053956	1.2464988	1.0137445
5.90	1.1468887	1.2665983	1.2991200	1.2473868	1.1193253	9.2609946^{-3}
6.25	9.6022400^{-3}	1.0729473	1.1129864	1.0821269	9.8637219^{-3}	8.3451189
6.55	8.1818869	9.2539070^{-3}	9.7084085^{-3}	9.5547098^{-3}	8.8386195	7.6305319
6.90	6.7275756	7.7368054	8.2393814	8.2363503	7.7596056	6.8621911
7.20	5.6447198	6.5999205	7.1302629	7.2311253	6.9245411	6.2512280
7.85	3.7594999	4.5954557	5.1470944	5.4015836	5.3654243	5.0592919

TABLE IV. $G^{o}_{4s,\,4s}$ $Z_{4s} = 2.50 \longrightarrow 5.00$

$r = 3.20 \longrightarrow 4.20.$

$G^{o}_{4s,4s}$

$r\backslash Z_{4s}$	2.5	3.0	3.5	4.0	4.5	5.0
3.0	1.2358037^{-1}	1.4507007^{-1}	1.6506257^{-1}	1.8316303^{-1}	1.9988902^{-1}	2.1605411^{-1}
3.1	1.2311615	1.4440270	1.6398410	1.8166741	1.9815977	2.1427314
3.2	1.2266652	1.4371226	1.6287439	1.8018625	1.9651388	2.1260632
3.3	1.2222409	1.4299739	1.6174061	1.7873932	1.9495101	2.1103502
3.4	1.2178476	1.4225474	1.6059515	1.7733079	1.9347736	2.0954624
3.5	1.2134090	1.4148221	1.5944763	1.7597468	1.9208471	2.0811966
3.6	1.2089172	1.4069085	1.5830696	1.7467901	1.9077159	2.0673003
3.7	1.2042900	1.3987990	1.5718371	1.7344026	1.8952514	2.0536707
3.8	1.1995494	1.3905287	1.5608405	1.7226275	1.8832902	2.0400700
3.9	1.1946521	1.3821598	1.5501474	1.7114611	1.8718027	2.0263017
4.0	1.1895853	1.3737227	1.5397784	1.7008505	1.8605703	2.0122518
4.1	1.1843818	1.3652961	1.5298223	1.6907463	1.8495450	1.9977786
4.2	1.1790184	1.3569169	1.5202631	1.6810628	1.8385419	1.9827486
4.3	1.1735384	1.3486560	1.5111100	1.6717511	1.8274220	1.9671792
4.4	1.1679277	1.3405449	1.5023580	1.6627185	1.8161439	1.9509340
4.5	1.1622300	1.3325934	1.4939921	1.6538403	1.8045800	1.9340173
4.6	1.1564406	1.3248458	1.4859816	1.6451154	1.7926855	1.9164152
4.7	1.1506124	1.3173405	1.4783385	1.6364200	1.7803576	1.8981570
4.8	1.1447689	1.3100926	1.4709300	1.6276693	1.7675885	1.8792737
4.9	1.1389117	1.3030827	1.4637955	1.6188378	1.7543392	1.8598124
5.0	1.1330850	1.2963246	1.4568376	1.6098014	1.7406156	1.8398113

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SCATTERING OF 20 MeV α-PARTICLES

BY

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CONTENTS

Synopsis

Focusing and analyzing magnets for bringing the external cyclotron beam to a shielded room were constructed. An ionization chamber for detecting scattered α's was constructed and the set-up was found to give a resolution of about 1 $^0/_0$ in energy.

The energy spectra of scattered α's were measured at 45°, 90°, and 135° for a number of elements. Peaks due to direct interaction processes were observed in all elements except the heaviest, where the α-particles cannot penetrate the barrier. Energy distributions corresponding to α-particles evaporated from the compound nucleus were observed for Ni, Cu, and Zn. From the shape of the spectra the level density for these elements was found, for excitation energies E^* in the region 4—11 MeV, to be proportional to exp $(E^*/_T)$ with T = const. rather than to exp $\sqrt{aE^*}$. This does not agree with the simple Fermi gas theory, but is consistent with recent theories taking into account the fact that the nucleons at low excitation energies cannot be regarded as free Fermi gas particles.

The cross section for evaporated α-particles was found to be almost the same at the three angles in high contrast to the single peaks due to direct interactions. Using the experimentally determined level density functions, the cross sections for (α, α') compound nucleus scattering were calculated by means of the statistical theory. The calculated cross sections agree with the measured values within a factor of two.

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1. Introduction

An abundance of information accumulated in the past ten years has clearly shown that the well-known theory of nuclear reactions based upon compound nucleus formation is quite inadequate to account for many of the phenomena observed, and a number of theories have been developed to account for special cases of so-called direct interactions, especially Butler's theory(1) of the stripping reaction and its extension to include various other types of stripping and pickup reactions. In many cases, these theories have had outstanding success, and no one can seriously doubt the validity of the mechanisms postulated in those cases. As matters now stand, additional explorations of direct interaction processes are vigorously under way in many laboratories. The results to be described below give evidence of the importance of both the compound nucleus mode and a direct interaction mode of inelastic scattering of α-particles from nuclei.

The original motivation for our efforts came from the work of Cohen(2) on the inelastic scattering of 23 MeV protons from medium Z and high Z nuclei, experiments which showed, among other things, a systematic enhancement of the intensity of scattered protons leaving the target nucleus with an excitation of 2 to 3 MeV. We started out to see whether similar results would be obtained in a study of the inelastic scattering of 20 MeV α-particles. Of course, the higher Coulomb barrier in our case would prevent us from obtaining comparable data above the medium region, but we hoped to shed some light upon the mystery posed by the proton work. As it turned out, our work, which covered relatively few nuclei in the medium Z range, yielded results similar to Cohen's in showing strong α-particle groups apparently corresponding to individual low-lying excited states, and in showing the onset of a continuum smoothly rising with increasing energy of excitation of the residual nucleus, but it cannot be said to reproduce the regularities in the intensity patterns found for various nuclei in the proton case.

2. Experimental Arrangement

The overall arrangement of the experimental apparatus is shown in Fig. 1. The 20 MeV deflected, analyzed, and focused α-particle beam of the Copenhagen cyclotron was used. The particle detector was an ionization chamber featuring fast electron collection and a Frisch grid. The scattering chamber had ports for supporting the ionization chamber at an angle of observation of 45°, 90°, or 135°. The beam was collected in a Faraday cup connected to an accurate and stable electronic integrator circuit.

Beam Handling System

Before the experiments could be undertaken it was necessary to obtain a deflected beam and to prepare a magnet system for handling it. This work required several months.

When the Copenhagen cyclotron was rebuilt, an internal deflector was installed inside one of the dees, but, up to the time when our plans began to develop, it had never been put into service. After some weeks of careful adjusting of the position controls of the deflector system, a fairly satisfactory set of operating conditions was found and a beam of 5 to 10 microamperes of α-particles was obtained at the opening in the stem of the second dee through which the deflected beam passed after leaving the dee containing the deflector plates. There was some trouble with deflector sparking, especially at the beginning of operation when a conditioning period of five to ten minutes was required before the full 40 to 50 KV potential difference could be applied.

The beam emerged from the dee chamber through a special valve and lock system just before the horizontal center line on Fig. 1. Ray-tracing experiments showed that it was diverging horizontally as if the rays came from a fairly well defined virtual source about 70 cm behind the exit port. To reduce the spreading of the beam a special lens was installed.

Gradient lens 1 has a focusing action on the horizontal motion of the particles. Its pole tips have flat surfaces tilted together at large radii. Flux for its field comes from the poles of the cyclotron through two stacks of iron flux bars trimmed empirically to terminate at such spots on the outer surfaces of the pole pieces of the gradient lens that the desired approximately constant gradient field distribution was obtained in the gap. Ray-tracing experiments showed that most of the particles emerging from gradient lens

1 were moving almost exactly parallel to each other horizontally, while diverging slightly vertically.

To cause the beam to converge horizontally, as well as to bend the beam into a more favourable direction for later use, gradient lens 2 was added.

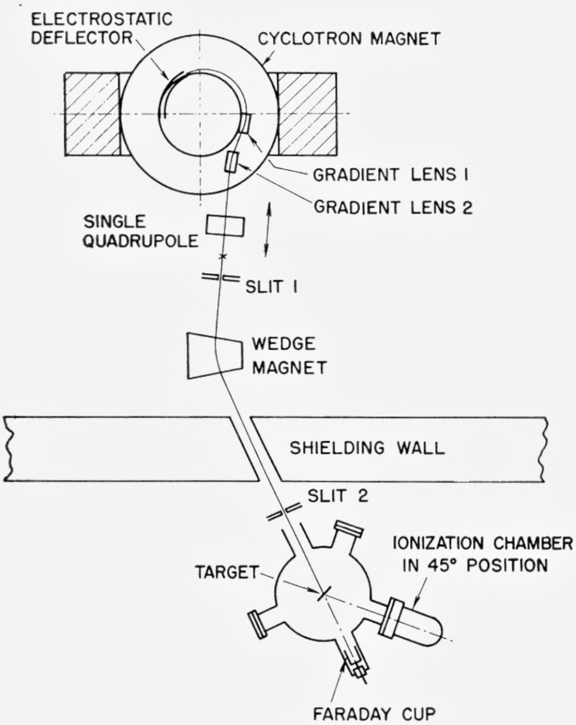

Fig. 1. Overall experimental arrangement, not drawn to scale.

This is a complete magnet situated between the coil tanks of the cyclotron magnet. Its field is in the reverse direction. Experience showed that the magnet could not function if placed within about 30 cm of the cyclotron magnet poles, apparently because of saturation effects. The position finally chosen is the closest one feasible. The current for the coils of gradient lens 2 comes directly from the cyclotron generator; in fact, the coils (of copper strips, 3 × 30 mm^2) are connected directly in series with the cyclotron magnet coils.

So far as the horizontal motion was concerned, gradient lenses 1 and 2 had the effect of producing a focus at the position indicated by the small x in Fig. 1. The fluorescent spot actually observed there on a quartz plate had a width of the order of 3 mm with a total vertical extent of about 5 cm. A vertical line of some sort was, of course, to be expected as a consequence of the slight initial vertical divergence of the beam and the inevitable vertical defocusing in gradient lenses 1 and 2. To complete the condensing of the beam a single quadrupole lens with hyperbolic pole tips was added. This lens has a defocusing action in the horizontal direction and a focusing action in the vertical direction. It was mounted on a cart which could easily be moved back and forth parallel to the direction of the beam; the adjustable position was necessary so that the relative effect of the quadrupole lens in the horizontal and vertical directions could be varied. This, together with a variation in the magnetizing current, permitted us to focus the beam as a spot centered on a predetermined point, the center of slit 1 in Fig. 1. The spot turned out to be somewhat fuzzy. It was about 7 mm wide and 12 mm high as judged by observations on a fluorescent plate.

Shortly after this part of the system was completed, some successful preliminary experiments were made with a scattering chamber placed inside the cyclotron room, just past slit 1, but as soon as possible the beam was brought through the shielding wall into an experimental room where the final measurements were made.

The wedge magnet was designed, according to the method of Cross(3), to have the same focal length in the vertical and horizontal directions and to focus an image of slit 1 at the position of slit 2. Of course, what is to be expected at slit 2 is a blurred energy spectrum of the α-particles emerging from slit 1, spread out in the horizontal direction. The particles passing through slit 2 should have a restricted energy spread, which in this case was to be of the order of a few tenths of a percent, the best figure being about 0.2 $^0/_0$ for very narrow slits. No measurement of the actual spread was ever made; the resolution of our ionization chamber spectrometer was insufficient to show the existence of an energy spread.

Because the magnet was designed by a simple method which could not take into proper account fringing field effects, especially those due to the rather extended air-cooled coils, it was mounted on a base which could be moved roughly at right angles to the direction of the beam, and in addition could be rotated. In making the final adjustments on the beam system we used both of these motions, together with variations in the positions of slit 2 (both directions) and the two controls for the quadrupole lens. We were never able to show that the wedge magnet worked as planned, but the quadrupole magnet gave an independent control of the vertical focal position, and a satisfactory current of the order of 0.1 microampere was obtained.

Unfortunately this much current could not always be obtained. A loss of current was sometimes accompanied by a lateral motion of the condensed beam across slit 1. A variable resistor shunted across the coils of gradient lens 2 helped to minimize the trouble, but was not sufficient. The most likely explanation for the variation in intensity is that very small variations in the positions and shapes of the iron vacuum chamber lids of the cyclotron from one period of use to another produced changes in the magnetic field of the cyclotron which, in turn, caused (a) a change in the radial oscillations of the particles while they were rotating, and (b) small variations in the trajectories of the particles after deflection. Similar effects have been observed elsewhere. This effect could presumably be reduced greatly by securing better the "fixed" spacing of the lids with respect to the magnet pole tips*.

The Ionization Chamber

The scattered α-particles were observed by means of a fast, electron collection type ionization chamber having the geometry shown approximately to scale in Fig. 2**. α-particles scattered from the foil in the center of the scattering chamber passed through a 1.2 mg/cm^2 mylar window coated on its inner surface with an electrically grounded semi-transparent evaporated film of aluminum. The window was tilted so that the particles entered at an angle of 23° with respect to the normal to its surface. The tilt was an unnecessary refinement added for reasons independent of this experiment. The collector was a ski-shaped strip of brass about 1 cm wide, supported by its connecting electrode. The grid was a 0.2 mm wire wound back and forth in 0.3 mm slots milled in a brass frame with a center-to-center spacing of 3 mm. The size of the opening in the frame was 4.0 cm × 12.5 cm. The grid structure was supported by its connecting electrode. The insulators were made of Teflon (CF_4). Another insulator (not shown) prevented accidental rotation of either the collector or the grid.

* W. P. Alford has shown that similar symptoms observed in the behaviour of the variable energy cyclotron at the University of Rochester were associated with changes in the lid positions and with quite strong variations in the amplitude of radial oscillations. Secure wedging of the lids cured the trouble.

** For a description of the operating principles of this kind of chamber, see Rossi and Staub, "Ionization Chambers" The McGraw-Hill, New York (1949) or Handbuch der Physik, XLV, Ch. 1; J. Springer, Berlin (1958).

The window was held in a special removable frame. The window-to-frame and frame-to-chamber seals were made with O ring gaskets, as were all the other removable seals. The window was supported by a polished brass surface containing 73 1 mm diameter holes drilled parallel to the direction of the scattered beam in a regular pattern, all lying within a 1.5 cm diameter circle.

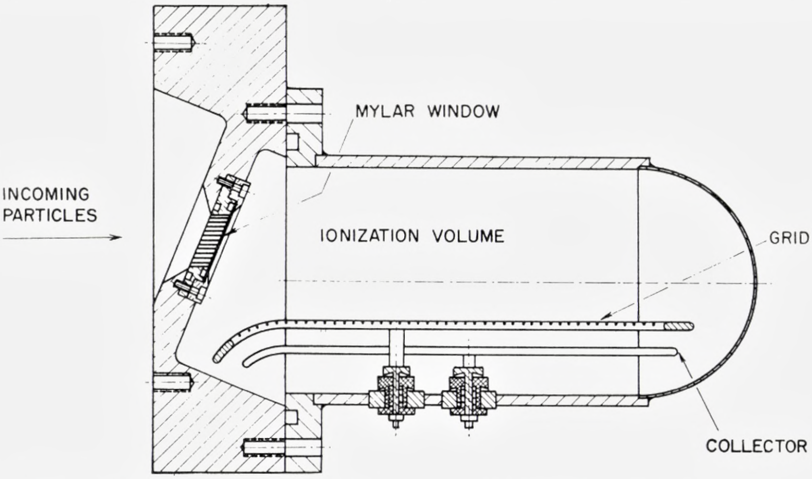

Fig. 2. Gridded ionization chamber used as the charged particle detector.

A hot calcium purifier (not shown) was connected by means of $^1/_4$ inch copper tubing to the top and bottom of the cylindrical section of the chamber wall so that the filling gas could circulate by thermal convection. The purifier was very effective in cleaning the gas, especially just after the chamber had been worked on, then reassembled. Even though meticulous care was taken in cleaning all chamber parts with organic solvents and with a water solution of detergent, the behaviour of the ionization chamber suggested that electronegative gases given off by the walls were steadily removed by the action of the purifier during the first day or so of its operation.

Various gases and mixtures were employed. The mixture most commonly used was argon plus 5 to 20 $^0/_0$ of CH_4. The pressure was ordinarily about 3 atmospheres. The grid was maintained at about +1500 volts, the collector at about +3000 volts. Under these conditions, good saturation curves were obtained after purification, there was no noticeable loss of electrons to the grid wires, and the pulse height resolution was excellent.

The preamplifier of an EKCO Type N568 amplifier was attached directly to the ionization chamber by means of a shield. The input wiring of the preamplifier was modified slightly to reduce capacitance. The amplifier proved exceptionally fine for our purposes. Its output was connected to a 99 channel Philips Balham pulse height analyzer.

The stability of the system against both long- and short-time drift of calibration was excellent. Careful measurements made with the help of a pulser based on a vibrating mercury relay showed an accurately linear input pulse height *vs* output pulse height relationship. All our experience with α-particles indicated that a linear relationship also exists between the energy lost by α-particles in the $A + CH_4$ mixture and the number of electrons collected, but this relationship was not the subject of an especially careful investigation.

The resolving power of the system was investigated by means of 5 MeV protons from the cyclotron scattered from a thin Al foil. Peaks from elastic scattering and inelastic scattering with the excitation of the states at 0.84 and 1.01 MeV were sharply resolved, with widths of about 80 keV (full width at half-maximum). With 8.8 MeV α's from a ThC' source or 20 MeV α's from the cyclotron the width was about 130—200 keV.

In most experiments, a continuous low-lying spectrum of pulses due to fast protons entering the chamber through the window, or generated in the chamber by neutrons passing through it (in many cases recoil protons from the CH_4 gas), was observed. The highest pulses of this sort were due to protons having just enough energy to traverse the length of the active volume of gas before coming to rest. Ordinarily, the corresponding energy limit was about 5 MeV.

3. Experimental Results

Carbon and Oxygen

The scattering from these substances has not been studied in detail, but, since both of them appear very frequently as impurities in targets, it was felt to be of some importance to know the rough appearance of the spectra. As an example, the spectrum obtained at 45° with a mylar target ($C_{10}\,(H_2O)_4$) is shown in Fig. 3. The peak indicated by an arrow on the right side of Fig. 3 was taken to be that due to elastic scattering from O^{16}. The expected positions for peaks corresponding to various known states of O^{16}, C^{12}, and C^{13} were then calculated. Some are indicated by arrows in Fig. 3. The peak at 6.1 MeV excitation may be due to either or both of the known levels in O^{16} at 6.05 and 6.13 MeV; the next peak similarly may be due to either or both of the levels at 6.9 and 7.1 MeV; and one we have attributed to the known level at 8.8 MeV. These assignments are strengthened by the fact that the four peaks disappear almost entirely if polystyrene is substituted for the mylar scattering foil.

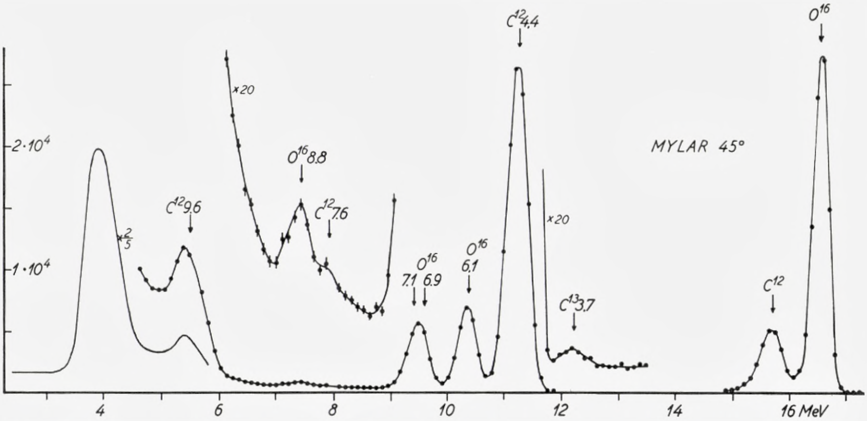

Fig. 3. Spectrum of α-particles scattered from a mylar foil 2.3 mg/cm². Scattering angle 45°. The abscissae are the energy dissipated by the scattered particles inside the ionization chamber, without corrections for absorption in the window of the ionization chamber and in the scattering foil.

In C^{12}, the first three known levels are 4.43, 7.6, and 9.6 MeV. They are all seen, the 4.43 MeV level very strongly, the corresponding peak being about five times higher than the elastic C^{12}-peak. The 9.6 MeV level also appears rather strongly, whereas the 7.6 MeV level is very weak. In fact, in the mylar curve, the latter is not even certainly detectable; however, when polystyrene is used as a target, the neighbouring O^{16}-peak has disappeared and now the C^{12}-level is clearly seen. To the right of the 4.43 MeV peak, a weak peak is seen; it is also seen in the polystyrene curve and we ascribe it to the second excited level in C^{13} (known levels in C^{13} are 3.09, 3.68, and 3.86 MeV in this region).

The position of the high peak at about 4 MeV depends on the pressure in the ionization chamber, which shows that it is caused by particles passing through the chamber. We think it is due to recoil protons from the hydrogen in the mylar target. Such protons would have about 6.3 MeV, but the range would be longer than the length of the ionization chamber, and hence only part of their energy would be spent in ionizing the gas in the ionization chamber.

Magnesium

Several preliminary short runs were made with a target of magnesium evaporated onto a thin gold foil. The well-known levels at 1.37 and

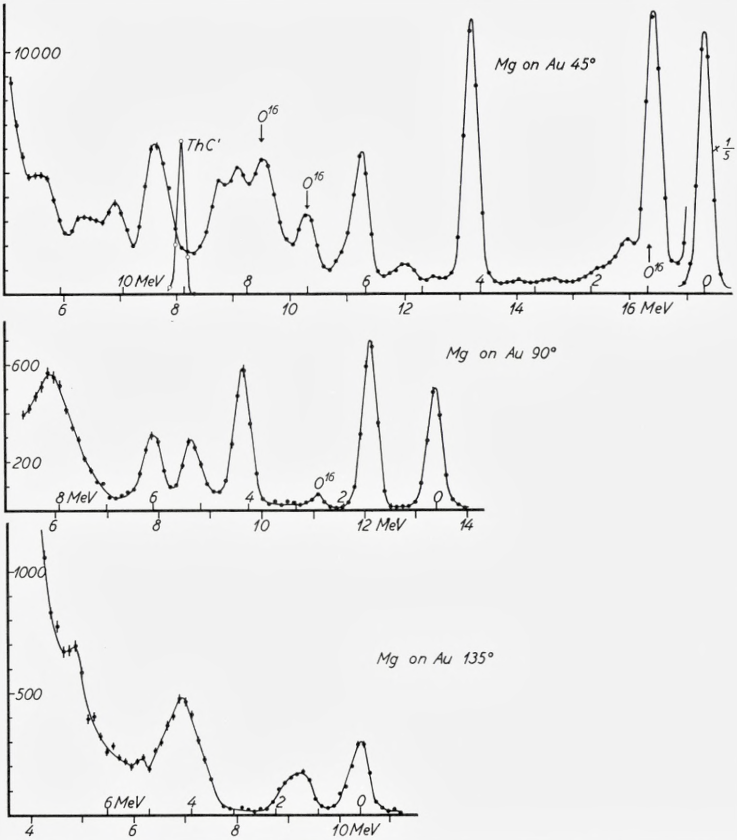

Fig. 4. Spectra of α-particles scattered from a layer of magnesium evaporated onto a 0.16 mg/cm^2 gold foil. The scale below the axis of abscissae gives the energy dissipated inside the ionization chamber. The scale above the axis gives the corresponding excitation energy of the residual nucleus, assuming that Mg^{24} is responsible for the scattering. For Mg^{26}, the scale values are 0.1—0.2 MeV too low. When calculating the scale, absorption in the chamber window and the scattering foil was taken into account. The scattering was assumed to take place in the mid-plane of the magnesium layer. Integrated doses of primary α's 50, 6, and 10 μ Coulomb for 45°, 90°, and 135°, respectively.

4.2 MeV in Mg^{24} are seen at all three angles (Fig. 4), though not with the same intensity ratio. In the 135° direction, these are the only ones visible above the proton background, whereas in the 90° direction three more peaks corresponding to higher excitation energies appear, and at 45° discrete peaks are seen for excitation energies up to more than 10 MeV.

At 45° the oxygen impurity in the target causes trouble. The two peaks corresponding to the 6 and 7 MeV levels in O^{16} are both too high as compared with the elastic peak, which shows that at least two peaks corresponding to levels in either of the magnesium isotopes in the region between 6.8—8 MeV have been concealed. The peak with $Q \sim 8.2$ MeV coincides rather closely with the expected position for a known level in Mg^{26} (8.28 MeV) and may perhaps be accounted for in this way. Also the peaks at excitation energies ~ 2.7 and 3.3 MeV may be ascribed to the less abundant isotopes $Mg^{25,\,26}$ (see Table 1). The peak at $Q = 6.06$ MeV almost coincides with the expected position for the 4.43 MeV level in C^{12}. However, a control run at 90° together with a comparison with mylar curves at 45° and 90° safely showed that not more than one third (probably much less) of the peak height could be due to carbon.

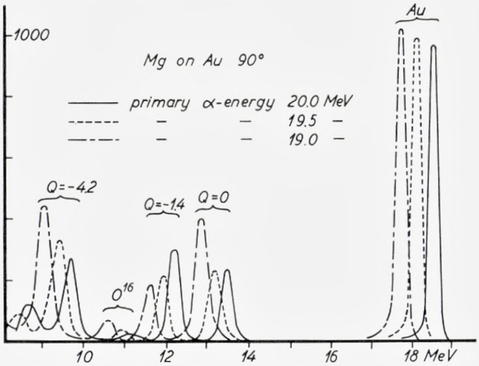

Fig. 5. Spectra of α-particles scattered from magnesium on gold at 90° for different energies of primary α-particles.

Though the present curves may be only of little value, a further study has been postponed to a later occasion, because it was felt that, in order to obtain more information, separated isotopes and, especially, more observation angles would be needed. To this decision also contributed the observation that the various peaks are strongly energy dependent. This is illustrated in Fig. 5 which shows the spectra obtained at 90° for slightly

Table 1. Magnesium on gold

Known levels in			Q-values of peaks found at		
Mg^{24} 79 %	Mg^{25} 10 %	Mg^{26} 11 %	45°	90°	135°
	0.58				
	0.98				
1.37			∼ 1.4	1.4	1.4
	1.61				
	1.96	1.83	(∼ 1.9)		
	2.57				
	2.74	2.97	∼ 2.7		
	2.80				
	3.40		∼ 3.3		
	3.90				
	3.97	3.97			
4.12	4.05		4.17	4.17	4.2
4.25	4.27	4.35			
	4.42				
	4.67				
4.8	4.86	4.86	∼ 4.8		
	4.96	4.92			
	5.15	5.27			
5.24	5.34	5.32	5.30	5.20	(5.2)
	5.54	5.50			
6.0	6.09	6.15	6.06	6.0	
	6.25				
6.4	6.54				∼ 6.6
6.9	6.95				
	7.04	7.29			
7.4					
		8.28	8.16	8.2	
8.5		8.55	∼ 8.5		
		8.93			
9.5			9.5		
		10.08	10.15		

All values in the table in MeV.

different energies of the incoming α-particles. They were degraded in energy by means of aluminum foils placed in the beam before it entered the scattering chamber. The height of the elastic Au-peak varies in the way to be expected from the Rutherford formula. But the heights of the three Mg-peaks vary in different ways.

Aluminum

The spectra obtained at three angles are shown in Fig. 6 and the results are summarized in Table 2. The small peak observed at 45° to the right of the elastic group is probably caused by an iron impurity in the target. As may be seen, the first five levels appear readily in all three directions. The next three levels give only a weaker response. For excitation energies higher than 4 MeV, the level spacing is so small that our energy resolution is insufficient to separate individual peaks and permit their assignment to known levels. For instance, looking at the peak at about 4.5—4.6 MeV, we cannot decide which of the three known levels 4.40, 4.50, and 4.58 MeV is responsible for it or whether more than one of these levels contribute to the spectrum. We cannot even know whether the same levels are responsible for corresponding peaks at different angles. However, peaks are seen up to excitation energies of 10 MeV and more, and since here the level spacing must be quite small, it is obvious that only a small fraction of the highly excited levels show up as single peaks. Therefore the fact that the Q-values corresponding to peaks in the 45°-curve and the 90°-curve are so closely the same seems to indicate that we have to do with the same levels, irrespective of the angle. An exception is the 4.81 MeV level, which is rather strong in the 135° direction, but hardly seen at the other angles. Another exception, the hump in the 135°-curve at about 7.2 MeV excitation energy, may be neglected, since it occurs in a position where the elastic peak from a possible C^{12} impurity would appear.

In Table 2 are given the ratios R_1 between the peak heights at 45° and 90° for some of the peaks. When calculating these values, the different effective thicknesses of the scattering foil at the two angles and the different channel widths were taken into account. The R_1-values show an interesting variation with the excitation energy. The ratios R_2 between peak heights at 90° and 135° are also given.

Nickel

Fig. 7 and Table 3 give the results for nickel. With two exceptions the peaks up to about 4 MeV correspond rather closely to known levels in Ni^{58},

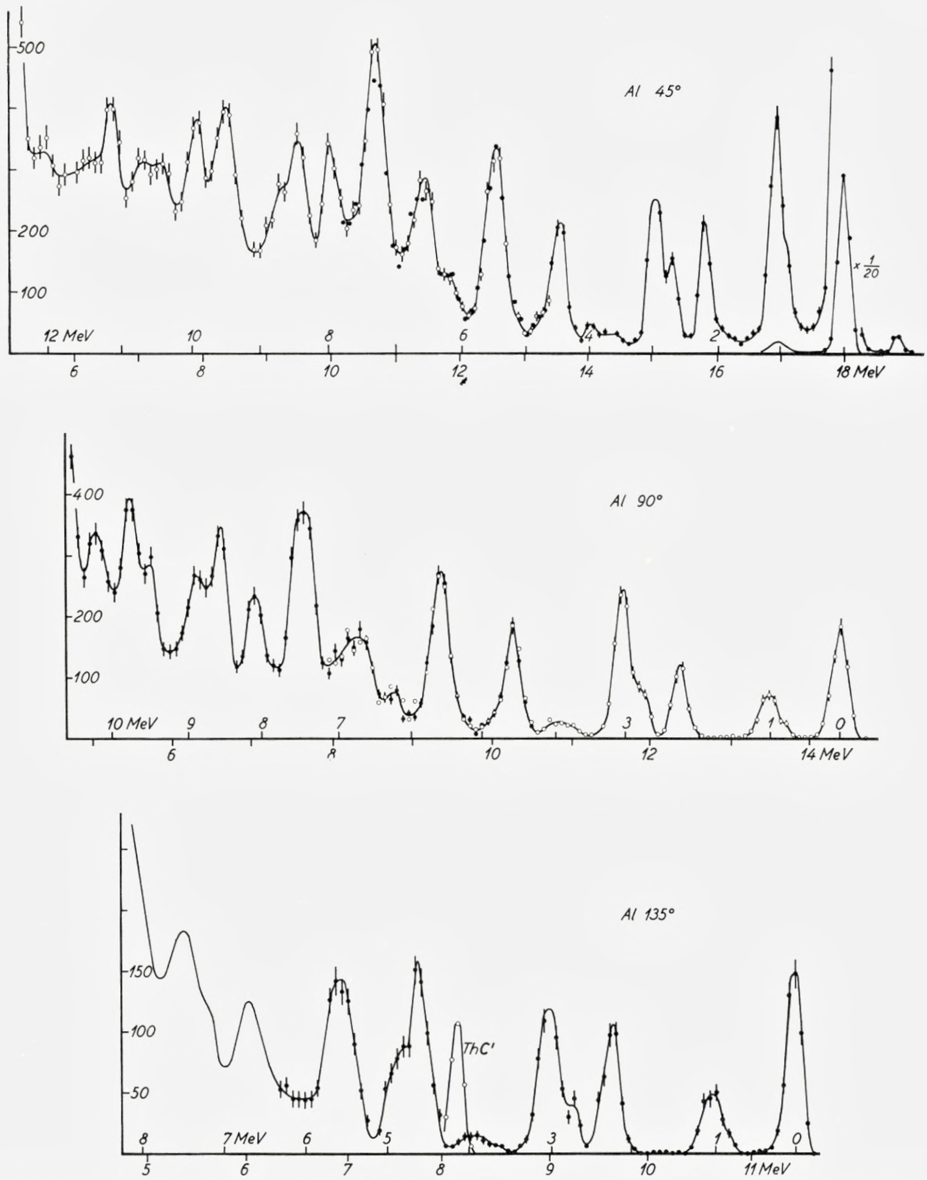

Fig. 6. Spectra of α-particles scattered from an aluminum foil 0.24 mg/cm^2. Integrated doses of primary α's 40, 40, and 30 μ Coulomb for 45°, 90° , and 135°, respectively. The steep rise in the curves in this figure and the following figures at the left end represents the inset of the proton background. The left part of the 135°-curve in this figure was obtained in a run with less dispersion and covering the whole spectrum.

TABLE 2. Aluminum

Known levels	*Q*-values of peaks				
	45°	90°	135°	R_1	R_2
	0	0	0	35	0.55
0.84	~ 0.8	~ 0.8	~ 0.8		
1.01	1.06	1.03	1.03	5.8	0.7
2.21	2.20	2.17	2.22	2.0	0.55
2.73	2.7	~ 2.7	~ 2.7	2.3	0.9
3.00	2.95	3.02	3.02	1.2	0.9
3.68	~ 3.7				
3.95 4.05	~ 4.0	~ 4	~ 3.9		
4.40 4.50 4.58	4.5	4.6	4.6	1.1	0.55
4.81	~ 4.8				
5.15 5.24					
5.41 5.42 5.49 5.55 5.62	5.5	5.6	5.6	1.3	0.9
5.88					
	~ 6.2	6.2			
	6.6	6.8	6.7	1.8	0.55
			7.2		
	7.3	7.4	7.5	1.5	
	8.0	8.1		1.6	
8.53 8.58 8.69	8.6	8.6		1.1	
8.89 8.94 9.03	~ 8.9	8.8			
9.06 9.17 9.21 9.23					
9.38 9.46 9.50 9.62 9.66	9.5	9.5		1.6	
	9.9	9.8		1.1	
		10.2			

$$R_1 = \frac{\text{peak height at } 45^\circ}{\text{peak height at } 90^\circ} \qquad R_2 = \frac{\text{peak height at } 90^\circ}{\text{peak height at } 135^\circ}$$

All other values in the table in MeV.

which would be expected, since it is the most abundant isotope (68 $^0/_0$). However, some of the peaks might just as well partly or totally be due to levels in other isotopes. Only in three cases can a safe correlation be established. In the 45-curve a bump is seen for $Q \sim 0.7$ MeV; it has appeared in several runs and we believe it to be real. It is probably due to the known level in Ni^{61}. In the 90°-curve the 1.33 MeV level in Ni^{60} appears. The 1.45 MeV level in Ni^{58} is seen at all three angles.

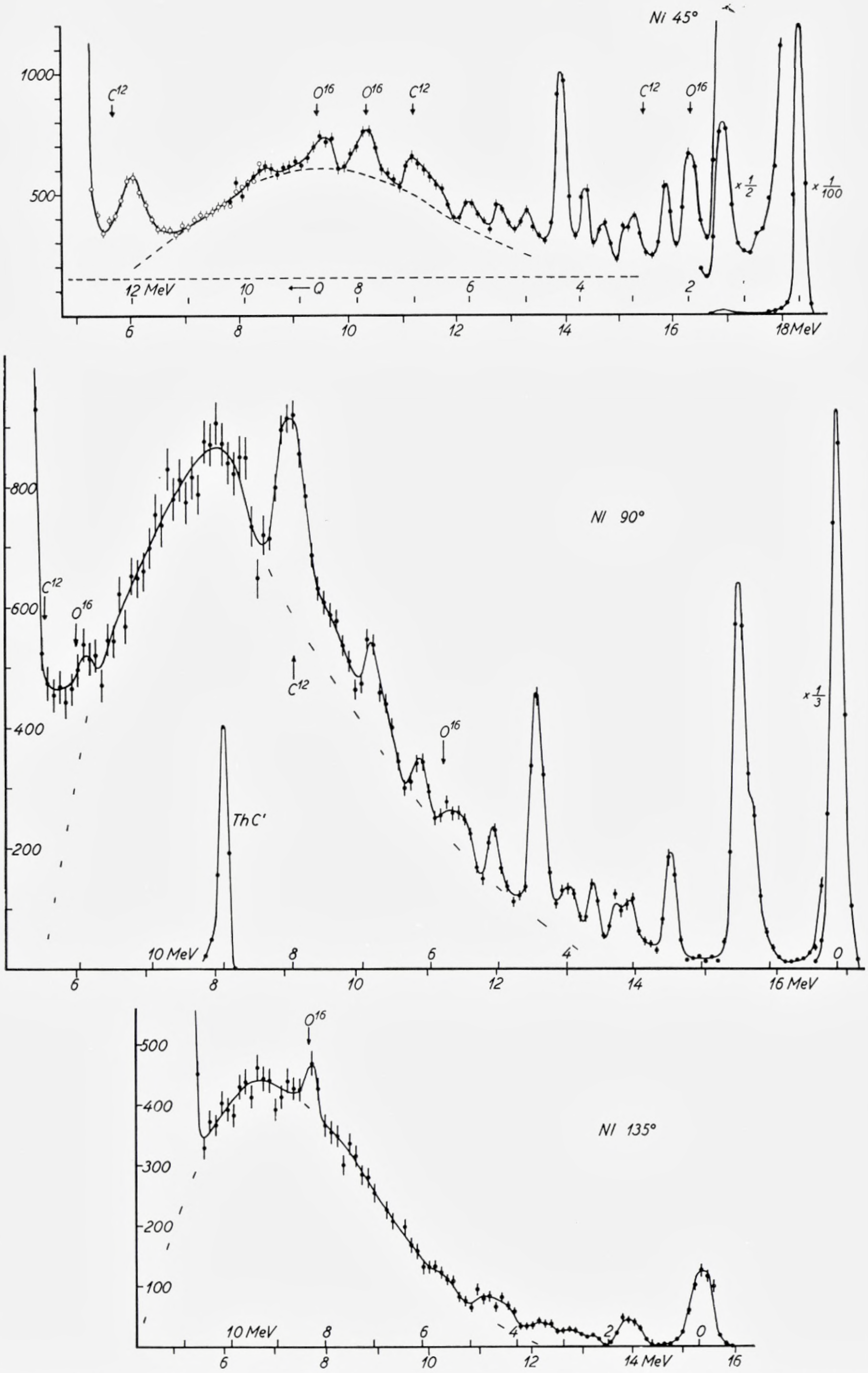

Fig. 7. Spectra of α-particles scattered from a nickel foil. Target thickness 0.5 μ for 45° and 90°, and 1.25 μ for 135°. Integrated doses of primary α's 100, 300, and 40 μ Coulomb for 45°, 90°, and 135°, respectively.

TABLE 3. Nickel

Known levels in			Cohen's peaks	Q-values of peaks		
Ni^{58} 68 %	Ni^{60} 26 %	Ni^{61} 1 %		45°	90°	135°
		0.7		~ 0.7		
	1.33				~ 1.3	
1.45			1.51	1.43	1.45	~ 1.55
	2.16					
	2.28					
2.46	2.50		2.50	2.44	2.44	
	2.62					
2.77						
2.90						
2.94						
3.04	3.12			3.00	3.03	
3.26	3.18		3.20	~ 3.2	3.27	
3.42	3.19					
	3.26					
	3.31					
	3.39					
3.52	3.59			3.6	3.6	
3.59	3.62					
3.63	3.67					
	3.73					
3.77	3.87			3.9	4.0	
3.90	3.89					
4.11	3.92					
	4.00					
	4.04					
	4.08					
				4.35	4.4	
				5.0	5.1	
				5.5	5.7	
				6.0	6.15	
				~ 6.7	6.9	

All values in the table in MeV.

In the 45°-curve, O^{16} gives a high elastic peak and two smaller peaks due to the excited states. The heights of the latter may be estimated from the height of the former, and thus a rough correction indicated by the dotted line can be performed. The arrows show the positions in which the various carbon and oxygen peaks should appear. The 4.43 MeV level in C^{12} is clearly seen; the elastic peak has a height only one fifth of the former and hence cannot be observed. The peak at about 6 MeV is not understood. Since we did not see it when using another Ni target it is probably due to some unknown impurity.

In the 90°-direction the elastic peak from C^{12} is quite strong, whereas O^{16} is hardly seen. In the 135°-direction the oxygen elastic peak clearly appears.

As will be seen later, a strong elastic peak is always accompanied by a tail which for lower energies runs almost horizontal with a height $\sim 0.1\ {}^0/_0$ of the elastic peak. The correction is indicated by the dashed line.

The most pronounced feature of the curves, especially in the backward direction and the 90°-direction, is the broad "continuous" distribution of α-particles with energies between 5 and 14 MeV emphasized by the more or less arbitrarily drawn dotted lines. Another striking feature is the absence of high peaks in the backward direction. Though the experimental arrangement may be partly responsible for the difference between forward and backward angles, a thicker target and reflection geometry having been used in the latter case, it is at the first sight evident that the relative intensity of the single peaks as compared to the intensity of the broad continuous distribution is very much smaller at 135° than at the other angles.

In Table 3 and the following tables our peak positions are compared with Cohen's results(5). He used 23 MeV protons and measured the energy of the scattered protons by means of a magnetic spectrometer with a resolution about twice as good as ours. In Ni the agreement is not particularly good, since we find more levels than he does, some of which are relatively rather strong.

Copper

The results for copper given in Fig. 8 and Table 4 are similar to those for nickel. In an experiment in which an absorber of 11 mg/cm² Al was placed between target and ionization chamber, it was determined that the broad continuous distribution was caused by α-particles. The absorber made the whole spectrum move far to the left, which would not have been

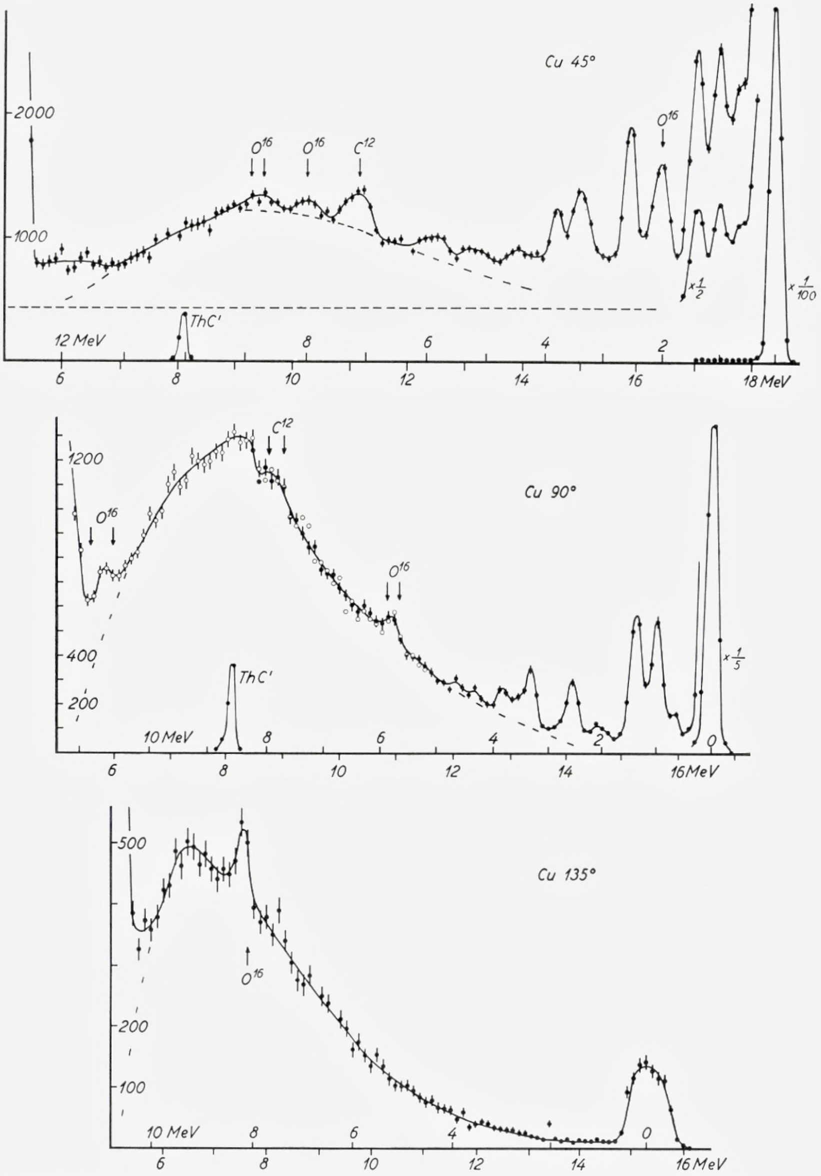

Fig. 8. Spectra of α-particles scattered from a copper foil 2.5 μ. Integrated doses of primary α's 60, 114, and 40 μ Coulomb for 45°, 90°, and 135°, respectively. The two sets of arrows in the 90°-curve give the expected positions for peaks due to oxygen and carbon impurities, assuming that (1) the impurities are located to a surface layer on the side of the foil looking away from the cyclotron or (2) that they are uniformily distributed in the foil.

TABLE 4. Copper

Known levels (4) in		Cohen's peaks	Q-values of peaks		
Cu^{63} 69 $^0/_0$	Cu^{65} 31 $^0/_0$		45°	90°	135°
0.67	0.77	0.70	~ 0.7	~ 0.7	
0.96	1.11	1.01	1.00	0.98	
1.33 1.41		1.38	1.37	1.34	
1.55 1.86	1.48 1.62 1.77				
2.01 2.06 2.08 2.09 2.21	2.09 2.10 2.21	1.97	(O^{16})	2.1	
2.34	2.28 2.35				
2.40 2.49 2.50 2.51 2.53 2.54	2.40 2.53 2.59 2.65	2.51	2.52	2.55	
17 levels	levels < 3.17				
3.21 3.22 3.25 3.29 3.31 3.37 3.40 3.42 3.43 3.46 3.48		3.26	3.4	3.33	
		3.72	3.8	3.85	
			~ 4.4	~ (4.35)	
				~ (4.65)	
			~ 5.2		
			~ 5.9	(O^{16})	

All values in the table in MeV.

the case had it been due to singly charged ions. Note the almost complete absence of any indication for single inelastic peaks at 135°. Note also the good agreement between Cohen's and our peak values in spite of the high number of known levels.

Zinc

Zinc was evaporated in vacuum onto a thin gold foil. The gold backing was only 0.16 mg/cm^2 but, nevertheless, it gives a considerable background.

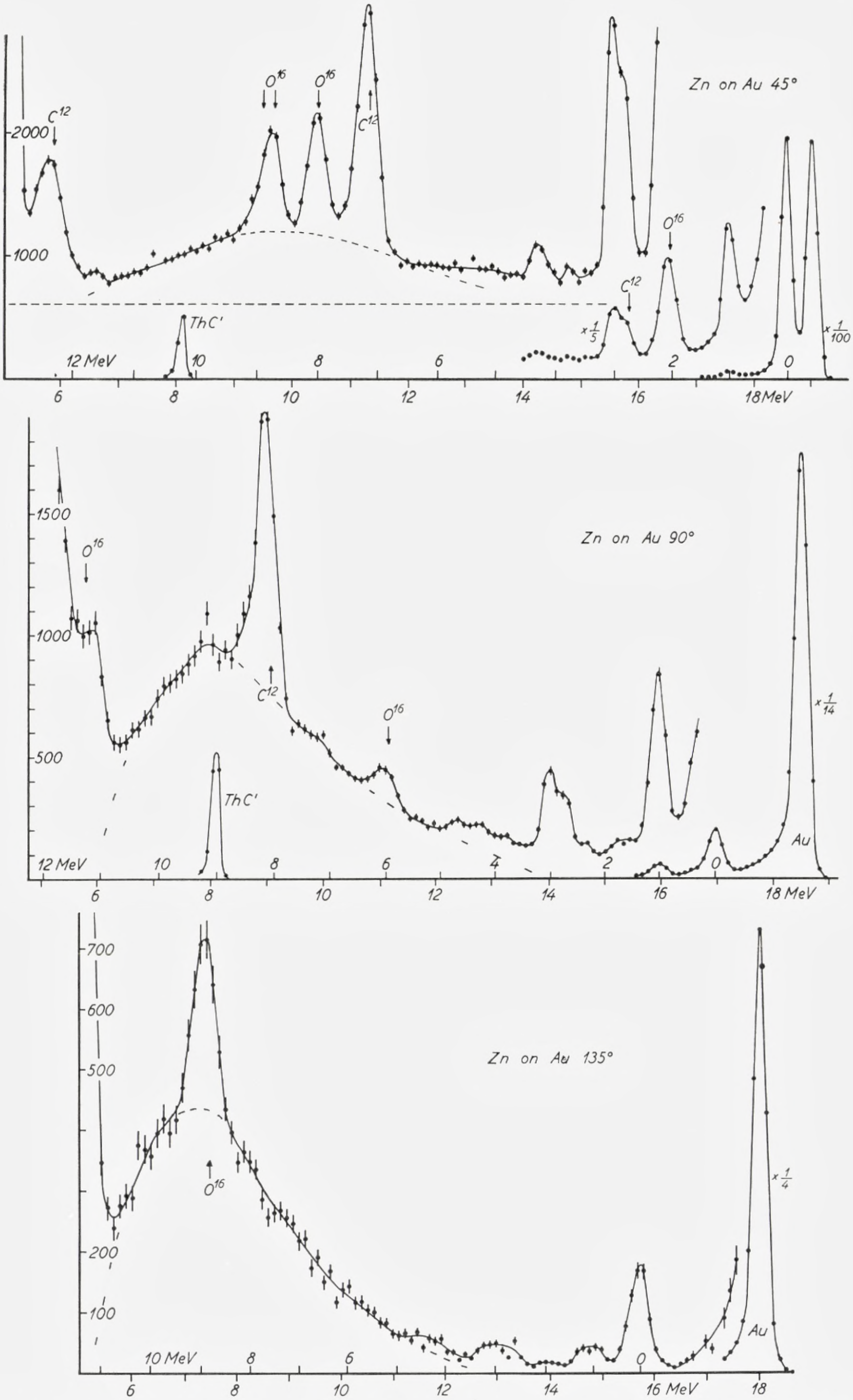

Fig. 9. Spectra of α-particles scattered from a layer of zinc evaporated onto a 0.16 mg/cm^2 gold foil. Integrated doses of primary α's 75, 160, and 60 μ Coulomb for 45°, 90°, and 135°, respectively.

TABLE 5. Zinc

Known levels in			Cohen's peaks in		Q-values of peaks		
Zn^{64} 49 %	Zn^{66} 28 %	Zn^{68} 19 %	Zn^{64}	Zn^{68}	45°	90°	135°
1	1.04	1.08	1.02	1.07	1.00	1.00	1.1
	1.38						
		1.91	1.83	1.98	(O^{16})	$\sim$ 1.7	
2.27			2.13	2.34	(O^{16})	$\sim$ 2.3	
				2.68	2.8	$\sim$ 2.7	
3.04			3.00		3.0	3.0	$\sim$ 3
3.43				3.47			
3.84?				3.8	3.8	(3.8)	
				4.1	4.3	(4.3)	4.5
				4.5			
						(4.7)	
				4.9			
				5.1			
				5.4			

All values in the table in MeV.

The thickness of the Zn-layer was only very roughly known, but from the absolute yield of elastically scattered α-particles it was estimated to be 1.1 mg/cm². The appearance of the spectra is dominated by the oxygen and carbon impurities which actually, however, only cause minor difficulties. In the 45°-curve the 4.43 and 9.6 MeV levels in C^{12} are seen, but not the elastic group, because it coincides with a real Zn-peak. Fig. 9 and Table 5 give the results.

Silver

The spectra obtained from silver are shown in Fig. 10. They differ markedly from the earlier spectra. Few strong levels appear. No continuous distribution is seen above background. Table 6 summarizes the results and compares them with Cohen's.

Some levels in Ag are known from Coulomb excitation, among others those at 320, 418, 306, and 412 keV. At 135° and 90° we find a peak, and

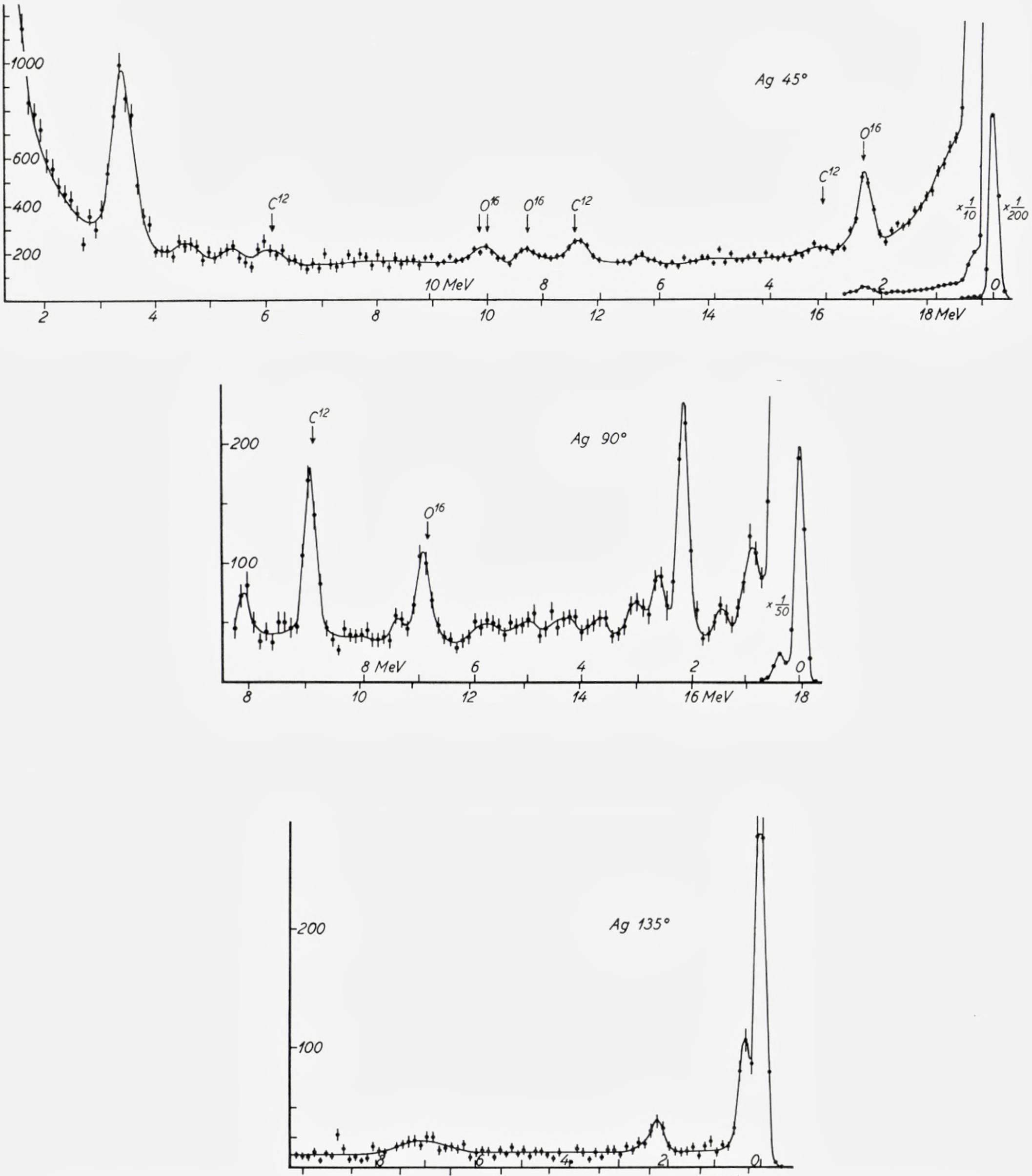

Fig. 10. Spectra of α-particles scattered from a silver foil. Target thickness 0.12 mg/cm² for 45°, 0.48 mg/cm² for 90° and 135°. Integrated doses of primary α's 100, 140, and 101 μ Coulomb for 45°, 90°, and 135°, respectively.

at 45° a bump on the curve, corresponding to about 350 keV. In Table 7, the estimated cross sections are compared with the calculated cross section for Coulomb excitation of the 400 keV-levels*. In view of the large experimental uncertainties the agreement is rather good for the 45°-direction. At 90°, and especially at 135°, the calculations may be expected to give too high values, since they are based upon the classical orbit picture and assuming the α-particle to move in Rutherford orbits. The experimental cross sections seem to vary in accordance with this. However, the results are insufficient to show whether Coulomb excitation is responsible for the peaks or whether other processes are involved.

TABLE 6. Silver

Known levels in		Cohen's peaks	Q-values of peaks		
Ag^{107}	Ag^{109}		45°	90°	135°
0.32 0.42	0.31 0.41	0.39	~ 0.4	~ 0.35	~ 0.3
		0.94		0.85	
		1.50		1.5	
		2.19	(O^{16})	2.18	2.20
				2.6	

All values in the table in MeV.

TABLE 7. Cross section in mb/ster. for the 3–400 keV levels in silver

	45°	90°	135°
Calculated for Coulomb excitation	4.2	3.0	2.5
Experimentally........................	7	1.3	0.1

A level at 2.19 MeV is observed; we find it both at 90° and 135°, whereas in the 45°-direction the O^{16} elastic peak makes observation impossible. In the 90°-curve are furthermore seen peaks at about 0.85, 1.5, and 2.6 MeV and several weaker peaks with Q-values $\geqslant 3$ MeV. The former are probably due to Ag; if they were caused by impurities they should be expected to appear also at 45°. The latter are probably also due to some

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* Our thanks are due Mag. BRO-JØRGENSEN for calculating the Coulomb cross sections for Ag and Au.

reactions taking place in the Ag nucleus, as will be made plausible by the following considerations.

In the 45°-curve we see an almost horizontal background with a height about 0.1 % of the height of the elastic peak*. The same background is found when using a target of gold or heavier elements and it may be assumed to be caused by a contamination in the primary α-beam of particles scattered along through the tube or by scattering of the secondary α's in the entrance diaphragm of the ionization chamber. For the heavier elements, the height of the background relative to the elastic peak is the same for all three angles. For silver, however, the "background" amounts to about 0.4—0.5 % in the 90°-curve and 3—4 % in the 135°-curve. Thus, in Ag at 45°, the tail accompanying the high elastic peak can account for the whole counting rate, and any inelastic scattering, except the peak at 3–400 keV, is overshadowed, whereas for the two other angles the counting rate is appreciably higher than would correspond to the tail.

In addition to the main background, the 45°-curve shows the O^{16} and C^{12} peaks known from the mylar curve. To the left of the 9.6 MeV C^{12} peak two other small peaks appear. The left one of these might be assigned to a known level of 10.75 MeV in C^{12}. The big peak $\sim$ 3.5 MeV probably represents recoil protons from a surface layer of water**.

Indium

We have used targets of evaporated In-layers on gold and aluminum. At 90° the gold backed target shows, besides the two elastic peaks, two inelastic peaks, both rather broad. At 45° the two inelastic peaks were not seen, but this may be due to the background. The aluminum backed target was not used for the 45°-direction; at the other two angles it shows four levels (see Fig. 11). The data are summarized in Table 8. The four levels we see were also observed by Cohen. He furthermore sees peaks at 0.63 and 3.07 MeV. In fact, in our curves there are indications of a peak at about 0.5 and another in the neighbourhood of 3 MeV, but the number of events is too small to establish their existence.

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* Since the peak widths are so small and the elastic peaks only cover a few channels, the peak height is not a good unit. What we find for Ag at 45° and for the heavier elements at all angles is that the height of the background per channel (using a specific channel width) is 0.065 % of the total number of counts in the elastic peak. This value was used when correcting the 45°-curves for Ni, Cu, and Zn.

** The ratio between the areas of this peak and of the O^{16} peak agrees within the limits of experimental errors with the corresponding ratio for the mylar curve. The amount of H_2O is 1.5 $\mu g/cm^2$.

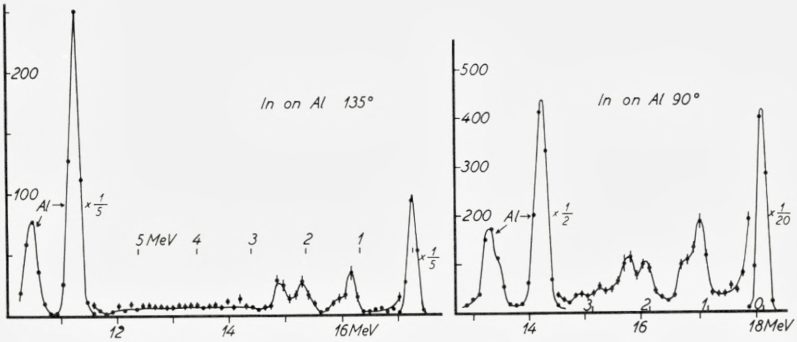

Fig. 11. Spectra of α-particles scattered from a layer of indium evaporated onto a 0.24 mg/cm^2 aluminum foil. Integrated dose of primary α's 60 and 150 μ Coulomb for 90° and 135°, respectively.

Gold

From the scattering spectra of gold, shown in Fig. 12, only one excited level can be identified. In the 90°-curve a peak is clearly seen at a position corresponding to the known 550 keV-level. A chemical analysis shows, however, the presence of silver in the gold foil, and the silver elastic peak should occur just here. Mag. B. Elbek kindly made a quantitative measurement. He used 4 MeV protons from the Van der Graff and measured the scattered protons by means of a heavy-particle spectrometer and photographic plates. The number of silver atoms in the gold is 15.3 $^0/_0$ of the total number of atoms. Since this is not sufficient to account for the observed peak we think we see the 550-keV level. It also appears in the

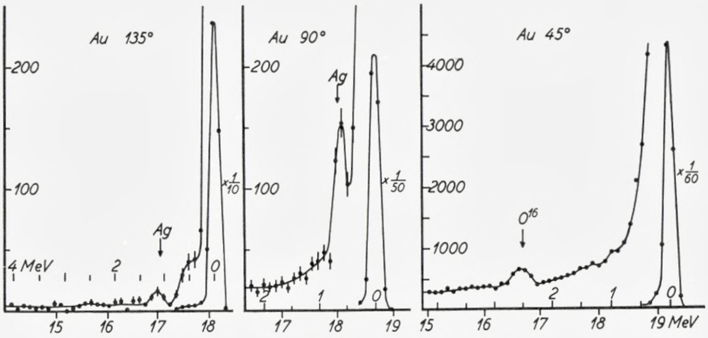

Fig. 12. Spectra of α-particles scattered from a gold foil 0.16 mg/cm^2. The foil contains 15 $^0/_0$ of silver. Integrated doses of primary α's 40, 40, and 100 μ Coulomb for 45°, 90°, and 135°, respectively.

135°-curve clearly separated from the Ag peak; at 45° the elastic peaks from Ag and Au coincide. Here, the 550-keV level is not very pronounced. However, one point lies much higher than the curve and, using the vertical difference between the point and the curve drawn, we obtain the cross section given in Table 9. Here are compared cross sections calculated for Coulomb excitation with the cross sections estimated from the curves. Of course, the "observed" cross sections are very uncertain, since they depend strongly on the way in which the tail of the elastic peak is drawn. Hence, the agreement is satisfactory.

TABLE 8. Indium

Known levels in In^{115} (96 %)	Cohen's peaks	Q-values of peaks	
		90°	135°
0.61	0.63		
0.92			
1.08 1.14	1.14	1.13	1.17
1.29			
	1.48	1.4	1.4
1.98	2.15	2.05	2.07
	2.43	2.43	2.5
	3.07		

TABLE 9. Cross sections in mb/ster. for the 550 keV level in gold

	45°	90°	135°
Calculated for Coulomb excitation	2.2	1.6	1.3
Experimentally	2.0	0.9	1.2

Lead and Bismuth

No inelastic scattering was observed in these elements. Curves for Pb on Au and for Bi on Au are very similar to those for pure Au, though the higher elastic peak obscures the 550 keV level in Au.

In Fig. 13 are shown the 45°-curve for Pb on Au, the 90°-curve for Bi on Au, and the 135°-curve for Bi on Al.

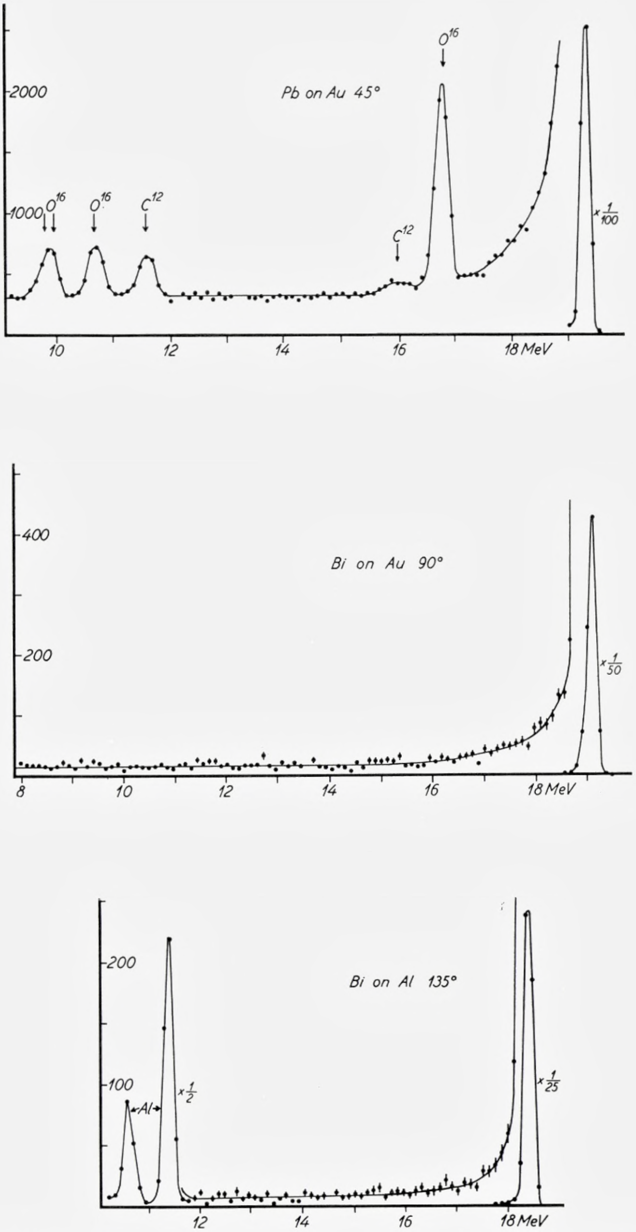

Fig. 13. Spectra of α-particles scattered from layers of lead and bismuth on gold and aluminum. Integrated doses of primary α's 20, 10.4, and 60 μ Coulomb for 45°, 90°, and 135°, respectively.

Width of Peaks

When ΔE is the full width at half maximum height we find for Au $\frac{\Delta E}{E} = 1.1\ {}^0/_0$. From the mylar curve (45°) we get for the elastic O^{16}-peak $\frac{\Delta E}{E} = 1.8\ {}^0/_0$. The mylar target was much thicker than the gold target, but with the transmission geometry used the peak widths should only be very slightly influenced by target thickness and, in fact, from the 45° Pb on Au curve, we find again for the combined Pb and Au peak the half-width 1.1 ${}^0/_0$ and for the O^{16} peak 1.8 ${}^0/_0$, the latter being corrected for background.

This difference in half-width is due to the geometry. The maximum angular spread caused by the finite size of the ionization chamber window is $\pm 1^\circ\!.4$, that due to the finite width of the target area $\sim \pm 0^\circ\!.5$, and that due to the primary beam $\sim \pm 0^\circ\!.5$. Thus, the total maximum angular spread is $\sim \pm 2^\circ\!.4$. At 45° scattering angle, this gives a maximum energy spread of 0.54 and 0.06 MeV for O^{16} and Au, respectively. Identifying, for simplicity, half maximum spread and half-width, one calculates from the half-width 0.21 MeV for gold a half-width for O^{16} of $\sqrt{0.21^2 + 0.24^2} = 0.32$ MeV or 1.8 ${}^0/_0$ of the energy of the elastically scattered α-particles, in agreement with the experimental value.

For some of the targets, for example Cu, the half-width of the elastic peak is somewhat bigger (50 ${}^0/_0$) than it would be for a thin homogeneous target. We do not know the reason, but suspect target inhomogeneity.

Cross Section for Elastic Scattering

The cross sections obtained for elastic scattering are given in Table 10. They are estimated to be correct within $\pm 20\ {}^0/_0$, the main contributions to the uncertainty coming from the beam measurement and from target thickness. No test of foil homogeneity was made.

For gold at 45° we find $\sigma = \sigma_R$, the Rutherford cross section. Within the estimated error the same is valid for 90°, but for 135° $\sigma < \sigma_R$. Looking at elements heavier than aluminum, the well-known variation⁽⁶⁾ of σ/σ_R is found. For each element it decreases with increasing scattering angle. It decreases with decreasing atomic number of the scatterer. For the lighter elements the cross section varies in a more irregular manner. For C^{12} at 90° our value agrees fairly well with RASMUSSEN, MILLER, and SAMPSON's value⁽⁷⁾. At 45° our values agree with the values of BLEULER and TENDAM⁽⁸⁾ and of

TABLE 10. Cross sections for elastic scattering

	45°			90°			135°		
	σ	σ/σ_R	E_1	σ	σ/σ_R	E_1	σ	σ/σ_R	E_1
Au	3900	1.1	20.0	250	0.85	20.0	70	0.65	19.8
Ag	1200	0.9	20.0	10	0.09	19.8	0.8	0.02	19.8
Zn	170	0.3	19.7	1.2	0.02	19.8	0.32	0.018	20.0
Cu	160	0.3	19.7	1.4	0.03	19.5	0.30	0.018	19.8
Ni	140	0.3	19.6	1.0	0.03	19.9	0.33	0.02	20.0
Al	17	0.22	20.1	0.57	0.07	20.2	0.8	0.22	20.0
O^{16}	45	1.6	19.9	0.3	0.1	20.0	6.4	4.0	19.9
C^{12}	4.6	0.3	19.9	3.9	2.2	20.0	3.2	3.5	19.9

σ is given in millibarns per steradian.

E_1 is the energy in MeV of the α-particles having traversed half the thickness of the scattering foil.

The thickness of the Zn-layer was chosen to 1.1 mg/cm^2 in order to obtain the above figures.

O. GAILAR(9) for Ag, Cu, and Al. For Ag we find somewhat lower values for σ/σ_R at 90° and 135° than Gailar, but since his α-energy (18.7 MeV) is lower than ours this should be expected. For Cu the agreement is good; for Al a comparison is not justified, since the cross section may vary considerably with energy.

4. Discussion

The elements we have studied may be divided into four groups:

I. The light elements C, O, Mg, and Al.
II. The medium light elements Ni, Cu, and Zn.
III. The medium heavy elements Ag and In.
IV. The heavy elements Au, Pb, and Bi.

Group I

The spectra of α-particles scattered from the elements of group I are composed of single peaks. For carbon and oxygen, these peaks correspond to known levels which are widely spread. For magnesium, peaks due to Mg^{24} are dominant, even though the rarer isotopes Mg^{25} and Mg^{26} have more low-lying excited states. For aluminum, the spectra are more complex, showing many closely packed peaks. Common to all spectra are single peaks seen up to excitation energies of about 10 MeV. We cannot see peaks for higher excitation energies, because we then get into the intense continuous spectrum due to protons.

Two possible processes through which one can imagine that scattering occurs have already been mentioned. The first involves compound nucleus formation followed by the evaporation of a particle. The second, the so-called direct interaction process, involves a collision between the incoming particle and one (or at most a few) nucleons. The first process requires a much longer average time per event than does the second one.

One way of determining which of these proposed mechanisms is effective in a particular case is to study the angular distribution of α-particles corresponding to a definite level in the residual nucleus. If the scattering occurs entirely through compound nucleus formation, a distribution symmetrical about 90° is expected, whereas if the direct interaction process is dominant, the angular distribution should be peaked more or less in the forward direction. For Mg^{24} and other light nuclei, WATTERS(10) has found results strongly supporting the direct interaction picture. The angular distributions show maxima and minima which may be largely accounted for by theoretical considerations(1).

When looking only at a few definite angles, as we have done, one may expect to find intensities of the various inelastic peaks varying in an irregular manner, since the intensity will depend on whether the particular angle is close to a maximum or to a minimum. Our results for C, O, and Mg are in accordance with this expectation.

For aluminum, however, we find a somewhat more regular variation. The ratio R_1 between peak heights at 45° and 90° (Table 2) is high (35) for the elastic peak. For the first excited state it is somewhat lower (5.8), and it decreases with increasing excitation energy until, for the fifth level, it reaches a value between one and two, and then remains fairly constant with further increasing excitation energy. For the low-lying levels, the lack of symmetry around 90° and the strong forward peaking may be taken as an indication of a direct interaction.

For the higher excitation energies, the fact that single peaks are observed may give rise to some speculation. Assuming the level spacing here to be quite small, which may be justified in view of the high angular momenta involved, this would seem to point to some mechanism different from compound nucleus formation. Professor AAGE BOHR has suggested that the α-particle stays long enough in the nucleus to transfer energy to a small number of nucleons, but not so long that the energy is distributed over a larger fraction of the nucleons. Another viewpoint would be to assume a somewhat higher level spacing comparable with our resolution. In this case, compound nucleus scattering would just give curves like ours with single peaks showing up on top of a continuous background. Anyhow, whether the single peaks are due to the one or the other process, we do see an increasing continuous background for excitation energies above some 4 MeV, and this background is interpreted as due to α-particles boiled off from the compound nucleus.

Group II

If the compound nucleus interpretation is correct, one might expect to find a similar behaviour for heavier nuclei, but with higher cross sections for the compound nucleus contribution because of the higher level densities. This agrees well with our results for Ni, Cu, and Zn. For these elements we see, in addition to the single peaks, a broad continuous distribution between 5 and 14 MeV, which we ascribe to compound scattering. The shape of this evaporation spectrum has been compared with the statistical theory, which gives the formula(11)

$$N(E)\,dE = \text{const.}\ \varrho(E^*)\cdot E\sigma_c(E)\,dE, \tag{I}$$

where E is the total kinetic energy of the evaporated α-particle and the residual nucleus in the center of mass system, N is the intensity of α-particles of this particular energy, $\sigma_c(E)$ is the cross section for formation of the compound nucleus when bombarding with α-particles of this energy, and $\varrho(E^*)$ is the level density of the residual nucleus at an excitation energy $E^* = E_0 - E$. E_0 is the energy in the entrance channel.

Rearranging the formula, we get

$$\log\varrho(E^*) = \log N(E) - \log\frac{\sigma_c(E)}{\pi\lambda\!\!\!^{-2}} + C. \tag{II}$$

The second term on the right side was calculated by means of table IV in the paper of Shapiro(12). The interaction radii 7.66, 7.81, and 7.86 Fermis for Ni, Cu, and Zn, respectively, determined by Kerlee, Blair, and Farwell(6), were used to obtain the values of the Coulomb barrier. Plotting $\log(N(E)) - \log\frac{\sigma_c(E)}{\pi\lambda\!\!\!^{-2}}$ against E^*, we get straight lines as shown in Fig. 14. We may then write

$$\varrho(E^*) = \text{const.} \times \exp. \frac{E^*}{T}, \tag{III}$$

where T is a constant. Defining in the usual way the nuclear temperature as $\left(\frac{d \log \varrho}{dE^*}\right)^{-1}$ we thus find this temperature T to be constant. The values found for T are given in Table 11.

Table 11. Nuclear temperature T in MeV as derived from the α-spectra

	135°	90°	45°
Ni	1.15	1.06	(1.16)
Cu	1.16	1.16	(1.25)
Zn	1.04	1.03	(1.15)

When calculating the temperature the experimental points were not directly used, but points were chosen on the dashed lines shown in Figs. 7—9. In this way, a separation between the α-particles scattered in direct interactions and *via* a compound nucleus was attempted, and also the peaks due to impurities were omitted. From the curves it is evident that the 45°-results are much more uncertain than the 90°–and 135°-results.

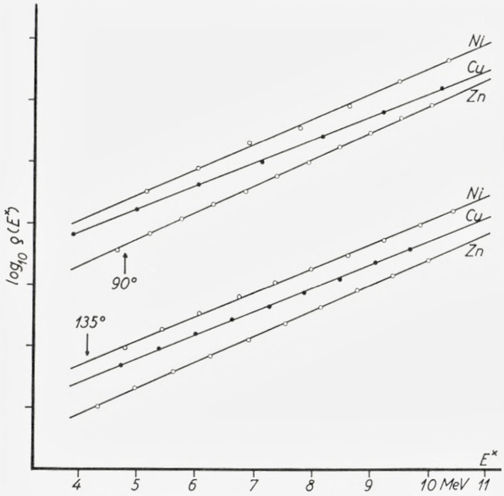

Fig. 14. Level density functions as obtained from the spectra of scattered α's from Ni, Cu, and Zn. The ordinate is $\log N(E) - \log \frac{\sigma_c(E)}{\pi \lambda\!\!\!^{-2}} = C + \log \varrho(E^*)$. The lines drawn correspond to $\varrho(E^*) \sim \exp \frac{E^*}{T}$ with the T-values given in Table 11.

The figures for 45° are given here mainly to show that compound scattering is also observed at this angle. An error in the earlier mentioned background associated with the high elastic peaks—the horizontal dashed lines—will influence the T-values. Another very likely reason for the higher temperatures found from the 45°-curves is that direct processes may play a larger role than would correspond to the dashed lines.

The error in R given by Kerlee, Blair and Farwell is $\Delta R = \pm 0.13$ Fermis, which gives $\Delta T = \pm 0.02$ MeV. For the 90°–and 135°–results, we estimate the total erorr to be $\Delta T \sim \pm 0.04$ MeV.

It is interesting to see that the temperature is higher for copper than for nickel and zinc. Since copper consists of two odd-even isotopes, whereas the predominant isotopes in nickel and zinc are even-even, such a difference would not be unexpected. However, the difference is not much outside the experimental uncertainty and further data are needed to ensure the significance of it.

It should be stressed that the estimates of temperature were obtained by treating our experimental results in the particular manner described, i. e., on the basis of a model of the reaction in which a sharply defined interaction radius $R = 7.66$ Fermis was assummed. Smaller R-values in a reasonable range also give approximately straight lines in the log ϱ *vs* E^* plots, but with slopes corresponding to lower temperatures, the T-values being roughly propertional to the R-values used. Significantly larger values of R, however, give curved lines in such plots.

For further comparison with the statistical theory, the cross section for compound nucleus scattering was calculated, using the expression

$$\sigma_{\alpha,\alpha'} = \sigma_{c,\alpha}(E_0) \times \frac{M_\alpha \int_0^{E_0} E\sigma_{c,\alpha}(E)\,\varrho_1(E^*)\,dE}{M_\alpha \int_0^{E_0} E\sigma_{c,\alpha}(E)\,\varrho_1(E^*)\,dE + 2M_p \int_0^{E_1} E\sigma_{c,p}(E)\,\varrho_2(E^*)\,dE + 2M_n \int_0^{E_2} E\sigma_{c,n}(E)\,\varrho_3(E^*)\,dE}. \quad \text{(IV)}$$

Here, $\sigma_{\alpha,\alpha'}$ is the cross section for compound nucleus scattering; $\sigma_{c,\alpha}(E)$, $\sigma_{c,p}(E)$, $\sigma_{c,n}(E)$ are the cross sections for formation of the compound nucleus when bombarding the respective residual nuclei with α-particles, protons, and neutrons, respectively, of energy E; M_α, M_p and M_n are the reduced masses of the α-particle, the proton, and the neutron, respectively; E_0 is the entrance channel energy (C. M. system); E_1 and E_2 are the maximum channel energies for outgoing protons and neutrons, respectively;

$\varrho_1(E^*)$, $\varrho_2(E^*)$, $\varrho_3(E^*)$ are the level density functions for the residual nuclei corresponding to α-, proton-, and neutron-emission, respectively, and the factor 2 for protons and neutrons takes into account the statistical weight due to spin.

Consider, for example, the scattering from Cu^{63}

$$Cu^{63} + \alpha \rightarrow (Ga^{67})^* \rightarrow \begin{cases} Cu^{63} + \alpha \\ Zn^{66} + p \\ Ga^{66} + n \end{cases}$$

We neglect γ-transitions. Deuteron emission is calculated to be negligibly small.

Now ϱ_1, ϱ_2, and ϱ_3 are the level density functions of Cu^{63}, Zn^{66}, and Ga^{66}. These are not known, but the temperatures may be expected to be nearly the same for neighbouring nuclei, as is also borne out by Table 11, and hence a good approximation should be to put

$$\varrho = \mathrm{K} \cdot exp\left(\frac{E^*}{1.08}\right) \qquad \text{(V)}$$

for all these nuclei. The proportionality factor K is, however, different for odd and even nuclei due to pairing correlations between the nucleons. This has roughly the effect of increasing the excitation energy by δ for odd-even and by $2\,\delta$ for odd-odd nuclei, where δ is half the pairing energy(14, 15, 18), or to increase ϱ by $exp\left(\frac{\delta}{T}\right)$ for odd-even and by $exp\left(\frac{2\,\delta}{T}\right)$ for odd-odd nuclei.

Since $\delta \approx T$, we therefore put for the nuclei here considered $\mathrm{K} = \mathrm{k}$, 3 k, and 9 k for even-even, odd-even, and odd-odd nuclei, respectively.

The E_1- and E_2-values were determined from Wapstra's tables(16). In evaluating the integrals, Shapiro's tables were used for $\sigma_{c,\alpha}$ and $\sigma_{c,p}$. For the nuclear radii were used $R = 1.414 \cdot A^{1/3} + 2.19$ Fermis, where the last term was omitted for protons and neutrons. For neutrons, the cross sections given in Blatt and Weisskopf(17) were used.

The calculations give for Cu^{63}

$$\sigma_{\alpha,\alpha'} = 0.954 \frac{14}{14 + 24 + 62} = 0.128 \text{ barns.}$$

The results of calculations for some target nuclei are given in Table 12, and in Table 13 the experimental cross sections are compared with the calculated values. The experimental cross sections are about equal for the three directions, as should be expected for compound nucleus scattering.

The slightly high values for 45° probably again show that the correction for direct processes, indicated by the dotted line, is insufficient. As the best value for the average cross section we take a weighted mean using arbitrary weight factors 2, 2, and 1 for 135°, 90°, and 45°, respectively.

TABLE 12

Target nucleus	Percentage of		
	α's	p's	n's
Ni^{60}	14	37	49
Cu^{63}	14	24	62
Cu^{65}	4	4	92
Zn^{66}	12	15	73

TABLE 13. σ in millibarn per steradian

Target	Experimental			Weighted mean	Calculated		
	135°*)	90°*)	45°*)		for		$\sigma exp/\sigma calc.$
Nickel	8.5	5.5	8.6	7.3	Ni^{60}	10.0	0.73
Copper	5.8	4.0	7.6	5.4	nat. Cu.	8.0	0.68
Zink	6.6	3.9	9.1	6.0	Zn^{66}	9.6	0.63

The angles are in the laboratory system. The cross sections have been corrected for C. M. motion.

The agreement between the absolute values of the calculated and the measured cross sections is better than to a factor of two, which is satisfactory. In view of the uncertainties in the parameters, one could hardly expect closer agreement, and the results show that we may be confident in regarding the α-particles as being evaporated from the compound nucleus. The ratio between the calculated cross sections for the three elements reproduce the experimental values to a much higher accuracy, which is further corroboration that, so far as the continuum is concerned, the scattering process proceeds mainly through compound nucleus formation.

It may be noted that, if the different odd-even factors in the expression (V) for ϱ had not been applied, the agreement between calculated and experimental absolute cross sections would have been poorer, and especially that $\sigma exp/\sigma calc.$ would have been twice as high for the copper as for the two other targets.

It may be argued that, although the previous considerations strongly support the statistical theory, the level density function $\varrho = k\ exp\left(\frac{E^*}{T}\right)$, where T is a constant, is not what should be expected. The free-particle Fermi gas theory predicts $\varrho = k\ exp\left((aE^*)^{\frac{1}{2}}\right)$. It would therefore seem to be interesting to plot $log\,N(E) - log\,\frac{\sigma_c(E)}{\pi\lambda\!\!\!^{-2}}$ as a function of $\sqrt{E^*}$. This is done in Fig. 15.

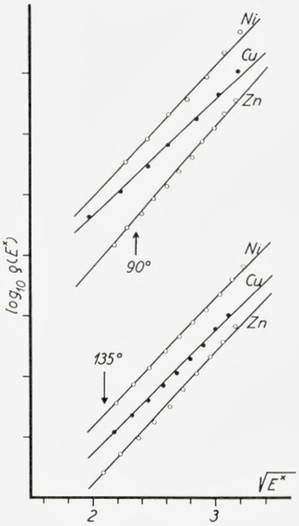

Fig. 15. The level density plotted as a function of $\sqrt{E^*}$.

The fit to straight lines is definitely worse in this plot than in Fig. 14; actually, in all cases, the points indicate a curved line. In passing, it may be mentioned that the use of smaller R-values would give stronger curvatures. In Fig. 15, the straight lines drawn for Ni, Cu, and Zn at 90° correspond to $a = 6.1$, 4.8, and 7.2, and at 135° to $a = 5.7$, 5.3 and 6.2, respectively, a being in MeV^{-1}. It is thought that the correlations between the motions of the nucleons are causing considerable deviations from the free-particle Fermi gas picture at low excitation energies, associated particularly with the existence of pairing effects. When these are taken into account, the nuclear temperature is expected to vary only slowly with energy in an intermediate energy range[*] [**](15, 18), and it is therefore not surprising that we find a nearly constant temperature in the range 4–10 MeV.

[*] V. F. Weisskopf: private communication.

[**] V. Strutinski: private communication.

In Fig. 16, we have attempted a comparison with some other experimental determinations of the level density of nuclei in the copper region. Here is plotted the ratio $\varrho(E^*):\varrho(1)$ between level densities at excitation energies E^* and 1 MeV. Curve a is the level density found in this experiment. Curve b is that found in (α, p) experiments by EISBERG, IGO, and WEGNER(19). Curve c is the one found by GUGELOT(20) by (p, p') scattering experiments. For the latter work it is now generally agreed, we think, that direct processes overshadow the compound scattering at small excitation energies. At high energies, curves a and c tend to become parallel; in the energy region 10–13 MeV the temperature as given by Gugelot is 1.2 MeV, in good agreement with our value of 1.1 MeV. For low energies, curves a and b agree fairly well, but for higher energies, a difference is observed which is not understood.

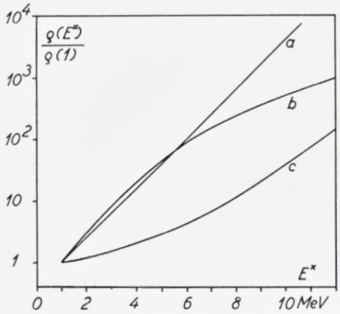

Fig. 16. Comparison with some other experimental level densities for elements in the copper region. Level density determined:

a) from (α, α') reactions is this work;
b) from (α, p) reactions (ref. 19) on Cu;
c) from (p, p') reactions (ref. 20) on Cu.

More recently, MARCH and MORTON(21) have studied (n, p) reactions in Fe^{54} and Fe^{56}, using 13.5 MeV neutrons; they found a shape of the energy distributions of emitted protons consistent with the statistical theory and corresponding to a temperature of about 1.2 MeV. In similar experiments, ALLAN(22) found for $Cu(n,p)$ Ni reactions a temperature of 1.0 MeV. ZUCKER(13), studying the reactions

$$_{13}\mathrm{Al}^{27}+{}_{7}\mathrm{N}^{14}\rightarrow{}_{20}\mathrm{Ca}^{41}\rightarrow\begin{cases}{}_{19}\mathrm{K}^{40}+p\\ {}_{18}\mathrm{A}^{37}+\alpha,\end{cases}$$

found for both residual nuclei densities $\varrho \sim exp\sqrt{aE^*}$. His results cover a large energy region. Replotting his values for $\frac{N(E)}{E\sigma_c(E)}$ as a function of E^*, we find in a limited interval—for α-particles between 5 and 12 MeV—rather good agreement with $\varrho \sim exp\ E^*/T$ with a temperature of about 1.5—1.6 MeV. Since the nuclei involved here are much lighter than in our case the higher temperature is not surprising. The interesting feature is that, in the energy interval covered in our experiments, also Zucker's results agree with a level density function $\varrho \sim exp\ E^*/T$ with a constant temperature, whereas his results show that, for higher excitation energies, the temperature varies with E^*.

Group III

For Ag and In, a calculation shows that the number of α-particles to be expected from compound nucleus scattering is orders of magnitude smaller due to the higher Coulomb barrier. In accordance with this evidence we do not see any evaporation distribution, but only a few single peaks probably due to direct interactions.

Group IV

For Au, Pb, and Bi, the Coulomb barrier is so high that the probability that an α-particle will penetrate it twice—in and out—is very small. Accordingly, we have observed no nuclear processes except Coulomb interactions, which we have seen only in Au.

These experiments were carried out at the Institute for Theoretical Physics, University of Copenhagen, and the authors wish to express their gratitude to the Director of the Institute, Professor NIELS BOHR, for his interest in the work. For many valuable discussions our thanks are due Dr. TORLEIF ERICSON, Dr. BEN MOTTELSON, Professor AAGE BOHR, and many others. We should also like to thank Mr. PHILIP DAM for his help in operating the cyclotron and Miss LISE BRYDE for doing most of the numerical calculations. One of us (HWF) also wishes to thank the Guggenheim Foundation and the United States Educational Foundation in Denmark for support during his year's stay at the Institute.

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EFFECT OF PAIRING CORRELATIONS ON NUCLEAR PROPERTIES

BY

S. T. BELYAEV

1742

København 1959
i kommission hos Ejnar Munksgaard

Synopsis.

A method analogous to that developed in the new theory of superconductivity is applied to nuclei in order to investigate the influence of the coherent pairing interaction on various nuclear properties, especially on collective motion. The finite size effects, in particular the shell structure of the single-particle levels, are considered. The pairing correlation between two nucleons in states of opposite angular momentum projections is taken into account by means of a canonical transformation from the original interacting nucleons to new independent quasi-particles.

For strongly deformed nuclei, the moment of inertia is rather sensitive to the effect of pairing correlations and is found to be reduced from the value for rigid rotation by a factor of the order of that observed. For nuclei in regions near closed shells, the pairing correlations give rise to a spherical equilibrium shape and low energy vibrational modes of excitations. The vibrational frequencies and inertial parameters obtained from the present model are in qualitative agreement with experimental data and fit the observed trends.

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CONTENTS

Introduction

The Fermi gas model, which neglects the interaction between nucleons, is the simplest microscopic model of the nucleus. The development of nuclear models has progressed by taking into account certain parts of the nucleon-nucleon interaction. The great successes of the shell model, in which the nucleons are assumed to move independently in a certain average potential, showed that evidently the main part of interaction can be treated as a spherically symmetrical, self-consistent field. In the unified nuclear model, developed by A. Bohr, B. Mottelson,1, 2) and others3), it is assumed that, from the remaining part of the nucleon-nucleon interaction, an additional self-consistent part may be extracted, which is non-spherical and time-dependent. This procedure makes it possible to explain many of the regularities in the low-lying nuclear levels in the language of collective excitations.

However, the real interaction between nucleons cannot be reduced simply to a self-consistent field. After separation of the self-consistent part, there remains some interaction between the particles. This residual interaction is rather weak, but it may play an important role in various nuclear properties4, 5).

Recent work in the theory of superconductivity6–8) has shown that even small interactions between Fermi particles may give rise to a basic change in the properties of the system, provided this interaction has a correlated coherent character. In a superconductor, the correlations between electrons arise from the interaction with the lattice vibrations and make possible quasi-bound states of electron pairs with equal and opposite momenta near the Fermi surface9). This leads to a modification of the Fermi sea and to the appearance of a gap in the originally continuous energy spectrum of the system.

After the appearance of the new theory of superconductivity the suggestion was made10) that the energy gap found in the spectra of even-even nuclei is caused by correlation effects of a similar type to those considered for the electron system in superconductors. Such correlations may also affect other nuclear properties, which have no analogue in superconductors, connected with the finite size of nuclei and the shell structure of the single particle levels. It is the aim of the present paper to investigate the effect of the pairing correlation on various nuclear phenomena, in particular, on collective nuclear excitations.

We extend the method of the new theory of superconductivity developed by N. Bogolyubov$^{7)}$ in order to apply it to the nuclear system. The physical basis of the analogy is the similarity between the pairing energy of two nucleons with opposite projections of angular momentum and quasi-bound states of electron pairs with equal and opposite momenta. The correlation effect between nucleons is taken into account by means of a canonical transformation from the original interacting nucleons to new independent quasi-particles — the elementary excitations. The ground state of the system in terms of the new quasi-particles is the "vacuum" state. The essential part of the pairing correlation enters into the "vacuum" energy and into the intrinsic structure of the quasi-particles. Therefore, even if the residual interaction between the quasi-particles is neglected, one may investigate the influence of the correlation interaction on various nuclear properties. The general idea of the treatment is to take into account the coherent part of the residual internucleon interaction, but, at the same time, to retain the simple description afforded by the independent-particle model (with a type of quasi-particles).

In the first part, we consider the general formulation of the problem and select the canonical transformation required to take into account the effects of correlation between nucleons.

An explicit solution of the equation for the transformation coefficients is given in the second part. Here are also given, in the approximation of independent quasi-particles, the energy and the wave function of the ground state of the system and of the single-particle excited states.

The problems concerning the nuclear equilibrium shape and collective excitations are considered in the third part. Here, the moment of inertia for nuclear rotations and the inertial parameter and restoring force for the quadrupole vibrations of spherical nuclei are found within the framework of the cranking model.

I. Canonical Transformation

1. Hamiltonian

We consider a system of nucleons which are moving in a certain axially symmetric self-consistent well. (For simplicity, we do not distinguish between neutrons and protons). As basic functions of the second quantization representation we choose the wave functions of a nucleon in this well. States, which differ only in the sign of the projections of angular momentum along the symmetry axis, are degenerate. We call such states "conjugate" states and mark them with the index $k\sigma = (k+;\ k-)$*.

The wave functions of the conjugate states are assumed to transform into each other by complex conjugation and exchange of the spinor components**.

Let us introduce the Fermi operators $a^+_{k\sigma}$; $a_{k\sigma}$ which create and destroy a particle in the state $k\sigma$. The Hamiltonian for the system of interacting particles is then

$$\left.\begin{aligned} H' = \sum_k \varepsilon_k \, (a^+_{k+} a_{k+} + a^+_{k-} a_{k-}) \\ -\frac{1}{2} \sum_{(k,\,\sigma)} \langle k_1 \sigma_1 k_2 \sigma_2 \,|\, G \,|\, k'_2 \sigma'_2 k'_1 \sigma'_1 \rangle \, a^+_{k_1\sigma_1} a^+_{k_2\sigma_2} a_{k'_2\sigma'_2} a_{k'_1\sigma'_1}, \end{aligned}\right\} \qquad (1)$$

where ε_k is the single-particle energy in the k-th state. (The sign of G is chosen to be positive for an attractive interaction).

The Hamiltonian (1) describes a system with a fixed number of particles N. Therefore, in a perturbation treatment in which H' is split into two parts, each of these parts must commute with N. The problem is essentially simplified if we make a transition from the system with fixed N ("N-system")

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* In fact, even symmetry of reflection in a plane is enough for the definition of the conjugate states. We speak of axial symmetry only for definiteness.

** If $\psi_+ = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$, then $\psi_- = \begin{pmatrix} \psi_2^* \\ -\psi_1^* \end{pmatrix}$. The transformation $\psi_+ \rightarrow \psi_-$ is equivalent to the time reversal T.

to one with a fixed value of the chemical potential λ ("λ-system"), which is described by the Hamiltonian

$$H = H' - \lambda N. \tag{2}$$

The choice of λ determines only the average value of N in the λ-system. Therefore, the solution which corresponds to the Hamiltonian, (2), will describe only average properties of nuclei and does not pretend to describe the individual nuclear properties for which one needs a fixed value of N. As will be shown later, the uncertainty in the value of N is small. In practice, the averaging is done only over a few neighbouring nuclei, either all even or all odd.

2. Canonical Transformation

Following the analogy with the model of a superconductor, we choose a canonical transformation of the form given by N. Bogolyubov[7)]. In our case, however, it is necessary to consider a transformation of a more general type, because the interparticle interaction in (1) in general contains not only pairing interactions, but a certain supplementary self-consistent field. Therefore, we perform the following preliminary transformation to remove the self-consistent field:

$$b_{\nu +} = \sum_k \varphi^*_{k\nu} a_{k+}; \quad b_{\nu -} = \sum_k \varphi_{k\nu} a_{k-}, \tag{3}$$

where the coefficients satisfy the conditions

$$\sum_k \varphi^*_{k\nu} \varphi_{k\nu'} = \delta_{\nu\nu'}; \quad \sum_\nu \varphi^*_{k\nu} \varphi_{k'\nu} = \delta_{kk'}. \tag{4}$$

The conjugate relationship defined above is preserved by this transformation. Inverting (3), we obtain

$$a_{k+} = \sum_\nu \varphi_{k\nu} b_{\nu +}; \quad a_{k-} = \sum_\nu \varphi^*_{k\nu} b_{\nu -}. \tag{5}$$

After the transformation to the new operators the Hamiltonian (2) takes the form

$$\left.\begin{aligned} H = &\sum_{\nu\nu'} (\varepsilon_{\nu\nu'} - \lambda\delta_{\nu\nu'}) (b^+_{\nu +} b_{\nu' +} + b^+_{\nu' -} b_{\nu -}) \\ &- \frac{1}{2} \sum_{\nu\sigma} \langle \nu_1\sigma_1 \nu_2\sigma_2 | G | \nu'_2\sigma'_2 \nu'_1\sigma'_1 \rangle b^+_{\nu_1\sigma_1} b^+_{\nu_2\sigma_2} b_{\nu'_2\sigma'_2} b_{\nu'_1\sigma'_1}, \end{aligned}\right\} \tag{6}$$

where

$$\varepsilon_{\nu\nu'} = \sum_k \varepsilon_k \, \varphi_{k\nu}^* \, \varphi_{k\nu'}, \tag{7}$$

and the interaction matrix element is taken between the new states.

The self-consistent field is caused by the correlation between a great number of states. The character of the transformation (3) has this physical interpretation. After separation of the self-consistent field, each state is assumed to be correlated only with its conjugate state. The interaction mixes the states of the conjugate pair. In order to take into account this effect we introduce, instead of $b_{\nu\sigma}$, the new Fermi operators

$$\left.\begin{aligned} \alpha_\nu &= U_\nu \, b_{\nu +} - V_\nu \, b_{\nu -}^+, \\ \beta_\nu &= U_\nu \, b_{\nu -} + V_\nu \, b_{\nu +}^+, \end{aligned}\right\} \tag{8}$$

where U_ν and V_ν are real numbers which obey the condition

$$U_\nu^2 + V_\nu^2 = 1. \tag{9}$$

The special choice of $U_\nu = 1$; $V_\nu = 0$ for the states above the Fermi surface $(\varepsilon_\nu > \lambda)$, and $U_\nu = 0$; $V_\nu = 1$ for $\varepsilon_\nu < \lambda$, leads to the well-known transformation from particles and holes to elementary excitations. The completely occupied Fermi sea goes to the "vacuum". In general, the new particles $(\alpha; \beta)$ are a superposition of a particle and a hole, and the "vacuum" corresponds to a modification of the Fermi sea.

The transformation inverse to (8) has the form

$$\left.\begin{aligned} b_{\nu +} &= U_\nu \alpha_\nu + V_\nu \beta_\nu^+, \\ b_{\nu -} &= U_\nu \beta_\nu - V_\nu \alpha_\nu^+. \end{aligned}\right\} \tag{10}$$

Inserting (10) into (6), we obtain a Hamiltonian with the following structure:

$$H = U + H_{20} + H_{11} + H_{\mathrm{int}}. \tag{11}$$

Here, U is a constant term

$$U = \sum_\nu \left(\varepsilon_{\nu\nu} - \lambda - \frac{1}{2} \sum_{\nu_1} \langle \nu \nu_1 | \overline{G} | \nu_1 \nu \rangle V_{\nu_1}^2 \right) 2 V_\nu^2 - \sum_{\nu\nu_1} \langle \nu \nu | G | \nu_1 \nu_1 \rangle U_{\nu_1} V_{\nu_1} U_\nu V_\nu. \tag{12}$$

The terms H_{20} and H_{11} are quadratic in the new operators

$$\left.\begin{aligned} H_{20} = & \sum_{\nu\nu'} \Big\{ \Big(\varepsilon_{\nu\nu'} - \lambda \delta_{\nu\nu'} - \sum_{\nu'} \langle \nu \nu_1 | \overline{G} | \nu_1 \nu' \rangle V_{\nu_1}^2 \Big) (U_\nu V_{\nu'} + V_\nu U_{\nu'}) \\ & - \sum_{\nu_1} \langle \nu \nu' | G | \nu_1 \nu_1 \rangle U_{\nu_1} V_{\nu_1} (U_\nu U_{\nu'} - V_\nu V_{\nu'}) \Big\} (\alpha_\nu^+ \beta_{\nu'}^+ + \beta_\nu \alpha_{\nu'}), \end{aligned}\right\} \tag{13}$$

$$\left.\begin{aligned} H_{11} = \sum_{\nu\nu'} \Big\{ \Big(\varepsilon_{\nu\nu'} - \lambda \delta_{\nu\nu'} - \sum_{\nu'} \langle \nu \nu_1 | \overline{G} | \nu_1 \nu' \rangle V_{\nu_1}^2 \Big) (U_\nu U_{\nu'} - V_\nu V_{\nu'}) \\ + \sum_{\nu_1} \langle \nu \nu' | G | \nu_1 \nu_1 \rangle U_{\nu_1} V_{\nu_1} (U_\nu V_{\nu'} + V_\nu U_{\nu'}) \Big\} (\alpha_\nu^+ \alpha_{\nu'} + \beta_{\nu'}^+ \beta_\nu). \end{aligned}\right\} \tag{14}$$

The matrix elements in (12)—(14) have the form

$$\left.\begin{aligned} \langle \nu_1 \nu_2 | G | \nu_2' \nu_1' \rangle &= \langle \nu_1 + \nu_2 - | G | \nu_2' - \nu_1' + \rangle - \langle \nu_1 + \nu_2 - | G | \nu_1' + \nu_2' - \rangle \\ \langle \nu_1 \nu_2 | \overline{G} | \nu_2' \nu_1' \rangle &= \langle \nu_1 \nu_2 | G | \nu_2' \nu_1' \rangle \\ &+ \langle \nu_1 + \nu_2' + | G | \nu_2 + \nu_1' + \rangle - \langle \nu_1 + \nu_2' + | G | \nu_1' + \nu_2 + \rangle. \end{aligned}\right\} \tag{15}$$

The last term in (11), H_{int}, contains products of four operators and describes the interaction between the new particles (α; β).
It may be written in the form

$$H_{\text{int}} = H_{40} + H_{31} + H_{22}, \tag{16}$$

where the subscripts indicate the relative numbers of creation and destruction operators in the corresponding term, e. g., the term H_{40} describes the creation of four particles from the vacuum (or the inverse process) and so on. (The explicit expression of H_{int} is given in Appendix A). In the following, we consider mainly the independent quasi-particle model, neglecting the interaction term H_{int}. Effects of this term will be briefly discussed at the end of Part II.

3. Choice of the Transformation Coefficients

Neglecting the interaction between the new particles, let us consider the Hamiltonian

$$H_0 = U + H_{20} + H_{11}. \tag{17}$$

Following the programme outlined in the Introduction, we choose the coefficients of the canonical transformations so as to make H_0 correspond to an independent-particle system. This is possible only if $H_{20} = 0$ and H_{11} is a function only of the occupation numbers of the new particles $\alpha_\nu^+ \alpha_\nu$ and $\beta_\nu^+ \beta_\nu$.* From (13) it follows that the first condition leads to the equation

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* The condition $H_{20} = 0$ may be easily shown to be exactly equivalent to the requirement of a minimum "vacuum" energy U. Therefore, the ground state of the system in terms of the new particles is a "vacuum" state. The excited states are characterized by definite numbers of new particles, elementary excitations.

$$\left.\begin{aligned} h_{\nu\nu'} \equiv \Big(\varepsilon_{\nu\nu'} - \lambda\delta_{\nu\nu'} - \sum_{\nu_1} \langle \nu\nu_1 \,|\, \bar{G} \,|\, \nu_1 \nu' \rangle V_{\nu_1}^2\Big) (U_\nu V_{\nu'} + V_\nu U_{\nu'}) \\ - \sum_{\nu_1} \langle \nu\nu' \,|\, G \,|\, \nu_1 \nu_1 \rangle U_{\nu_1} V_{\nu_1} (U_\nu U_{\nu'} - V_\nu V_{\nu'}) = 0\,. \end{aligned}\right\} \tag{18}$$

The solution of (18) for $\nu' \neq \nu$ is equivalent to the diagonalization of the matrix $h_{\nu\nu'}$. It can be carried out by arbitrary U_ν, V_ν only with an appropriate choice of the coefficients in the transformation (3), i. e., the states ν. The quantities U_ν, V_ν might then be determined from the diagonal part of (18). In the general case, the choice of the states ν depends on U_ν, V_ν, and the two transformations are not independent of each other. The quantity $h_{\nu\nu'}$ in (18) is a linear combination of two non-diagonal matrices

$$\tilde{\varepsilon}_{\nu\nu'} = \varepsilon_{\nu\nu'} - \sum_{\nu_1} \langle \nu\nu_1 \,|\, \bar{G} \,|\, \nu_1 \nu' \rangle V_{\nu_1}^2, \tag{19}$$

$$\Delta_{\nu\nu'} = \sum_{\nu_1} \langle \nu\nu' \,|\, G \,|\, \nu_1 \nu_1 \rangle U_{\nu_1} V_{\nu_1}. \tag{20}$$

From (19) it is seen that $\tilde{\varepsilon}_{\nu\nu'}$ is the energy of a particle in a self-consistent field*. The diagonalization of $\tilde{\varepsilon}_{\nu\nu'}$ corresponds to the transition to the single-particle eigenstates in this new field. Generally, it does not lead to the diagonalization of $\Delta_{\nu\nu'}$ (and, therefore, $h_{\nu\nu'}$). But, in many cases of practical interest, the diagonalization of the single-particle energy $\tilde{\varepsilon}_{\nu\nu'}$ gives rise to the following selection rule for the interaction matrix element:

$$\langle \nu\nu' \,|\, G \,|\, \nu_1 \nu_1 \rangle = 0 \quad \text{for} \quad \nu' \neq \nu. \tag{21}$$

(In the *jj*-shell model, $\nu \to m_j$ and Eq. (21) is a consequence of the conservation of the angular momentum). This makes both $\tilde{\varepsilon}_{\nu\nu'}$ and $\Delta_{\nu\nu'}$ simultaneously diagonal. There remain then in the sum in (14) only the terms with $\nu' = \nu$, and H_{11} takes the form of a Hamiltonian for independent particles. For simplicity, we restrict ourselves to this case**.

Assuming the diagonalization of $\tilde{\varepsilon}_{\nu\nu'}$ and $\Delta_{\nu\nu'}$ to be fulfilled, we obtain from (12)—(14)

$$U = \sum_\nu (\tilde{\varepsilon}_\nu - \lambda)\, 2 V_\nu^2 - \sum_\nu \Delta_\nu U_\nu V_\nu + \sum_{\nu\nu'} \langle \nu\nu' \,|\, \bar{G} \,|\, \nu' \nu \rangle V_{\nu'}^2 V_\nu^2, \tag{22}$$

---

* If the Fermi sea is not modified, the sum in (19) spreads only over the occupied states for which $V_\nu^2 = 1$. In the general case, V_ν^2 describes the average distribution of the particle among the states.

** In the general case, one more transformation of the type (3) is needed for the diagonalization of H_{11}. It corresponds to the separation of a self-consistent field of the new quasi-particles α and β.

$$H_{20} = \sum_{\nu} \left\{ (\tilde{\varepsilon}_\nu - \lambda)\, 2\, U_\nu V_\nu - \Delta_\nu (U_\nu^2 - V_\nu^2) \right\} (\alpha_\nu^+ \beta_\nu^+ + \beta_\nu \alpha_\nu), \tag{23}$$

$$H_{11} = \sum_{\nu} \left\{ (\tilde{\varepsilon}_\nu - \lambda) (U_\nu^2 - V_\nu^2) + \Delta_\nu\, 2\, U_\nu V_\nu \right\} (\alpha_\nu^+ \alpha_\nu + \beta_\nu^+ \beta_\nu), \tag{24}$$

where $\tilde{\varepsilon}_\nu$ and Δ_ν are diagonal terms of (19) and (20),

The condition $H_{20} = 0$, which determines U_ν and V_ν, has now the form

$$(\tilde{\varepsilon}_\nu - \lambda)\, 2\, U_\nu V_\nu - \Delta_\nu (U_\nu^2 - V_\nu^2) = 0. \tag{25}$$

4. Analysis of the Equation for $U_\nu V_\nu$

It is convenient to use an alternative form of equation (25). To obtain this, we express U_ν and V_ν through Δ_ν from (25) and (9):

$$\left.\begin{aligned} 2\, U_\nu V_\nu &= \frac{\Delta_\nu}{\sqrt{(\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta_\nu^2}}; & U_\nu^2 - V_\nu^2 &= \frac{\tilde{\varepsilon}_\nu - \lambda}{\sqrt{(\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta_\nu^2}} \\ U_\nu^2 &= \frac{1}{2}\left[1 + \frac{\tilde{\varepsilon}_\nu - \lambda}{\sqrt{(\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta_\nu^2}}\right]; & V_\nu^2 &= \frac{1}{2}\left[1 - \frac{\tilde{\varepsilon}_\nu - \lambda}{\sqrt{(\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta_\nu^2}}\right]. \end{aligned}\right\} \tag{26}$$

Using (26) and (20), we find the following equation for Δ_ν:

$$\Delta_\nu = \frac{1}{2} \sum_{\nu'} \frac{\langle \nu\nu \,|\, G \,|\, \nu'\nu' \rangle}{\sqrt{(\tilde{\varepsilon}_{\nu'} - \lambda)^2 + \Delta_{\nu'}^2}} \Delta_{\nu'}. \tag{27}$$

To make clear the physical sense of the quantity Δ_ν, let us consider the energy of a quasi-particle E_ν. From (24) and (26) follows

$$E_\nu = \sqrt{(\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta_\nu^2}. \tag{28}$$

As is seen from (28), in the case of a continuous spectrum, the quantity Δ_ν is an energy gap in the spectrum of the quasi-particles. For a discrete spectrum $\tilde{\varepsilon}_\nu$, it is meaningful to speak of a gap only for values of Δ_ν which are greater than the distances between the levels $\tilde{\varepsilon}_\nu$.

The equation (27) has a trivial solution:

$$\Delta_\nu = 0 \quad \text{or} \quad U_\nu V_\nu = 0, \tag{29}$$

which corresponds to the sharp Fermi surface. If we choose in this case

$$\left.\begin{aligned} U_\nu = 1;\ V_\nu = 0 \quad \text{for} \quad \tilde{\varepsilon}_\nu > \lambda, \\ U_\nu = 0;\ V_\nu = 1 \quad \text{for} \quad \tilde{\varepsilon}_\nu < \lambda, \end{aligned}\right\} \tag{30}$$

then the new quasi-particles α, β should correspond to the old particles outside the Fermi sea and to the old holes inside. If the interaction is sufficiently weak, the trivial solution (30) remains the only solution of (27).

However, if the inequality

$$\frac{1}{2}\sum_{\nu'} \frac{\langle \nu\nu \,|\, G \,|\, \nu'\nu' \rangle}{|\, \tilde{\varepsilon}_{\nu'} - \lambda \,|} > 1 \tag{31}$$

is fulfilled, then there is also a non-trivial solution of (27), which corresponds to the modification of the Fermi sea (the analogy of the superconducting state)*.

The equation (27) contains two matrix elements of the two-body potential which play entirely different roles. The matrix element $\langle \nu\nu' | G | \nu'\nu \rangle$ is shown from (19) to contribute only to the self-consistent field. The matrix element $\langle \nu\nu | G | \nu'\nu' \rangle$ ("pairing interaction"), on the contrary, determines a qualitatively new effect which corresponds to a modification of the Fermi sea. From (31) one can see that this modification is possible only if the pairing interaction for sufficiently many states has a coherent character, e. g., for a sufficiently broad region of the states the matrix element $\langle \nu\nu | G | \nu'\nu' \rangle$ must have the same sign, because otherwise there will occur a cancellation.

Lets us expand the two-body interaction potential in spherical harmonics

$$G(\vec{r}_1 - \vec{r}_2) = \sum_l G^l(r_1 r_2) P_l(\cos\vartheta_{12}). \tag{32}$$

and ask the question: "Which part of the two-body interaction contributes to a self-consistent field and which part determines a coherent pairing interaction?"

We believe that the following considerations may provide a qualitative understanding of this point. Assume that the spherically symmetric part of the interparticle interaction has determined a certain self-consistent isotropic field. The single-particle levels in this field are degenerate and characterized by the value of the angular momentum j (shell model). Let us consider the particles in the same level j, neglecting their interaction

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* Eq. (27) differs from the analogous equation in ref. 7 for a superconductor by the character of the spectrum $\tilde{\varepsilon}_\nu$. In the case of the superconductor, the continuous spectrum allows a non-trivial solution of (27) for any value of the interaction.

with the particles in the other shells. The term with $l = 2$ (quadrupole) gives an essential contribution to a self-consistent field producing an ellipsoidal deformation which splits the single-particle levels[20)]. But its contribution to the pairing interaction is small, because it connects only the nearest levels ($|\nu - \nu'| \leqslant 2$), which might not be enough to satisfy the inequality (31). The term in (32) with $l = 4$ connects the more distant levels ($|\nu - \nu'| \leqslant 4$), but its contribution to the self-consistent field is not so important, and so on. Therefore, the main contribution to the pairing interaction is from the high harmonics of the two-particle potential. The self-consistent field, on the other hand, is essentially determined by the low harmonics.

II. Ground State and Single-Particle Excitations

1. Solution of the Equation for Δ_ν

We assume that the condition (31) is fulfilled and that a non-trivial solution of the equation (27) exists. For an explicit solution of (27), assumptions have to be made about the character of the single-particle spectrum $\tilde{\varepsilon}_\nu$. For strongly deformed nuclei, where the shell structure almost completely vanishes, the distribution of the single-particle levels is approximately uniform in each interval, and the average level density is a smooth function of the energy. The sum in (27) spreads practically only over an effective region of the coherent interaction where the matrix element $\langle \nu \nu | G | \nu' \nu' \rangle$ differs appreciably from zero. The single-particle levels of spherical and not strongly deformed nuclei exhibit a shell structure*, i. e., are divided into sharply separated groups[11)]. The most essential contribution to the sum (27) is given, in this case, by transitions between the states in the same shell. Neglecting the transitions between different shells (which will be discussed later), we can treat each shell independently. Therefore, in both cases, we have to consider a separated group of levels with approximately uniform distribution. For strongly deformed nuclei, this level group, determined by the effective region of interaction, may be assumed to be symmetrical with respect to the Fermi surface. In the second case, the level group coincides with the shell and may, in particular, reduce to one highly degenerate level. The position of the Fermi energy, in this case, is not fixed and depends on the number of particles in the shell. (A symmetrical position corresponds

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* We do not necessarily here mean *j*-shells.

approximately to a half-filled shell). We shall consider this general case, keeping in mind that the case of strongly deformed nuclei is equivalent simply to a half-filled shell.

To simplify the problem, we assume that the matrix element $\langle \nu\nu | G | \nu'\nu' \rangle$ is constant for the transitions between any levels inside the shell. With this assumption, the equation (27) for Δ (which is now constant) takes the form

$$1 = \tfrac{1}{2} G \sum_{\nu} \frac{1}{\sqrt{(\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta^2}}. \tag{33}$$

For Δ larger than the distance between levels, which is the case we are interested in, the sum in (33) can be replaced by an integral. Then, we get

$$1 = \frac{G}{2} \int_a^b \varrho(\varepsilon) \frac{d\varepsilon}{\sqrt{\varepsilon^2 + \Delta^2}} \tag{34}$$

where

$$a = \varepsilon' - \lambda; \quad b = \varepsilon'' - \lambda \tag{35}$$

and ε', ε'' determine the boundaries of the shell.

Defining a certain average level density $\bar{\varrho}$, according to

$$\bar{\varrho} \int_a^b \frac{d\varepsilon}{\sqrt{\varepsilon^2 + \Delta^2}} = \int_a^b \frac{\varrho(\varepsilon)\, d\varepsilon}{\sqrt{\varepsilon^2 + \Delta^2}}, \tag{36}$$

and introducing the dimensionless quantity

$$\eta = (\bar{\varrho} G)^{-1}, \tag{37}$$

we obtain from (34)

$$\sinh^{-1}\frac{b}{\Delta} - \sinh^{-1}\frac{a}{\Delta} = 2\eta \tag{38}$$

and, therefore,

$$\Delta = \frac{1}{\sinh 2\eta} [b^2 + a^2 - 2ab \cosh 2\eta]^{1/2}. \tag{39}$$

2. Influence of the neighbouring shells

Up to now, we have not taken into account the matrix elements $\langle \nu\nu | G | \nu'\nu' \rangle$ between different shells. Here, we consider briefly their effect. By separating out those terms of the sum (27), for which ν' is in the shell nearest to the Fermi surface (λ-shell), we can rewrite the equation (27) in the following form:

$$\Delta_\nu = \frac{1}{2}\sum_{\nu'}^{\lambda} \frac{\langle \nu\nu \,|\, G \,|\, \nu'\nu' \rangle}{\sqrt{(\tilde{\varepsilon}_{\nu'} - \lambda)^2 + \Delta_{\nu'}^2}}\,\Delta_{\nu'} + \frac{1}{2}\sum_{\nu'}{}' \frac{\langle \nu\nu \,|\, G \,|\, \nu'\nu' \rangle}{\sqrt{(\tilde{\varepsilon}_{\nu'} - \lambda)^2 + \Delta_{\nu'}^2}}\,\Delta_{\nu'}. \qquad (40)$$

Treating the last term as a perturbation, we may in this term replace $\Delta_{\nu'}$ by Δ_ν, determined from the main part of (40). Further, in the denominator of this term, Δ_ν^2 can be neglected, since the distance between shells is greater than the gap*. The equation (55) may then be expressed as

$$\left.\begin{aligned} \Delta_\nu = \frac{1}{2}\sum_{\nu'}^{\lambda} \frac{\Delta_{\nu'}}{\sqrt{(\tilde{\varepsilon}_{\nu'} - \lambda)^2 + \Delta_{\nu'}^2}} \Bigg\{ & \langle \nu\nu \,|\, G \,|\, \nu'\nu' \rangle \\ & + \frac{1}{2}\sum_{\nu''}{}' \frac{\langle \nu\nu \,|\, G \,|\, \nu''\nu'' \rangle \langle \nu''\nu'' \,|\, G \,|\, \nu'\nu' \rangle}{|\, \tilde{\varepsilon}_{\nu''} - \lambda \,|} \Bigg\}. \end{aligned}\right\} \qquad (41)$$

Eq. (41) has the same form as the corresponding equation in which intershell transitions are neglected, but with a new value of the interaction. Therefore, the influence of other shells only increases the effective interparticle interaction.

The efficiency of the pairing interaction depends on the region of interaction, i. e., on the number of states connected by the transitions $\langle \nu\nu \,|\, G \,|\, \nu'\nu' \rangle$, and on the value of the matrix element. Inclusion of intershell transitions means, in fact, some extension of the interaction region, but, as it has been shown just now, it can be described as an effective increase in the value of the matrix element. It is of interest to see how this solution for Δ, in the case when the shell structure disappears, goes into solution with the unrenormalized matrix element, but with an extended region of interaction. For simplicity, we consider the case of a uniform level density inside the shells and assume a constant matrix element for all transitions in an energy region $(-\omega, \omega)$ measured from the Fermi surface λ. Then, we have for the last term in (40)

$$\frac{1}{2}\Delta\left(\int_{-\omega}^{a-\delta} + \int_{b+\delta}^{\omega}\right)\frac{G\varrho\, d\varepsilon}{\sqrt{\varepsilon^2 + \Delta^2}},$$

where δ is the distance between the shells. Neglecting the quantity Δ in the square root, and performing the integration, we obtain for the equation (40)

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* This is, in fact, the condition for the existence of a shell structure in our treatment.

$$\sinh^{-1}\frac{b}{\Delta}-\sinh^{-1}\frac{a}{\Delta}=2\,\eta-ln\frac{\omega^2}{(b+\delta)\,(\delta-a)}\equiv 2\,\eta_{\mathrm{eff}}\,.$$

In the limiting case of $\eta_{\mathrm{eff}} \gg 1$, one finds for Δ

$$\Delta = 2\sqrt{-ab}\,e^{-\eta_{\mathrm{eff}}} = 2\,\omega\sqrt{\frac{ab}{(b+\delta)\,(a-\delta)}}\,e^{-\eta}$$

which, for $\delta \to 0$, goes into the usual solution for a system with uniform level density (Fermi gas).

The matrix element $\langle \nu\nu|G|\nu'\nu'\rangle$ decreases with the atomic number as A^{-1}. On the other hand, in heavy nuclei, the distance between the shells decreases and intershell transitions become more essential. Therefore, the effective interaction parameter G decreases somewhat more slowly than A^{-1}.

3. Elimination of the Chemical Potential

The operator for the total number of particles in the system has the form

$$\left.\begin{aligned} N=\sum_{k\sigma} a_{k\sigma}^{+}\,a_{k\sigma}=\sum_{\nu} 2\,V_\nu^2+\sum_{\nu}(U_\nu^2-V_\nu^2)\,(\alpha_\nu^{+}\,\alpha_\nu+\beta_\nu^{+}\,\beta_\nu)\\ +\sum_{\nu} 2\,U_\nu\,V_\nu\,(\alpha_\nu^{+}\,\beta_\nu^{+}+\beta_\nu\,\alpha_\nu)\,.\end{aligned}\right\}\qquad(42)$$

The average number of particles in the ground state ("vacuum") is determined by the constant term in (42). Comparing it with a given value N, we find the following equation which determines λ:

$$\sum_{\nu} 2\,V_\nu^2=\sum_{\nu}\left(1-\frac{\hat{\varepsilon}_\nu-\lambda}{\sqrt{(\tilde{\varepsilon}_\nu-\lambda)^2+\Delta^2}}\right)=N \qquad (43)$$

or, replacing the sum by an integral,

$$\int_a^b\left(1-\frac{\varepsilon}{\sqrt{\varepsilon^2+\Delta^2}}\right)\varrho\,(\varepsilon)\,d\varepsilon=N. \qquad (44)$$

We shall approximate the level density $\varrho(\varepsilon)$ by a straight line, taking into account only the first derivative $\varrho'(\varepsilon)$. Introducing two parameters

$$\varrho_0=\frac{1}{2}\,[\varrho\,(b)+\varrho\,(a)]\,;\qquad \xi=\frac{\varrho\,(b)-\varrho\,(a)}{\varrho\,(b)+\varrho\,(a)}, \qquad (45)$$

we have in this approximation

$$\varrho(\varepsilon) = \varrho_0 \left[1 - \xi \frac{b+a}{b-a} + \frac{2\,\xi}{b-a}\,\varepsilon\right]. \tag{46}$$

The average density ϱ_0 is connected with the total number of pairing states in the shell Ω by the condition

$$\varrho_0 \left(\varepsilon'' - \varepsilon'\right) = \Omega. \tag{47}$$

Performing the integration in (44) and inserting for Δ the expression (39), we get

$$\left.\begin{aligned} 1 - \frac{N}{\Omega} - \frac{b+a}{b-a}\tanh\eta - \frac{\xi}{2}\left(1 - \frac{2\,\eta}{\sinh 2\,\eta}\right)\coth\eta \\ + \frac{\xi}{2}\left(\frac{b+a}{b-a}\right)^{2}\left(1 - \frac{2\,\eta}{\sinh 2\,\eta}\right)\tanh\eta = 0. \end{aligned}\right\} \tag{48}$$

It is convenient to introduce the quantity χ_N according to

$$b + a = (b-a)\,\chi_N \coth\eta = (\varepsilon'' - \varepsilon')\,\chi_N \coth\eta. \tag{49}$$

Inserting (49) into (48), one finds the following equation for χ_N:

$$\chi_N - \tfrac{1}{2}\,\xi\gamma(\eta)\,\chi_N^2 = 1 - \frac{N}{\Omega} - \tfrac{1}{2}\,\xi\gamma(\eta), \tag{50}$$

where

$$\gamma(\eta) = \coth\eta\left(1 - \frac{2\,\eta}{\sinh 2\,\eta}\right). \tag{51}$$

From (50) follows

$$\chi_N = 2\,\frac{1 - \dfrac{N}{\Omega} - \dfrac{\xi}{2}\gamma}{1 + \sqrt{1 - 2\,\xi\gamma\left(1 - \dfrac{N}{\Omega}\right) + \xi^2\gamma^2}}. \tag{52}$$

From (45) and (51), one can see that $|\xi| \leqslant 1$ and $0 \leqslant \gamma < 1$. Thus, from (52) it follows that $|\chi_N| \leqslant 1$. The limiting values ± 1 are reached on the boundaries of the shell ($N = 0$ and $N = 2\,\Omega$):

$$\chi_N = \left\{\begin{array}{rl} 1 & \text{for } N = 0, \\ 0 & \text{for } N = (1 - \frac{1}{2}\,\xi\gamma), \\ -1 & \text{for } N = 2\,\Omega. \end{array}\right\} \tag{53}$$

Thus, the quantity χ_N characterizes the occupation of the shell and may be called "occupation factor". For the uniform level density ($\xi = 0$),

$$\chi_N \rightarrow \chi_N^0 = 1 - \frac{N}{\Omega}. \tag{54}$$

The chemical potential λ may be expressed from (49) and (35) as

$$\lambda = \frac{\varepsilon'' + \varepsilon'}{2} - \frac{1}{2}(\varepsilon'' - \varepsilon')\,\chi_N \coth\eta. \tag{55}$$

The average density $\bar{\varrho}$ introduced in (36) (and therefore η) in general depends on N. Inserting (46) into (36) and performing the integration, we find

$$\bar{\varrho} = \varrho_0\left[1 - \xi\chi_N\left(\coth\eta - \frac{1}{\eta}\right)\right]. \tag{56}$$

With the aid of (55) or (49) λ can be eliminated from all final results.

4. Criterion for the Existence of a Gap

Eliminating λ from (39) we get for Δ[*]

$$\Delta = \frac{\varepsilon'' - \varepsilon'}{2\sinh\eta}(1 - \chi_N^2)^{1/2}{}^{**}. \tag{57}$$

This result has been obtained with the assumption that Δ is not smaller than the distance between levels. This condition may be written as $\Delta\varrho_0 > 1$ or, with the aid of (57) and (47), as

$$\frac{\Omega}{2\sinh\eta}(1 - \chi_N^2)^{1/2} > 1. \tag{58}$$

This inequality gives the condition for a modification of the Fermi sea and for the existence of an energy gap for the nucleus. To estimate the left side of (58), we may use the expression (54) for χ_N and obtain

$$\frac{1}{2\sinh\eta}\sqrt{N(2\Omega - N)} > 1. \tag{59}$$

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[*] We avoid calling Δ an "energy gap". It will be seen later, that in the case $\eta < 1$, the energy gap is determined by another quantity.

[**] Far from the boundaries of the shell, where $\chi_N^2 \ll 1$, (57) coincides with the solution in references 6, 7 for a superconductor if $(\varepsilon'' - \varepsilon')$ is identified with the region of the coherent interaction (see also pages 14–15).

In the case of $\eta \gg 1$, (59) is satisfied only by a sufficiently broad region of coherent interaction, i. e., for sufficiently large values of $N(2\Omega - N)$. On the other hand, if $\eta \lesssim 1$, this condition is always fulfilled.

5. Energy of the Ground State

The energy of the ground state (of the "vacuum") is the quantity U given by (22). The last term in (22) is connected with the energy of the selfconsistent field. We shall come to this term later and consider here only the two first terms in (22), i. e.,

$$U' = \sum_{\nu} (\tilde{\varepsilon}_{\nu} - \lambda)\, 2 V_{\nu}^2 - \sum_{\nu} \varDelta_{\nu} U_{\nu} V_{\nu}. \tag{60}$$

The sum over closed shells, for which $\varDelta_{\nu} = 0$; $V_{\nu} = 1$, gives

$$U'_{cl} = 2 \sum_{\nu}{}' (\tilde{\varepsilon}_{\nu} - \lambda) = 2 \sum_{\nu}{}' \tilde{\varepsilon}_{\nu} - \lambda N_{cl}. \tag{61}$$

Using the constancy of $\varDelta_{\nu}$ and replacing the sum by an integral, we get for the unfilled λ-shell

$$U'_{\lambda} = \int_a^b \left(1 - \frac{\varepsilon}{\sqrt{\varepsilon^2 + \varDelta^2}}\right) \varrho(\varepsilon)\, \varepsilon\, d\varepsilon - \frac{\varDelta^2}{G}.$$

After the integration and subsequent elimination of λ with the help of (49), we find

$$U'_{\lambda} = -\frac{\Omega}{4} (\varepsilon'' - \varepsilon') (1 - \chi_N)^2 \left[\coth \eta - \frac{\xi}{3} (2 + \chi_N)\right]. \tag{62}$$

The quantity U corresponds to the ground state of the auxiliary Hamiltonian (2) with the chemical potential. The energy which corresponds to the original Hamiltonian according to (62) and (55) is given by

$$\left.\begin{aligned} W_{\lambda} = U'_{\lambda} + \lambda N_{\lambda} = \frac{1}{2} \left[\varepsilon' + \varepsilon'' + \frac{\xi}{3} (\varepsilon'' - \varepsilon')\right] N_{\lambda} \\ -\frac{\Omega}{4} (\varepsilon'' - \varepsilon') (1 - \chi_N^2) \left[\coth \eta + \frac{\xi}{3} \chi_N (1 - 3\gamma(\eta) \coth \eta) - \frac{\xi^2}{3} \gamma(\eta)\right]. \end{aligned}\right\} \tag{63}$$

The last term in (63) contains the factor $(1 - \chi_N^2)$ and disappears for the closed shell, which has, thus, the energy

$$W_{cl} = \frac{1}{2} \left[\varepsilon' + \varepsilon'' + \frac{\xi}{3} (\varepsilon'' - \varepsilon')\right] 2\,\Omega. \tag{64}$$

It is known that the energy of the closed shell in the first approximation does not change for a small variation $\delta\beta$ of the equilibrium deformation. Therefore, the quantity

$$\varepsilon_\lambda = \frac{1}{2}\left[\varepsilon' + \varepsilon'' + \frac{\xi}{3}(\varepsilon'' - \varepsilon')\right]$$

is at least quadratic in $\delta\beta$*.

In the absence of the interaction ($\eta \to \infty$; $\gamma \to 1$), it follows from (63) that

$$W_\lambda = \varepsilon_\lambda N - \frac{\Omega}{4}(\varepsilon'' - \varepsilon')(1 - \chi_N^2)\left[1 - \tfrac{2}{3}\xi\chi_N - \tfrac{1}{3}\xi^2\right]. \tag{65}$$

In the opposite limiting case $\eta < 1$, one finds

$$\left.\begin{aligned} \gamma \approx \frac{2}{3}\eta; \quad \chi_N \approx \chi_N^0 - \frac{\xi}{3}\Theta_N\eta - \frac{2}{3}\xi^2\chi_N^0\Theta_N\eta^2 \\ \varepsilon'' - \varepsilon' \approx \Omega G\eta\left[1 - \frac{\xi}{3}\chi_N^0\eta + \frac{\xi^2}{g}\Theta_N\eta^2\right], \end{aligned}\right\} \tag{66}$$

where χ_N^0 is given by (54), and

$$\Theta_N = 1 - (\chi_N^0)^2 = \frac{2N}{\Omega}\left(1 - \frac{N}{2\Omega}\right). \tag{67}$$

Inserting (66) in (63) and restricting ourselves to η^2-terms, we find

$$W_\lambda = \varepsilon_\lambda N - \frac{1}{4}\Omega^2 G\Theta_N - \frac{\Omega^2}{12}G\Theta_N\left(1 - \frac{\xi^2}{3}\Theta_N\right)\eta^2. \tag{68}$$

For small deformations β of a spherical nucleus, $\eta \approx (\varepsilon'' - \varepsilon')/\Omega G \sim \beta$. The expression (65) is thus a linear function of β. On the other hand, (68) is proportional to β^2. Therefore, the pairing interaction changes the dependence of the energy of the outside nucleons on deformation. This turns out to be very important for the problem of the nuclear equilibrium shape. (See Part III).

6. Energy Spectrum of Quasi-Particles

The ground state of the system expressed in terms of the quasi-particles $\alpha\beta$ is a vacuum. Acting on the vacuum wave function by the operators α^+ and β^+, we get excited states with one or more quasi-particles. Such states we shall denote as single-particle excited states. The energy of these

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* For a correct approximation the quantity ξ must be chosen to satisfy this condition.

states measured relative to the ground state is given by the sum of the quasi-particle energies E_ν.

From (28), (55), and (57) we find for E_ν

$$\left.\begin{aligned} E_\nu^2 &= (\tilde{\varepsilon}_\nu - \lambda)^2 + \Delta^2 \\ &= \frac{1}{4}(\varepsilon'' - \varepsilon')^2 (1 - \chi_N^2)(\coth^2 \eta - 1) + \left[\tilde{\varepsilon}_\nu - \frac{\varepsilon' + \varepsilon''}{2} + \frac{1}{2}(\varepsilon'' - \varepsilon')\chi_N \coth \eta\right]^2. \end{aligned}\right\} \quad (69)$$

In the absence of a pairing interaction, E_ν coincides with the particle energy measured relative to the Fermi surface:

$$E_\nu^0 = |\tilde{\varepsilon}_\nu - \lambda^0| = \pm(\tilde{\varepsilon}_\nu - \lambda_0) = \pm\left\{\tilde{\varepsilon}_\nu - \tfrac{1}{2}(\varepsilon'' + \varepsilon') + \tfrac{1}{2}(\varepsilon'' - \varepsilon')\bar{\chi}_N\right\}, \quad (70)$$

where $\bar{\chi}_N = \chi_N(\eta = \infty)$. With the aid of (70), the expression (69) takes the form

$$\left.\begin{aligned} E_\nu^2 = \frac{1}{4}(\varepsilon'' - \varepsilon')^2 \Big\{ &\coth^2 \eta - 1 + (\chi_N - \bar{\chi}_N)^2 - 2\chi_N \bar{\chi}_N (\coth \eta - 1) \\ &\pm \frac{4E_\nu^0}{\varepsilon'' - \varepsilon'}(\chi_N \coth \eta - \bar{\chi}_N) + \frac{4E_\nu^{02}}{(\varepsilon'' - \varepsilon')^2}\Big\}. \end{aligned}\right\} \quad (71)$$

In the limit of $\eta \gg 1$ (weak interaction or small level density), we get

$$E_\nu \approx \sqrt{(\varepsilon'' - \varepsilon')^2 (1 - \chi_N^2) e^{-2\eta} + E_\nu^{02}} = \sqrt{\Delta^2 + E_\nu^{02}}. \quad (72)$$

In this case, the value of the energy gap is given by the quantity Δ. Because of the factor $(1 - \chi_N^2)$ the gap disappears, in this case, at closed shells.

In the opposite limiting case of $\eta < 1$, it follows from (71) that

$$E_\nu = \sqrt{\tfrac{1}{4}\Omega^2 G^2 \pm \chi_N^0 \Omega G E_\nu^0 + E_\nu^{02}}. \quad (73)$$

In (73) the role of the gap is played by the quantity $^1/_2\, \Omega G$. It does not depend on the number of particles in the shell and does not coincide with Δ which, for $\eta \langle 1$, is equal to

$$\Delta \approx \frac{1}{2}\Omega G (1 - (\chi_N^0)^2)^{1/2} = \frac{1}{2}\Omega G \Theta_N^{1/2}. \quad (74)$$

For the first excited states, E_ν^0 is of the order of the distance between single-particle levels (in the absence of degeneracy $E_\nu^0 \sim \varrho^{-1}$). Therefore, the terms in (73) containing E_ν^0 are small. These terms determine the level density of the quasi-particles above the gap. For small E_ν^0, we have from (73)

$$E_\nu \approx \frac{1}{2}\Omega G \pm \left(\chi_N^0 \pm \frac{E_\nu^0}{\Omega G}\right) E_\nu^0. \quad (75)$$

(The term, quadratic in E_ν^0, may be important only in the middle of the shell, where $\chi_N^0 \approx 0$). Comparing the level density ϱ for the quasi-particles with that for the original non-interacting particles ϱ^0, one finds

$$\varrho^0/\varrho \approx \chi_N^0 + \frac{2\,E_\nu^0}{\Omega G} = 1 - \frac{N}{\Omega} \pm \frac{2\,E_\nu^0}{\Omega G}. \tag{76}$$

Near the closed shell, where $|\chi_N^0| \sim 1$, the ratio (76) is of the order of unity. As one moves away from closed shells, the level density of quasi-particles increases and in the middle of the shell becomes of the order of $\Omega\varrho^0$.

7. Wave Functions of the Ground- and Excited States

We consider now the question of the meaning of the wave functions of the ground- and excited states in terms of the old particles. Let us introduce the wave function of the vacuum state of the old particles $\Psi_0^{(0)}$, for which $a_{k\sigma}\Psi_0^{(0)} = 0$. The first transformation (3), which removes the self-consistent field, does not mix up creation and destruction operators and, therefore, does not change the vacuum state. After introduction of the operators α_ν and β_ν, the new vacuum state Ψ_0 is defined by the equations

$$\left.\begin{aligned} \alpha_\nu \Psi_0 &= (U_\nu b_{\nu+} - V_\nu b_{\nu-}^+)\,\Psi_0 = 0, \\ \beta_\nu \Psi_0 &= (U_\nu b_{\nu-} + V_\nu b_{\nu+}^+)\,\Psi_0 = 0. \end{aligned}\right\} \tag{77}$$

It is easy to prove that these equations are satisfied by the function

$$\Psi_0 = \prod_\nu (U_\nu + V_\nu b_{\nu+}^+ b_{\nu-}^+)\,\Psi_0 = 0. \tag{78}$$

In this representation, the wave functions of the excited states with only one quasi-particle have the form

$$\left.\begin{aligned} \alpha_\nu^+ \Psi_0 &= \prod_{\nu' \neq \nu} (U_{\nu'} + V_{\nu'} b_{\nu'+}^+ b_{\nu'-}^+)\, b_{\nu+}^+ \Psi_0^{(0)}, \\ \beta_\nu^+ \Psi_0 &= \prod_{\nu' \neq \nu} (U_{\nu'} + V_{\nu'} b_{\nu'+}^+ b_{\nu'-}^+)\, b_{\nu-}^+ \Psi_0^{(0)}, \end{aligned}\right\} \tag{79}$$

and the function corresponding to the excitation of the pair is

$$\alpha_\nu^+ \beta_\nu^+ \Psi_0 = \prod_{\nu' \neq \nu} (U_{\nu'} + V_{\nu'} b_{\nu'+}^+ b_{\nu'-}^+)\,(U_\nu b_{\nu+}^+ b_{\nu-}^+ - V_\nu)\,\Psi_0^{(0)}\,{}^{*}. \tag{80}$$

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* The expressions (78)—(80) are similar to those obtained in reference 6 for a superconductor.

As it follows from (78), Ψ_0 describes a superposition of states with different numbers of particles. This is true also for the functions (79) and (80). It must be pointed out that (78) and (80) are formed only by states with even numbers of particles. The functions (79), on the contrary, describe only superpositions of states with odd N. Therefore, these functions belong to different physical systems.

The "vacuum" function Ψ_0 describes the ground state only of the even-N system (even-even nuclei). Excited states in such systems contain an even number of quasi-particles α^+ or β^+ and are separated from the ground state by twice the energy gap.

For the odd-N systems, the ground state is given by the lowest of the states (79), i. e., the state with one quasi-particle, say $\alpha^+_{\nu_0}\,\Psi_0$. The excitations of this odd quasi-particle, which are obtained by acting with the operators $\alpha^+_{\nu}\,\alpha_{\nu_0}$ or $\beta^+_{\nu}\,\alpha_{\nu_0}$, have no energy gap.

Therefore, the excitation spectra in even-even and odd nuclei turn out to be completely different. On the other hand, the properties connected with the energy of the ground state exhibit no essential differences, since the energy of the odd particle may be neglected with comparison to the "vacuum" energy.

8. Uncertainty in the Number of Particles

To estimate the uncertainty in the number of particles in the states (78)—(80), one can consider the average quadratic fluctuation of N, say, in the "vacuum" state Ψ_0. Using for N the expression (42), one easily finds

$$\langle N^2\rangle - \langle N\rangle^2 = \sum_{\nu} 4\,U_\nu^2 V_\nu^2 = \sum_{\nu} \frac{\Delta_\nu^2}{\Delta_\nu^2 + (\tilde{\varepsilon}_\nu - \lambda)^2}. \tag{81}$$

For simplicity, we restrict ourselves to the case of a uniform level density ($\xi = 0$). Replacing the sum in (81) by an integral, we find, after some elementary calculations,

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{\Omega}{\sinh\eta}\,\Theta_N^{1/2}\tan^{-1}\left(\Theta_N^{1/2}\sinh\eta\right), \tag{82}$$

where Θ_N is the occupation factor (67). In the limiting case of $\eta \gg 1$, we get

$$\langle N^2\rangle - \langle N\rangle^2 \approx \pi\,\frac{\Omega}{2\sinh\eta}\,\Theta_N^{1/2} \qquad (\eta \gg 1). \tag{83}$$

This expression differs from the left side of the inequality (58) only by the factor π. Therefore, for this case, we can write

$$\langle N^2 \rangle - \langle N \rangle^2 \approx \pi \varrho \Delta \qquad (\eta \gg 1). \tag{84}$$

For strongly deformed nuclei for which this case is realized, the value $\varrho \Delta$ is significantly smaller than N, the number of the particles in the un closed shell.

In the case of $\eta < 1$, (82) takes the form

$$\langle N^2 \rangle - \langle N \rangle^2 \approx \Omega \Theta_N = 2N\left(1 - \frac{N}{2\Omega}\right); \quad (\eta < 1). \tag{85}$$

For $N = 2$ (one pair), δN, the average width of the distribution is approximately 2, i. e., there are admixed practically only the nearest even neighbours. In the middle of the shell ($N \sim \Omega$) the width is of the order of $\sqrt{N}$.

One might suspect that the uncertainty of N, in spite of its smallness, is of principal importance, because it might permit solutions which are impossible for fixed N. It must be pointed out that the removal of the condition $N = \text{const}$ by the introduction of the chemical potential λ does not extend the scope of possible solutions. This method means only a replacement of the system under consideration (N-system by λ-system). There are no physical reasons to expect a significant change in the ground state and in the properties of quasi-particles caused by this replacement. We can see this in the limiting case $\eta = 0$ (complete degeneracy), where our results may be compared with the exact solution*. The energy spectrum of the system with N particles is given in this case by[12).

$$W_m^N = -\frac{1}{2}\Omega G N\left(1 - \frac{N-2}{2\Omega}\right) + \Omega G m\left(1 - \frac{m-1}{\Omega}\right). \tag{86}$$

The corresponding expression in our case (λ-system) follows from (68) and (73) by substituting $\eta = 0$, $E_\nu^0 = 0$, $\varepsilon_\nu = 0$ by

$$W_m^\lambda = -\frac{1}{2}\Omega G N\left(1 - \frac{N}{\Omega}\right) + \Omega G m \tag{87}$$

(the last term corresponds to m excited pairs). Comparing (86) and (87) it is seen that relative corrections both to the ground state and to excited states are of the order of Ω^{-1} **.

---

* The Hamiltonian is given by $H = -G \sum_{\nu\nu'} b^+_{\nu+} b^+_{\nu-} b_{\nu'-} b_{\nu'+}$

** The interaction, H_{int}, between quasi-particles gives corrections of the same order. Therefore, in the approximation of independent quasi-particles, the equations (87) and (86) do not differ from each other.

9. Effect of the Residual Interaction between Quasi-Particles

The nature of the canonical transformations performed above might be explained in the following way. The interaction between the original particles contains a coherent pairing energy. This interaction, in principle, could be treated in a direct way by rejecting of the independent-particle model. We had another aim, namely to keep this model, but to take into account the pairing interaction, or at least its main part, by introducing a new type of independent particles. The pairing energy, which was an interparticle interaction, then determines the intrinsic structure of the quasi-particles.

With the aid of the canonical transformations, we can take into account the pairing interaction only in the form of the matrix elements $\langle \nu\nu|G|\nu'\nu'\rangle$. The question might quite naturally arise as to whether these matrix elements are the main part of the pairing interaction. Other matrix elements could possibly cause results which are basically different.

The residual interaction between the new quasi-particles is described by the Hamiltonian H_{int} (16). To answer the questions mentioned above one might treat H_{int} as a perturbation. In our case, the perturbation treatment has a special feature, since the coefficients of the canonical transformation U_ν, V_ν have to be corrected in each order. In the second order in H_{int}, the structure of the equation (27) for Δ_ν does not change, but the matrix element $\langle \nu\nu|G|\nu'\nu'\rangle$ is replaced by an expression of the form*

$$\langle \nu\nu \,|\, G \,|\, \nu'\nu'\rangle + \sum_{\nu_1\nu_1'} \frac{\langle \nu\nu_1 \,|\, G \,|\, \nu_1'\nu'\rangle \langle \nu_1\nu \,|\, G \,|\, \nu'\nu_1'\rangle}{E_\nu + E_{\nu'} + E_{\nu_1} + E^{\nu_1'}} U_{\nu_1} V_{\nu_1} U_{\nu_1'} V_{\nu_1'}.$$
$$+ \text{ terms of similar form}$$

In other words, the graphs of the perturbation theory correct the pairing interaction. One can expect that the sum of the graphs would lead to replacing the matrix element $\langle \nu\nu|G|\nu'\nu'\rangle$ by a certain effective pairing interaction, but not to a basic change of the results**. In this sense, the influence of the residual interaction H_{int} on the properties of the ground state and the quasi-particles is not essential.

* See the analogous analysis for a superconductor in reference 13.

** The analogous procedure in the Brueckner-Bethe theory of nuclear matter [14] leads to a replacement of the interaction matrix elements by those of the transition matrix. A similar situation might be pointed out also in the theory of superfluidity in a Bose system. In reference 15, a spectrum of quasi-particles has been obtained with the aid of a canonical tranformation. The sum of graphs of the perturbation theory, which has been performed in ref. 16, gave the same result but with replacement of the interaction matrix elements by exact scattering amplitudes.

Besides that, the interaction between quasi-particles contains the low harmonics of the nucleon-nucleon interaction (32) which remains almost untouched by the canonical transformation. These harmonics, which give rise to collective excitations in nuclei, require other methods of consideration20). On the other hand, collective excitations in nuclei can be treated directly in the framework of the unified nuclear model by introducing a time-dependent deformed self-consistent field.

III. Collective Excitations in Nuclei

The nature of collective excitations in nuclei and the methods of their investigation are explained in detail in the literature (see, e. g., Chapter V of reference 3). We briefly sketch some essential points which will be needed later.

Let us introduce a parameter which describes a particular type of the collective motion. Using the adiabatic character of the collective motion one may first consider the intrinsic motion of the nucleus for a fixed value of ϑ. The energy eigenvalues for this motion are denoted by $W_i(\vartheta)$. Then, the Hamiltonian of the collective motion is given approximately by

$$H_{\text{coll}} = W_i(\vartheta) + \frac{1}{2} B_i(\dot{\vartheta})^2, \tag{88}$$

where the inertial parameter $B_i(\vartheta)$, obtained by the adiabatical perturbation theory, is given by17)

$$B_i(\vartheta) = 2\hbar^2 \sum_{j \neq i} \frac{|\langle j \left| \frac{\partial}{\partial \vartheta} \right| i \rangle|^2}{W_j - W_i}. \tag{89}$$

The potential energy of the collective motion $W_i(\vartheta)$ and the inertial parameter $B_i(\vartheta)$ are essentialy determined by the intrisic nucleon motion and their calculation is possible, in practice, only for simple models. It is known that the hydrodynamical model of irrotational flow gives too small a value for $B(\vartheta)$. The independent-particle model (using an oscillator potential) leads to a very large value of $B(\vartheta)$ for rotations (rigid-body moment of inertia) and to a very small $B(\vartheta)$ for vibrations, which violates the adiabatic condition.

Below, the parameters of the collective motion will be found for the model of independent quasi-particles (which is equivalent to a model of the old particles with the pairing interaction included). It is not our aim to make here a detailed investigation of the collective excitations or a comparison of the results with experimental data. The main problem is to establish what role the pairing interaction plays in collective nucleon motion and what qualitative results it leads to.

1. Dependence of the Nuclear Energy on the Deformation

Here, we restrict ourselves only to the axially symmetric quadrupole deformations. In the liquid drop model, the deformation is defined in a natural way as a deviation of the uniform drop from the spherical shape, and is uniquely connected with the nuclear quadrupole moment*. In single-particle models where one considers the nucleons in a certain potential well, such a simple picture is valid only for nuclei with closed shells. In the presence of particles in an unfilled shell, the nucleus does not behave as a homogeneous system. The nuclear quadrupole moment is not determined only by the deformation of the well, but depends essentially on the configuration of the particles in the unfilled shell. The energy of the nucleus will also depend, in this case, on both factors. However, one must take into account the self-consistent nature of the nuclear potential. Self-consistency requires that the distribution of the potential must be the same as the density distribution (which is the consequence of the short range nucleon-nucleon forces). Therefore, for a given value of the eccentricity of the well, only such configurations of the outside nucleons are allowed, which provide the same eccentricity of the density.

In Section II. 5, we have not used this self-concistency argument; therefore the ground-state energy obtained there applies to the system in an external potential. In order to introduce the self-consistency, we now ask for the lowest state of the system with a fixed value of the quadrupole moment. Due to a relatively small coupling between the closed-shell core and the outside nucleons, we shall consider the deformations of these two components as distinct degrees of freedom and shall be looking for the nuclear energy as a function of two deformation parameters, say, the quadrupole moments both for the closed-shell core and the outside nucleons.

Let us assume, first, that the closed-shell core is spherical and undeformable. In this case, we have to find the energy of the lowest state of the outside nucleons for a fixed value of their quadrupole moment Q_λ (which, in this case, represents the total nuclear moment Q). To satisfy the subsidiary condition of a constancy of Q, we add to the Hamiltonian the term $-\mu \hat{Q}$,

---

* Here and below, we mean the quadrupole moment of the mass, but not that of the charge.

where $\hat{Q}$ is the quadrupole moment operator, and look for the ground state of the Hamiltonian

$$\overline{H} = H - \mu \hat{Q}. \tag{90}$$

Then, the Lagrangian multiplier μ has to be eliminated by using the condition $\langle \hat{Q} \rangle = Q$.

The quadrupole moment $\hat{Q}$, represented by the sum of the single-particle operators, has the form

$$\left.\begin{aligned} \hat{Q} = \sum_{\nu} q_{\nu\nu} 2 V_{\nu}^{2} + \sum_{\nu\nu'} q_{\nu\nu'} (U_{\nu} U_{\nu'} - V_{\nu} V_{\nu'}) (\alpha_{\nu}^{+} \alpha_{\nu'} + \beta_{\nu'}^{+} \beta_{\nu}) \\ + \sum_{\nu\nu'} q_{\nu\nu'} (U_{\nu} V_{\nu'} + V_{\nu} U_{\nu'}) (\alpha_{\nu}^{+} \beta_{\nu'}^{+} + \beta_{\nu} \alpha_{\nu'}), \end{aligned}\right\} \tag{91}$$

where $q_{\nu\nu'}$ are the matrix elements of the single-particle quadrupole moment. We neglect, as always, the interaction between quasi-particles and consider instead of H the Hamiltonian $H_0 = U + H_{20} + H_{11}$. Comparing (90) with (22)—(24) one can see that the inclusion of the term $-\mu \hat{Q}$ is simply equivalent to a renormalization of the single-particle energy $\varepsilon_{\nu\nu'} \rightarrow (\varepsilon_{\nu\nu'} - \mu q_{\nu\nu'})$. Assuming that the new single-particle energy has been diagonalized by an appropriate choice of the states ν, we get the Hamiltonian of the form (22)—(24), where the levels $\tilde{\varepsilon}_{\nu}$ are given by

$$\tilde{\varepsilon}_{\nu} = \varepsilon_{\nu} - \sum_{\nu'} \langle \nu\nu' \,|\, \bar{G} \,|\, \nu'\nu \rangle V_{\nu'}^{2} - \mu q_{\nu\nu}. \tag{92}$$

In producing the deformation of nuclei, the quadrupole part of the interaction between particles (the term $l = 2$ in (32)) is of great importance. The main effect of this quadrupole interaction can be described as an interaction of each particle with the total nuclear quadrupole moment. Therefore, we assume that

$$\sum_{\nu'} \langle \nu\nu' \,|\, \bar{G} \,|\, \nu'\nu \rangle V_{\nu'}^{2} = \varkappa Q q_{\nu\nu}, \tag{93}$$

where $\varkappa$ is a constant coefficient.* **

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* In the unified nuclear model, the analogous expression is considered as a coupling energy of a single particle to the nuclear surface. Comparing (93) with the equation (II. 26) of ref. 2 ($W_{\text{coupl}} = -k \beta Y_{20}$), we obtain the following relation between $\varkappa$ and the "coupling constant" k:

$$\varkappa = \frac{5}{12} \frac{k}{A R_0^2 \overline{r^2}}, \tag{93}$$

where we have used the connection between β and Q (see below, Eq. (105)) and the equation $q = 4 \sqrt{\frac{\pi}{5}}\, Y_{20} \overline{r^2}$. The equation (93′) implies, in particular, that $\varkappa$ is proportional to $A^{-7/3}$.

** The-single particle energy in a potential well is given by the same equations (92), (93), provided the quantity Q means the quadrupole moment of the potential. Identification of Q with the particle quadropole moment leads to the self-consistency discussed above.

Inserting (93) in (92) one finds for the single-particle-levels

$$\tilde{\varepsilon}_\nu = \varepsilon_\nu - (\mu + \varkappa Q)\, q_{\nu\nu} \equiv \varepsilon_\nu - \tilde{\mu}\, q_{\nu\nu}. \tag{94}$$

The quantity ε_ν, according to (7), is given by $\varepsilon_\nu = \sum_k \varepsilon_k^0 \varphi_{k\nu}^* \varphi_{k\nu}$, where ε_k^0 is the energy of the degenerate single-particle levels in the spherical nucleus, and $\varphi_{k\nu}$ are the coefficients which transform the single-particle wave functions in the spherical field to those in the deformed field. The splitting of ε_ν by the deformation is caused only by the change of the single-particle wave functions and can be neglected for the outside nucleons for which the main splitting is caused by the last term in (94), associated with the direct quadrupole interaction. (Cf. an explicit solution in Appendix B).

The energy of the ground state of the auxiliary Hamiltonian (90) is given by the quantity U in (22). The lowest state with a given value of the quadrupole moment Q of the original Hamiltonian has the energy

$$W(Q) = U + \lambda N + \mu Q. \tag{95}$$

With the aid of (22), (43), and (95) we obtain

$$W(Q) = \sum_\nu \varepsilon_\nu \, 2 V_\nu^2 - \frac{1}{2} \varkappa Q^2 - \frac{\Delta^2}{G}, \tag{96}$$

where Δ is given by (57). The first term in (96) corresponds to the energy of non-interacting particles, while the last two terms represent the energy of the quadrupole and pairing interactions.

According to (91) and (94) the quadrupole moment of the outside nucleons is given by

$$Q_\lambda = \sum_\nu^{\lambda} q_{\nu\nu} \, 2 V_\nu^2 = \frac{1}{\tilde{\mu}} \sum_\nu^{\lambda} (\varepsilon_\nu - \tilde{\varepsilon}_\nu) \, 2 V_\nu^2.$$

Neglecting the splitting of ε_ν, we may replace ε_ν by the average energy of the λ-shell $\varepsilon_\lambda = \frac{1}{2}\left[(\varepsilon'' + \varepsilon' + \frac{\xi}{3}(\varepsilon'' - \varepsilon')\right]$. With the aid of (43) we find

$$Q_\lambda = \frac{1}{\tilde{\mu}} (\varepsilon_\lambda - \lambda) N - \frac{1}{\tilde{\mu}} \sum_\nu^{\lambda} (\tilde{\varepsilon}_\nu - \lambda) \, 2 V_\nu^2. \tag{97}$$

Replacing the sum in (97) by an integral we obtain, after calculations similar to those performed in Part II,

$$Q_\lambda = q_0 A(\eta), \tag{98}$$

where

$$q_0 = \max q_{\nu\nu} - \min q_{\nu\nu} = q(\varepsilon') - q(\varepsilon'') = \frac{\varepsilon'' - \varepsilon'}{\tilde{\mu}} \tag{99}$$

is the amplitude of the single-particle quadrupole moment, and

$$A(\eta) = \frac{\Omega}{4}(1-\chi_N^2)\left[\left(1-\frac{\xi^2}{3}\right)\gamma(\eta) - 2\,\xi\chi_N\left(\gamma(\eta)\coth\eta - \frac{2}{3}\right)\right] \qquad (100)$$

where the function $\gamma(\eta)$ is given by (51). The equation (98) connects the quadrupole moment of the outside nucleons with the parameter η. Therefore, the equation (96) gives the nuclear energy as a function of η in the case of a spherical undeformable closed-shell core.

Now, let us go to the general case and consider also deformations of the core. Here, we require fixed values of the quadrupole moments both for the outside nucleons and the closed-shell core, and introduce into the Hamiltonian two Lagrangian multipliers

$$\overline{H} = H - \mu\hat{Q}_\lambda - \mu'\hat{Q}_{cl}, \qquad (101)$$

where Q_{cl} is the quadrupole moment of the closed shells. The equation (93) is valid also in this case, provided Q means the total quadrupole moment. The expressions (92) and (94) now correspond to the outside nucleons; for the closed shells, one needs simply to replace μ by μ'. After simple calculation, one finds that the energy of the lowest state with given values of Q_λ and Q_{cl} is given by the equation (96), where Q is now the total quadrupole moment ($= Q_{cl} + Q_\lambda$) and the sum in the first term is extended over the closed shells as well as the unfilled λ-shell.

The single-particle quadrupole moment $q_{\nu\nu}$ can be written, for small deformations of the self-consistent field, as

$$q_{\nu\nu} = q_{\nu\nu}^0 + q_{\nu\nu}^{(1)}, \qquad (102)$$

where $q_{\nu\nu}^0$ is determined by wave functions in the spherical field, and $q_{\nu\nu}^{(1)}$ is a correction caused by a dependence of the wave functions on the deformation. For the closed shells, $\sum_\nu{}' q_{\nu\nu}^0 = 0$, and therefore Q_{cl} is determined only by the quantity $q_{\nu\nu}^{(1)}$ which is proportional to the deformation. On the other hand, the quantity $q_{\nu\nu}^0$ gives the main contribution to the quadrupole moment of the outside nucleons Q_λ. The contribution of the quantity $q_{\nu\nu}^{(1)}$ to the value of Q_λ turns out to be small, as $\frac{\varepsilon''-\varepsilon'}{\varepsilon_F}$, where ε_F is the Fermi energy (see Appendix B). Thus, we can use, for Q_λ, the expression (98), where the dependence of the single-particle wave functions on the deformation was neglected.

The first term in (96) corresponds to the energy of non-interacting particles, provided one considers their new distribution among the levels ($V^2 \neq 0,1$). The dependence of this term on the deformation of the field is caused only by a change in the single-particle wave functions. This leads to a quadratic dependence for small deformations. Choosing the value of the quadrupole moment of the closed-shell core as the deformation parameter, one may write

$$\sum_{\nu} \varepsilon_{\nu}\, 2 V_{\nu}^2 = W_0 + \frac{1}{2} k Q_{cl}^2, \tag{103}$$

where W_0 and k do not depend on the deformation*. Inserting (103) in (96), one finds

$$W(Q) = W_0 + \frac{1}{2}(k-\varkappa) Q^2 - k Q Q_{\lambda} + \frac{1}{2} k Q_{\lambda}^2 - \frac{\Delta^2}{G}. \tag{104}$$

Let us introduce the deformation β which is associated with the total quadrupole moment Q by the equation²⁾

$$Q = \frac{3}{\sqrt{5\pi}} A R_0^2 \beta \equiv \bar{Q} \beta, \tag{105}$$

where A is the atomic number and R_0 is the nuclear radius. Inserting (98) and (105) in (104), we obtain

$$W(Q) = W_0 + \frac{1}{2}(k-\varkappa)\bar{Q}^2 \beta^2 - k q_0 \bar{Q} \beta \Lambda(\eta) + \frac{1}{2} k q_0^2 \Lambda^2 - \frac{\Delta^2}{G}. \tag{106}$$

The equation (106) determines the nuclear energy as a function of the deformation β and the parameter η associated with the configuration of the outside nucleons.

2. Equilibrium Shape of the Nucleus

In the absence of pairing interaction ($\eta \to \infty$) one finds from (57) and (100)

$$\frac{\Delta^2}{G} \approx 0 \quad \text{and} \quad \Lambda(\eta) \approx \frac{\Omega}{4}(1-\bar{\chi}_N^2)\left[1 - \frac{2}{3}\xi \bar{\chi}_N - \frac{\xi^2}{3}\right], \tag{107}$$

---

* The quantities W_0 and k depend somewhat on the occupation of the unfilled shell. We shall neglect this weak dependence. In order to add to the understanding of the nature of these coefficients, as well as of the approximation made in the derivation of equation (104), a particular problem is solved explicitly in Appendix B.

where $\bar{\chi}_N = \chi_N(\eta = \infty)$. The energy $W(Q)$ in this case depends on β only. The equilibrium deformation β_0 always differs from zero, except in the case of the completely closed shell. Therefore, the spherical shape turns out to be unstable for any number of outside nucleons and the deformation increases smoothly when the occupation of the shell increases.

For a fixed value of η, the equilibrium deformation β_0 determined from (106) is equal to

$$\beta_0(\eta) = \frac{q_0}{(1-\varkappa/k)\,\overline{Q}}\,\Lambda(\eta). \tag{108}$$

This equation can be written as

$$Q_\lambda = (1-\varkappa/k)\,Q, \tag{108'}$$

which indicates that the quantity $\varkappa/k$ describes the polarizability of the core by the outside nucleons*.

In the case of equilibrium between β and η, $W(Q)$ takes the form of

$$W(Q) = W_0 - \frac{\varkappa q_0^2}{2(1-\varkappa/k)}\,\Lambda^2(\eta) - \frac{\Delta^2}{G}. \tag{109}$$

This equation is seen to be equivalent to (96), (98). The only effect of the deformable core ($k \neq \infty$) is an effective increase in the quadrupole force $\left(\varkappa_{\mathrm{eff}} = \dfrac{\varkappa}{1-\varkappa/k}\right)$.

For small η, one finds from (57) and (100)

$$\left.\begin{aligned} \frac{\Delta^2}{G} &\approx \frac{\Omega^2}{4}G\Theta_N - \frac{\Omega^2}{12}G\Theta_N\left(1-\frac{\xi^2}{3}\right)\eta^2 \\ \Lambda(\eta) &\approx \frac{\Omega}{6}\left(1-\frac{\xi^2}{3}\right)\Theta_N\eta \end{aligned}\quad (\eta < 1).\right\} \tag{110}$$

Combining (109) and (110) we get

$$W(Q) = W_0 - \frac{\Omega^2}{4}G\Theta_N + \frac{1}{2}C_\eta\eta^2. \tag{111}$$

where

$$C_\eta = \frac{\Omega^2}{6}G\Theta_N\left(1-\frac{\xi^2}{3}\right)\left[1-\frac{\varkappa q_0^2}{6G(1-\varkappa/k)}\left(1-\frac{\xi^2}{3}\right)\Theta_N\right]. \tag{112}$$

---

* The quantity $\varkappa/k$ can be estimated empirically from the values of the quadrupole moment for nuclei with one particle outside of closed shells (e. g., O^{17} or Bi^{209}). These nuclei exhibit quadrupole moments of the order of single-particle values, which implies that $\varkappa/k \sim 0.5$.

The stability of the spherical shape depends on the ratio of the two terms in the square brackets of (112). The first term, which is associated with the pairing interaction, tends to produce stability. The second term gives the effect of the quadrupole interaction between nucleons and, in the case of attraction ($\varkappa > 0$), tends to produce instability of the spherical shape. Introducing the quantity Θ_{N_0} by the equation

$$\frac{1}{\Theta_{N_0}} = \frac{\varkappa q_0^2}{6\,G(1-\varkappa/k)}\left(1-\frac{\xi^2}{3}\right), \tag{113}$$

we can rewrite (112) in the form

$$C_\eta = \frac{\Omega^2}{6}\,G\,\Theta_N\left(1-\frac{\xi^2}{3}\right)(1-\Theta_N/\Theta_{N_0}). \tag{114}$$

The quantity Θ_{N_0} represents the value of the occupation of the unfilled shell required to make the spherical shape unstable. The value of Θ_{N_0} changes from shell to shell. If $\Theta_{N_0} > 1$, then the nucleus remains spherical for any occupation of this shell.

When the condition $\Theta_{N_0} < \Theta_N \leqslant 1$ is fulfilled, the spherical nucleus is unstable. The equilibrium deformation is determined in this case by the extremum of (109) for $\eta \neq 0$. To simplify the calculations, we restrict ourselves to the case of uniform level density ($\xi = 0$). Using (57), (100), and (113), one finds from (109)

$$W(Q) = W_0 - \frac{\Omega^2}{4}\,G\,\Theta_N\left(\frac{\eta^2}{\sinh\eta} + \frac{3}{4}\,\Theta_N/\Theta_{N_0}\cdot\gamma^2\right). \tag{115}$$

The extremum of (115) is determined by the equation

$$\left(\coth\eta_0 - \frac{1}{\eta_0}\right)\left[1-\frac{3}{2}\,\Theta_N/\Theta_{N_0}\cdot\frac{\gamma(\eta_0)}{\eta_0}\right] = 0. \tag{116}$$

The solution corresponding to the first factor in (116) gives an extremum for $\eta_0 = 0$. Since $3\gamma/2\eta < 1$, the second solution of (116) occurs only for $\Theta_N > \Theta_{N_0}$. Using this solution, one finds the equilibrium deformation β_0 from (108):

$$\beta_0 = \frac{\Omega\,q_0\,\Theta_N}{4\,(1-\varkappa/k)\,\overline{Q}}\,\gamma_0'. \tag{117}$$

In the absence of pairing interaction, the equilibrium deformation is given by the same equation (117) without the factor γ_0. Therefore, this factor represents a relative reduction of the equilibrium deformation arising from the

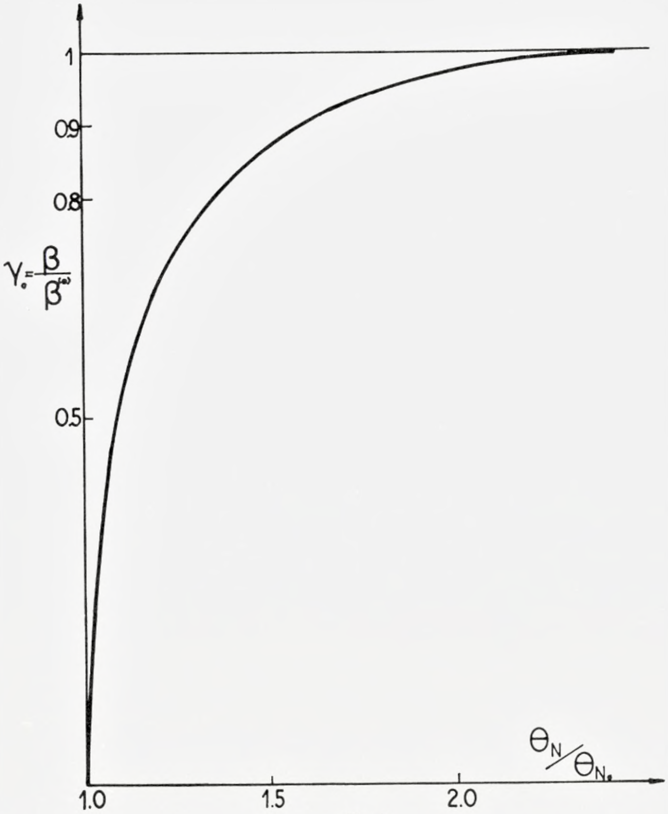

Fig. 1

Fig. 1. Relative reduction of the equilibrium deformation arising from the pairing interaction.

The figure shows the ratio of the equilibrium deformation to that in the absence of pairing interaction, in the region of deformed nuclei ($\Theta_N < \Theta_{N_0}$). The reduction factor γ_0 is obtained from the equation (116).

pairing interaction. The function $\gamma_0\,(\Theta_N/\Theta_{N_0})$, determined from the equation (116), rises rapidly with increasing occupation Θ_N near Θ_{N_0} and quickly approaches its limiting value $\gamma_0 = 1$. (see Fig. 1). Near the point of instablity, one finds

$$\gamma_0 \approx \frac{2\,\Theta_{N_0}}{3\,\Theta_N}\sqrt{\frac{15}{2}\left(1-\frac{\Theta_{N_0}}{\Theta_N}\right)}; \qquad \left(\eta_0 = \sqrt{\frac{15}{2}\left(1-\frac{\Theta_{N_0}}{\Theta_N}\right)} \lesssim 1\right) \tag{118}$$

and from (117) it follows that

$$\beta_0 \approx \frac{q_0\,\Omega\Theta_{N_0}}{6\,(1-\varkappa/k)\,\overline{Q}}\sqrt{\frac{15}{2}\left(1-\frac{\Theta_{N_0}}{\Theta_N}\right)}. \tag{119}$$

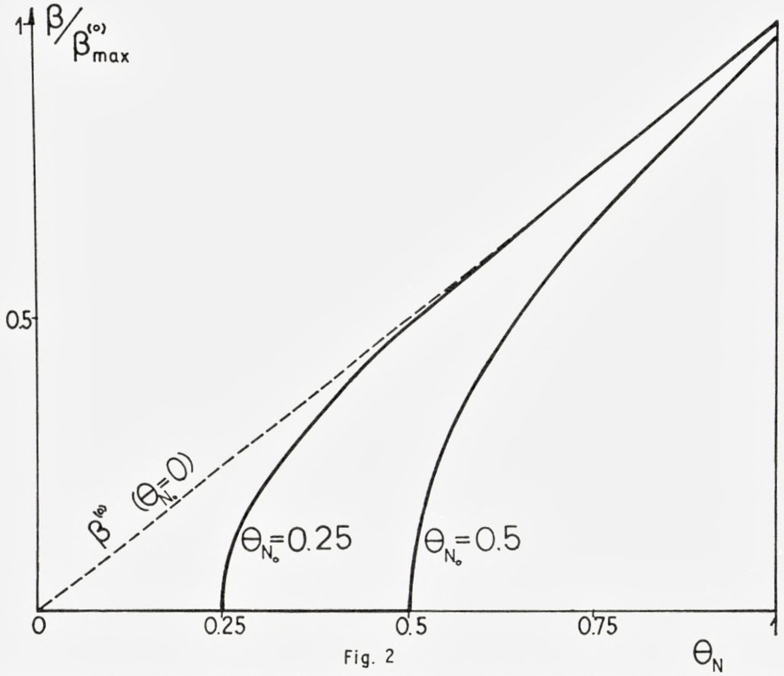

Fig. 2

Fig. 2. Dependence of the equilibrium deformation on the occupation of the unfilled shell. The equilibrium deformation β_0 is plotted as a function of the occupation factor Θ_N for two different values of the quantity Θ_{N_0} given by (113).
The dashed line shows the deformation $\beta^{(0)}$ in the absence of pairing interaction. The maximum value of $\beta^{(0)}$ (for a half-filled shell, i.e., $\Theta_N = 1$) is chosen as a unit.

Therefore, the transition from the spherical nucleus to the deformed one is rather sharp. The minimum value of the possible deformation may be estimated from (119) by setting $N = N_0 + 1$ (i. e. $(1-\Theta_{N_0}/\Theta_N) \approx N_0^{-1}$):

$$\beta_{\min} \approx \frac{q_0}{3(1-\varkappa/k)\,\overline{Q}}\sqrt{\frac{15}{2}N_0}. \tag{120}$$

For large values of Θ_N/Θ_{N_0}, one finds from (116)

$$\gamma_0 \approx 1-2\,(3\,\Theta_N/\Theta_{N_0}-1)\exp(-3\,\Theta_N/\Theta_{N_0}) \tag{121}$$

and, therefore,

$$\beta_0 \approx \frac{q_0\,\Omega\Theta_N}{6\,(1-\varkappa/k)\,\overline{Q}}\left\{1-2\,(3\,\Theta_N/\Theta_{N_0}-1)\,\exp\,(-3\,\Theta_N/\Theta_{N_0})\right\}. \tag{122}$$

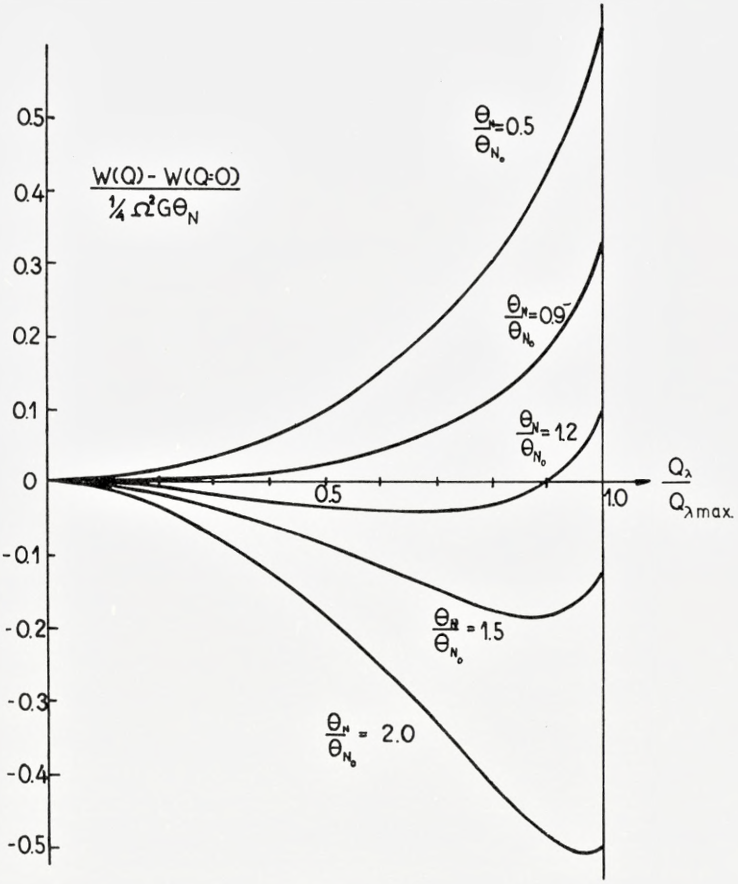

Fig. 3

Fig. 3. Dependence of the nuclear energy on the configuration of the particles in the unfilled shell.

The figure shows the nuclear energy as a function of the quadrupole moment of outside nucleons for five different occupation factors. The energy is measured as the difference from that in a spherical nucleus, in units $\frac{1}{4}\Omega^2 G\Theta_N$ (total pairing energy in the spherical nucleus). The quadrupole moment, Q_λ, is plotted in units of its maximum value $Q_{\lambda\,\max} = q_0 \frac{\Omega}{4}\Theta_N$. (The weak dependence of Q_λ on the change in wave functions upon deformation has been neglected).

In this region (near the middle of the shell), the main dependence β_0 of the occupation is given in (122) by the quantity Θ_N; thus, we may write approximately

$$\beta_0 \approx \beta_{\max} \Theta_N, \tag{123}$$

where $\beta_{\max}$ is the value of the deformation for the maximum occupation of the shell ($\Theta_N = 1$):

$$\beta_{\max} \approx \frac{q_0 \Omega}{6(1-\varkappa/k)\overline{Q}}. \tag{124}$$

Consequently, the values of the equilibrium deformation have a lower bound and change smoothly near the middle of the shell.

The equilibrium deformation β_0 as a function of the occupation factor Θ_N is illustrated in Fig. 2, where the dashed line corresponds to the absence of pairing interaction.

It is of interest to point out the dependence of $\beta_{\min}$ and $\beta_{\max}$ on the atomic number A. Since the quantity $\varkappa \sim A^{-7/3}$ (cf. footnote, p. 29) and $G \sim A^{-1}$*), $q_0 \sim R_0^2 \sim A^{2/3}$, it follows from (113) that Θ_{N_0} is independent of A (and, therefore, $N_0 \sim \Omega \sim A^{2/3}$). From (105) we have also $\overline{Q} \sim A^{5/3}$. Using these facts, we obtain from (120) and (124)

$$\beta_{\min} \sim A^{-2/3}; \quad \beta_{\max} \sim A^{-1/3}, \tag{125}$$

which is in agreement with the observed trends**.

The dependence of the nuclear energy on the configuration of the outside particles (for the equilibrium deformation of the core), which is given by the equation (115), is illustrated in Fig. 3. The value of the quadrupole moment of the outside nucleons is chosen as the variable. Due to the finite nature of the quadrupole moment Q_λ, the curves have terminal points. This fact may violate the possibility for vibrations of outside nucleons in a deformed field.

3. Inertial Parameter

As is seen from (89), for the calculation of the inertial parameter $B(\vartheta)$ it is necessary to know the dependence of the ground-state wave function on the collective parameter ϑ. To this end, we consider ψ_0 in the representation of occupation numbers of the old particles (78)

$$\Psi_0 = \prod_\nu (U_\nu + V_\nu b_{\nu+}^+ b_-^+) \Psi_0^{(0)}. \tag{126}$$

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* Here, we neglect effects of intershell transitions, which changes this dependence to some degree (cf. p. 17).

** For strongly deformed nuclei, the levels of different shells cross[11]. Redistribution of the particles might occur, however, only when the levels of the low shell cross the empty levels of the unfilled shell. The number of such crossings is rather small, and we may expect that they do not change qualitatively the results concerning the equilibrium deformation.

The change of the parameter ϑ means a certain variation of the self-consistent field; in the rotational case, it is equivalent to a certain rotation; in the case of quadrupole vibrations of a spherical nucleus, it is a quadrupole deformation, and so on. In the general case, we can associate with ϑ a certain operator of the infinitesimal displacement K^{ϑ}. The associated variation of the self-consistent field changes the single-particle states and, therefore, the operators of the old particles $b^+_{\nu\sigma}$. Since the $b^+_{\nu\sigma}$ correspond to independent particles, the operator K^{ϑ} expressed in terms of $b^+_{\nu\sigma}$ may be represented by a sum of single-particle operators

$$K^{\vartheta} = \sum_{\nu\nu'} k^{\vartheta}_{\nu\nu'} \left(b^+_{\nu+} b_{\nu'+} \pm b^+_{\nu'-} b_{\nu-}\right), \tag{127}$$

where $k^{\vartheta}_{\nu\nu'} = \langle \nu + \,|\, k^{\vartheta} \,|\, \nu' + \rangle$ is the matrix element of the single-particle operator. The sign $\pm$ is due to the condition

$$\langle \nu' - | k^{\vartheta} | \nu - \rangle = \pm \langle \nu + | k^{\vartheta} | \nu' + \rangle$$

and is defined by the behaviour of the operator k under time reversal.

In addition to the change in the wave functions of the original particles, the deformation causes a shift of the single-particle energy levels, which gives rise to a change in U_ν and V_ν. Therefore, the total effect of the deformation can be written in the following form:

$$\frac{\partial}{\partial\vartheta} = -\,i\,K^{\vartheta} + \left(\frac{\partial}{\partial\vartheta}\right)_b, \tag{128}$$

where the last derivative is taken, keeping the operators $b_{\nu\sigma}$ constant. Performing in (127) the transition to the operators α, β we get

$$\left.\begin{aligned} K^{\vartheta} = \sum_{\nu} k^{\vartheta}_{\nu\nu} (1 \pm 1)\, V^2_\nu + \sum_{\nu\nu'} k^{\vartheta}_{\nu\nu'} (U_\nu U_{\nu'} \mp V_\nu V_{\nu'}) (\alpha^+_\nu \alpha_{\nu'} \pm \beta^+_{\nu'} \beta_\nu) \\ + \sum_{\nu\nu'} k^{\vartheta}_{\nu\nu'} (U_\nu V_{\nu'} \pm V_\nu U_{\nu'}) (\alpha^+_\nu \beta^+_{\nu'} \pm \beta_\nu \alpha_{\nu'}). \end{aligned}\right\} \tag{129}$$

The result of the operation of K^{ϑ} on the vacuum state is given by

$$K^{\vartheta} \Psi_0 = \sum_{\nu} k^{\vartheta}_{\nu\nu} (1 \pm 1)\, V^2_\nu \cdot \Psi_0 + \sum_{\nu\nu'} k^{\vartheta}_{\nu\nu'} (U_\nu V_{\nu'} \pm V_\nu U_{\nu'})\, \alpha^+_\nu \beta^+_\nu \Psi_0. \tag{130}$$

Now, consider the last operator in (128). From (126) it follows that

$$\left(\frac{\partial \Psi_0}{\partial\vartheta}\right)_b = \sum_{\nu} \left(\frac{\partial U_\nu}{\partial\vartheta} + \frac{\partial V_\nu}{\partial\vartheta} b^+_{\nu+} b^+_{\nu-}\right) \prod_{\nu' \neq \nu} (U_{\nu'} + V_{\nu'} b^+_{\nu'+} b^+_{\nu'-})\, \Psi^{(0)}_0. \tag{131}$$

With the aid of the normalization condition $U^2 + V^2 = 1$, the first factor inside the sum takes the form

$$\frac{\partial U_\nu}{\partial \vartheta} + \frac{\partial V_\nu}{\partial \vartheta} b^+_{\nu+} b^+_{\nu-} = -\frac{1}{V_\nu} \frac{\partial U_\nu}{\partial \vartheta} (U_\nu b^+_{\nu+} b^+_{\nu-} - V_\nu). \tag{132}$$

Thus, by comparing (131) with (80), we get

$$\left(\frac{\partial \Psi_0}{\partial \vartheta}\right)_b = -\sum_\nu \frac{1}{V_\nu} \frac{\partial U_\nu}{\partial \vartheta} \alpha^+_\nu \beta^+_\nu \Psi_0. \tag{133}$$

As it is seen from (130) and (133), $\frac{\partial}{\partial \vartheta}$ causes transitions from the vacuum only to states with two quasi-particles

$$\left\langle \alpha^+_\nu \beta^+_{\nu'} \left| \frac{\partial}{\partial \vartheta} \right| 0 \right\rangle = -ik^\vartheta_{\nu\nu'} (U_\nu V_{\nu'} \pm V_\nu U_{\nu'}) - \frac{\delta_{\nu\nu'}}{V_\nu} \frac{\partial U_\nu}{\partial \vartheta}. \tag{134}$$

There is no interference between two terms in (134) provided the diagonal matrix element $k^\vartheta_{\nu\nu}$ is equal to zero. In this case, the inertial parameter for the vacuum state is given by

$$\begin{aligned} B(\vartheta) &\equiv B_1 + B_2 \\ &= 2\hbar^2 \sum_{\nu\nu'} \frac{|k^\vartheta_{\nu\nu'}|^2 (U_\nu V_{\nu'} \pm V_\nu U_{\nu'})^2}{E_\nu + E_{\nu'}} + \hbar^2 \sum_\nu \frac{1}{V_\nu^2} \left(\frac{\partial U_\nu}{\partial \vartheta}\right)^2 \frac{1}{E_\nu}, \end{aligned} \tag{135}$$

where E_ν is the energy of a quasi-particle (71). The expression (135) defines the inertial parameter for even-even nuclei. The ground state of odd nuclei is given by the function of the form (79), say, $\alpha^+_{\nu_0} \psi_0$. Performing similar calculations with this function we get

$$\left.\begin{aligned} B_{\text{odd}} &= 2\hbar^2 \sum_{\substack{\nu\nu' \\ \nu' \neq \nu_0}}{}' \frac{|k^\vartheta_{\nu\nu'}|^2 (U_\nu V_{\nu'} \pm V_\nu U_{\nu'})^2}{E_\nu + E_{\nu'}} \\ &+ \hbar^2 \sum_{\nu \neq \nu_0} \left(\frac{1}{V_\nu} \frac{\partial U_\nu}{\partial \vartheta}\right)^2 \frac{1}{E_\nu} + 2\hbar^2 \sum_{\nu \neq \nu_0} \frac{|k^\vartheta_{\nu\nu_0}|^2 (U_\nu U_{\nu_0} \mp V_\nu V_{\nu_0})}{E_\nu - E_{\nu_0}}. \end{aligned}\right\} \tag{136}$$

This expression can be rewritten in the form

$$B_{\text{odd}} = B_1 + B_2 + B_3, \tag{136'}$$

where B_1 and B_2 are given by (135) and correspond to even-even nuclei.

The term B_3, which determines the difference in the inertial parameters for neighbouring even-even and odd-A nuclei, is then given by

$$\left.\begin{aligned} B_3 = 2\hbar^2 \sum_{\nu \neq \nu_0} \frac{|k^{\vartheta}_{\nu\nu_0}|^2}{E_\nu^2 - E_{\nu_0}^2} \{ [(U_\nu^2 - V_\nu^2)(U_{\nu_0}^2 - V_{\nu_0}^2) \pm 4\, U_\nu V_\nu U_{\nu_0} V_{\nu_0}]\, E_\nu + E_{\nu_0} \} \\ - \frac{\hbar^2}{E_{\nu_0}} \left(\frac{1}{V_{\nu_0}} \frac{\partial U_{\nu_0}}{\partial \vartheta} \right)^2. \end{aligned}\right\} \quad (136'')$$

The two terms in (135) have an essentially different nature. In terms of original particles a nuclear deformation, which corresponds to the collective parameter ϑ, gives rise, in the first place, to single-particle transitions into the higher states and, secondly, to a change of the Fermi sea without particle excitations. B_1 corresponds to the first effect. The pairing interaction does not change the structure of this term, but makes only quantitative alterations, which are connected with the new energy spectrum and the new distribution of the particles ($U_\nu, V_\nu \neq 0{,}1$). The term B_2 is connected with the change of the Fermi sea by the deformation. This qualitatively new effect is caused by the pairing interaction and disappears for non-interacting particles (when $U_\nu, V_\nu = \text{const}$). In the case of rotations, the term B_2 is equal to zero, since U_ν, V_ν do not depend on the nuclear orientation. For vibrations, on the other hand, the term B_2 will be shown to make the main contribution in the inertial parameter. Therefore, the pairing interaction basically changes the character of the vibrational motion.

4. Rotational Moment of Inertia

In the case of rotations of axially symmetric nuclei about an axis perpendicular to the nuclear symmetry axis, the mass parameter B gives the moment of inertia J. In this case, k is the operator of the particle angular momentum j_x. Therefore, one finds from (135) for the moment of inertia of even-even nuclei

$$J = 2\hbar^2 \sum_{\nu\nu'} \frac{|(j_x)_{\nu\nu'}|^2}{E_\nu + E_{\nu'}} (U_\nu V_{\nu'} - V_\nu U_{\nu'})^2. \quad (137)$$

Since j_x changes sign under time reversal, the sign $(-)$ has been chosen in (135).

In the absence of the pairing interaction, we have $U_\nu, V_\nu = 1{,}0$ and $E_\nu = E_\nu^0 = |\varepsilon_\nu - \lambda|$, and (137) takes the form

$$J^{(0)} = 4\hbar^2 \sum_{\nu\nu'} \frac{|(j_x)_{\nu\nu'}|^2}{E_\nu^0 + E_{\nu'}} U_\nu^2 V_{\nu'}^2 = 4\hbar^2 \sum_{\varepsilon_\nu > \lambda > \varepsilon_{\nu'}} \frac{|(j_x)_{\nu\nu'}|^2}{\varepsilon_\nu - \varepsilon_{\nu'}}, \quad (138)$$

which coincides with the ordinary value for the moment of inertia in an independent-particle model.

Inserting the expressions (26) for U_ν, V_ν in (137), we get for the case with a constant gap Δ:

$$J = \hbar^2 \sum_{\nu\nu'} \frac{|(j_x)_{\nu\nu'}|^2}{E_\nu + E_{\nu'}} \left[1 - \frac{\Delta^2 + (\varepsilon_\nu - \lambda)(\varepsilon_{\nu'} - \lambda)}{E_\nu E_{\nu'}}\right]. \tag{139}$$

In order to analyse this expression we split it into two parts. $J = J' + J''$, where

$$J' = 2\hbar^2 \sum_{\varepsilon_\nu > \lambda > \varepsilon_{\nu'}} \frac{|(j_x)_{\nu\nu'}|^2}{E_\nu + E_{\nu'}} \left(1 + \frac{E_\nu^0 E_{\nu'}^0 - \Delta^2}{E_\nu E_{\nu'}}\right), \tag{140}$$

$$J'' = \hbar^2 \Delta^2 \sum_{(\varepsilon_\nu - \lambda)(\varepsilon_{\nu'} - \lambda) > 0} \frac{|(j_x)_{\nu\nu'}|^2}{E_\nu + E_{\nu'}} \quad \frac{(\varepsilon_\nu - \varepsilon_{\nu'})^2}{E_\nu E_{\nu'}(E_\nu E_{\nu'} + E_\nu^0 E_{\nu'}^0 + \Delta^2)}. \tag{141}$$

J' contains only transitions connecting states below with those above the Fermi surface. Comparing (138) and (140) one can see that $J' \leqslant J^{(0)}$ (an equality is achieved for non-interacting particles, when $\Delta = 0$). A decrease of J' with respect to $J^{(0)}$ occurs, in the first place, because of an increase of the energy denominator and, secondly, owing to the modification of the Fermi sea. (The probability of finding an occupied state below the Fermi surface and an empty state above has decreased). The term J'' contains transitions only on one side of the Fermi surface and gives a relatively small contribution for strongly deformed nuclei.

To estimate the term J' we rewrite (140) in the form

$$J' = 4\hbar^2 \sum_{\varepsilon_\nu > \lambda > \varepsilon_{\nu'}} \frac{|(j_x)_{\nu\nu'}|^2}{E_\nu^0 + E_{\nu'}^0} \left[\frac{E_\nu^0 + E_{\nu'}^0}{E_\nu + E_{\nu'}} \cdot \frac{1}{2}\left(1 + \frac{E_\nu^0 E_{\nu'}^0 - \Delta^2}{E_\nu E_{\nu'}}\right)\right]. \tag{142}$$

Assuming that $(j_x)_{\nu\nu'}$ is a sharp function of ν and ν', we may take out of the sum the smoothly changing factor in the square brackets, evaluating it for certain average values E_ν^0 and $E_{\nu'}^0$. Assuming that $\bar{E}_\nu^0 \approx \bar{E}_{\nu'}^0 = E^0$, we obtain

$$J'/J_{\mathrm{rig}} = \left(1 + \frac{\Delta}{E^0}\right)^{2-3/2}, \tag{143}$$

where J_{rig} is the moment of inertia in the absence of the interaction ($\Delta \to 0$) which coincides with the moment for rigid rotations. It is seen that the moment of inertia is rather sensitive to the effect of the pairing correlations;

thus, for $\Delta \approx (0.7-0.8)\,E^0$, which approximately corresponds to the situation in the most strongly deformed nuclei, one obtains $J'/J_{\mathrm{rig}} \approx \frac{1}{2}$.

In order to estimate the term J'', we assume that the matrix element $j_{\nu\nu'}$ connects the levels, separated by the same energy as in (143), namely, $\varepsilon_{\nu'} - \varepsilon_{\nu} \approx 2\,E^0$. Then, introducing a certain average distance of such two levels from the Fermi surface,

$$E^0_{\bar{\nu}} \approx \frac{\varepsilon_\nu + \varepsilon_{\nu'}}{2} - \lambda$$

and using the approximate relations

$$\begin{gathered} E_\nu E_{\nu'} \approx E^2_{\bar{\nu}} = E^{02}_{\bar{\nu}} + \Delta^2 \\ E_\nu + E_{\nu'} \approx 2\,E_{\bar{\nu}} = 2\sqrt{E^{02}_{\bar{\nu}} + \Delta^2}, \end{gathered}$$

we obtain from (141)

$$J'' = \hbar^2 \Delta^2 \sum_{\lambda < \varepsilon_{\nu'} < \varepsilon_\nu} \frac{|j_{\nu\nu'}|^2}{\varepsilon_\nu - \varepsilon_{\nu'}} \quad \frac{(\varepsilon_\nu - \varepsilon_{\nu'})^3}{(E^{02}_{\bar{\nu}} + \Delta^2)^{5/2}}.$$

Assuming, further, that the value of $|j_{\nu\nu'}|^2$ does not strongly vary in the effective region of the sum, and taking into account that, in this case,

$$4\,\hbar^2 \frac{|j_{\nu\nu'}|^2}{\varepsilon_\nu - \varepsilon_{\nu'}} \approx J^{(0)}$$

we find

$$J''/J^{(0)} \approx \frac{1}{4}\Delta^2 (2\,E^0)^3 \sum_{\bar{\nu} > \bar{\nu}_F} \frac{1}{(E^{02}_{\bar{\nu}} + \Delta^2)^{5/2}}. \tag{144}$$

For simplicity, we consider an oscillator-like level scheme, where $E^0_{\bar{\nu}} = 2\,E^0 \bar{\nu}$ $(\bar{\nu} = 1,2\ldots)$. For strongly deformed nuclei, when $\frac{\Delta}{2\,E^0} < 1$, the terms in the sum (144) decrease very rapidly, and we may restrict ourselves only to the first term. Then, we obtain

$$J''/J^{(0)} \approx \frac{1}{16}\left(\frac{\Delta}{E^0}\right)^2; \quad \left(\frac{\Delta}{2\,E^0} < 1\right),$$

which is very small compared to the ratio (143). When we go to less deformed nuclei, the ratio $\frac{\Delta}{2\,E^0}$ increases and more transitions make a significant contribution to the moment of inertia. In the case of $\frac{\Delta}{2\,E^0} \gg 1$, all transitions inside the energy region Δ are almost equivalent, but only one of them is included in J' (viz. that which crosses the Fermi surface). Therefore, we can expect that, in this case, the J''-term becomes larger than J' by the factor $\sim \frac{\Delta}{E^0}$ (which represents the number of effective transitions). For $\frac{\Delta}{2E^0} > 1$, we can replace the sum in (144) by an integral. Then, we obtain

$$J''/J^{(0)} \approx \frac{2}{3}\left(\frac{E^0}{\Delta}\right)^2; \quad \left(\frac{\Delta}{2E^0} > 1\right),$$

which confirms our expectation.

5. Inertial Parameter for Quadrupole Vibrations of Spherical Nuclei

As has been shown above, deviations of nuclei from the spherical equilibrium shape can be characterized by two parameters: the quadrupole moment of the closed-shell core Q_{cl} and that of the outside nucleons Q_λ (or by the parameter η proportional to Q_λ). The deformation associated with Q_{cl} changes only single-particle states, so that it contributes only to the term B_1 in (135). In the harmonic oscillator model, the operator K in this term is proportional to the single-particle quadrupole moment. Since the quadrupole transitions inside one shell are forbidden, the value B_1 in this case is very small, because the energy denominator is large. Let us introduce the deformation β' of the closed-shell core connected with Q_{cl} by the equation (105). Then the inertial parameter B_β, related to β' in the absence of pairing interaction coincides with that for the oscillations of an irrotational liquid drop[19)]

$$B_{\text{irr}} = \frac{3}{8\pi} A m R_0^2 \tag{145}$$

(m is the nucleon mass, R_0 and A are the radius and the atomic number of the nucleus). One might expect that this result is not sensitive to the model. The pairing interaction does not significantly change the value of $B_{\beta'}$.

The inertial coefficient B_η related to η is given only by the term B_2 in (135)

$$B_\eta = \hbar^2 \sum_\nu \left(\frac{1}{V_\nu}\frac{\partial U_\nu}{\partial \eta}\right)^2 \frac{1}{E_\nu}. \tag{146}$$

The parameter B_η is absent for non-interacting particles and, therefore, is of special interest.

Using (26) and (28) we obtain

$$\frac{1}{V_\nu}\frac{\partial U_\nu}{\partial \eta} = \frac{1}{2\,U_\nu V_\nu}\frac{\partial U_\nu^2}{\partial \eta} = \frac{1}{2\,E_\nu^2}\left[\Delta\frac{\partial}{\partial \eta}(\varepsilon_\nu - \lambda) - (\varepsilon_\nu - \lambda)\frac{\partial \Delta}{\partial \eta}\right]. \tag{147}$$

In the case of vibrations of spherical nuclei, we are interested in the value B_η for $\eta = 0$. The expansion of Δ for small η, as can be seen from (110), does not contain a linear term and therefore $\frac{\partial \Delta}{\partial \eta}$ vanishes for $\eta = 0$. The quantity $\varepsilon_\nu - \lambda$ for small η is given by

$$\varepsilon_\nu - \lambda \approx \frac{1}{2}\,\Omega G \chi_N^0 + \Omega G \frac{\varepsilon_\nu - \varepsilon_\lambda}{\varepsilon'' - \varepsilon'}\,\eta. \tag{148}$$

The average energy of the λ-shell, in the first approximation, is not shifted by the deformation. The ratio $(\varepsilon_\nu - \varepsilon_\lambda)/(\varepsilon'' - \varepsilon')$ remains constant for small η and, therefore,

$$\frac{\partial}{\partial \eta}(\varepsilon_\nu - \lambda) \approx \Omega G \frac{\varepsilon_\nu - \varepsilon_\lambda}{\varepsilon'' - \varepsilon'}. \tag{149}$$

With the aid of (149) and (147) we get from (146)

$$B_\eta = \frac{1}{4}\hbar^2 \sum_\nu \frac{\Delta^2}{E_\nu^5}(\Omega G)^2 \left(\frac{\varepsilon_\nu - \varepsilon_\lambda}{\varepsilon'' - \varepsilon'}\right)^2. \tag{150}$$

Inserting in (150) the values of Δ and E_ν, which for $\eta \ll 1$ are given by

$$\Delta \approx \frac{1}{2}\,\Omega G \Theta_N^{1/2}; \qquad E_\nu \approx \frac{1}{2}\,\Omega G,$$

we get

$$B_\eta = \frac{2\,\hbar^2 \Theta N}{\Omega G} \sum_\nu \left(\frac{\varepsilon_\nu - \varepsilon_\lambda}{\varepsilon'' - \varepsilon'}\right)^2. \tag{151}$$

Replacing the sum in (151) by an integral, we obtain

$$B_\eta = \frac{\hbar^2}{6\,G}\left(1 - \frac{\xi^2}{3}\right)\Theta_N. \tag{152}$$

The equation (152) contains the value of the interaction G in the denominator. It must be pointed out that the transition in (152) to the limit $G \to 0$ is not valid, since the condition $\eta \approx (\varepsilon'' - \varepsilon')/\Omega G < 1$ has been used in its calculation. As can be seen from the exact formula (146), $B_\eta \to 0$ for

$G \to 0$. When G decreases, then the number of outside particles, needed to make the spherical shape unstable, also descreases. For a certain value of G, the spherical shape becomes unstable even for one outside pair ($N = 2$), which makes the inertial parameter (152) meaningless. The minimum value of G in the equation (152) can be estimated from (113) if one requires that $\Theta_{N_0} > \Theta_2$, which leads to

$$G \quad > \frac{2}{3} \quad \frac{1 - \frac{\xi^2}{3}}{1 - \varkappa/k} \quad \frac{\varkappa q_0^2}{\Omega} \approx \frac{\varkappa q_0^2}{\Omega}. \tag{153}$$

To analyze the quantity B_η we compare it with the mass coefficient B_{irr} (145). To this purpose, we need a relation between η and the equivalent deformation of the nucleus in the hydrodynamical model. Assuming the equilibrium ratio between β and η we get from (108) and (110)*

$$\left(\frac{\eta}{\beta}\right)_{\text{eq}} = \frac{6\,\bar{Q}\,(1 - \varkappa/k)}{q_0\left(1 - \frac{\xi^2}{3}\right)\Omega\Theta_N}. \tag{154}$$

From (145), (152), and (154) it follows that

$$\left(\frac{\eta}{\beta}\right)^2 \frac{B_\eta}{B_{\text{irr}}} \approx \frac{16\,\pi\,(1 - \varkappa/k)^2}{1 - \frac{\xi^2}{3}} \cdot \frac{\hbar^2}{mR_0^2}\left(\frac{\bar{Q}}{q_0 A}\right)^2 \frac{A}{\Omega^2 G\,\Theta_N}. \tag{155}$$

Using (105), and setting $q_0/R_0^2 = 2$; $\xi = 1$ according to the oscillator model, one obtains from (155)

$$\left(\frac{\eta}{\beta}\right)^2 \frac{B_\eta}{B_{\text{irr}}} \approx 100 \text{ MeV } (1 - \varkappa/k)^2 \frac{A^{1/3}}{\Omega G N}. \tag{156}$$

The ratio (156) is significantly larger than unity and is in qualitative agreement with the observed trends. Thus, for the single particle, excitation energy $\Omega G \approx 1.5$ MeV and $\varkappa/k = 0.5$, $A^{1/3} = 5$; $N = 6$ the ratio is equal to 10 and decreases when the number of outside particles increases.

6. Normal Vibrations of Spherical Nuclei

The potential energy of collective vibrations is given by (104). Introducing the variables η and β' (the deformation of the core, associated with Q_{cl} by: $Q_{cl} = \bar{Q}\beta'$), we obtain for small η

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* In the general case, the equilibrium polarizability of the core $\varkappa/k$ may be replaced by $\alpha\varkappa/k$, where $0 \leqslant \alpha \leqslant 1$.

$$\left.\begin{aligned} W(Q) = W_0 - \frac{\Omega^2}{4} G\Theta_N + \frac{1}{2}(k-\varkappa)\,\bar{Q}^2\beta'^2 - \frac{\Omega}{6}\varkappa q_0 \bar{Q}\left(1-\frac{\xi^2}{3}\right)\Theta_N \beta'\eta \\ + \frac{\Omega^2}{12} G\Theta_N\left(1-\frac{\xi^2}{3}\right)\left[1-\frac{\varkappa q_0^2}{6\,G}\left(1-\frac{\xi^2}{3}\right)\Theta_N\right]\eta^2. \end{aligned}\right\} \tag{157}$$

As has been established in the previous section, the kinetic energy has the form

$$T = \frac{1}{2} B_\eta \dot{\eta}^2 + \frac{1}{2} B_{\beta'} \dot{\beta}'^2, \tag{158}$$

where B_η is given by (152). Because of the smallness of the coefficient $B_{\beta'}$, the second term in (158) is much smaller than the first one. Making use of this fact in the transformations of (157) and (158) to the normal vibrations, we obtain for the normal coordinates*

$$\alpha_1 \approx \sqrt{B_\eta}\left\{\eta + \frac{\varkappa q_0 \Omega\Theta_N}{6\,(k-\varkappa)\,\bar{Q}}\left(1-\frac{\xi^2}{3}\right)\frac{B_{\beta'}}{B_\eta}\beta'\right\}, \tag{159}$$

$$\alpha_2 \approx \sqrt{B_{\beta'}}\left\{\beta' - \frac{\varkappa q_0 \Omega\Theta_N}{6\,(k-\varkappa)\,\bar{Q}}\left(1-\frac{\xi^2}{3}\right)\eta\right\}. \tag{160}$$

The corresponding eigenfrequencies are given by

$$\omega_1 = \sqrt{\frac{C_\eta}{B_\eta}}; \qquad \omega_2 = \sqrt{\frac{(k-\varkappa)\,\bar{Q}^2}{B_{\beta'}}}, \tag{161}$$

where C_η is determined by (112) or (114).

The normal vibration of the first type ($\alpha_2 = 0$) preserves the equilibrium relation between β' and η. Indeed, using (98) and (110) and employing the relation between β' and Q_{cl}, one may write the condition $\alpha_2 = 0$ as

$$Q_{cl} = \frac{\varkappa}{k-\varkappa} Q_\lambda \quad \text{or} \quad Q_\lambda = (1-\varkappa/k)\,Q, \tag{162}$$

which is equivalent to the equilibrium relation (108'). Therefore, in the vibration of the first type, the closed-shell core adjusts itself adiabatically to the deformation of the outside nucleons. According to (161), (114), and (152), the energy of this vibration is given by

$$\hbar\omega_1 = \Omega G \sqrt{1-\frac{\Theta_N}{\Theta_{N_0}}} \tag{163}$$

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* In terms of these coordinates the Hamiltonian of collective vibrations is given by $H_{coll} = T + W(Q) = \frac{1}{2}(\dot{\alpha}_1^2 + \dot{\alpha}_2^2 + \omega_1^2\alpha_1^2 + \omega_2^2\alpha_2^2)$.

and decreases as the occupation of the shell increases. Only when Θ_N approaches the value Θ_{N_0}, needed to give instability of the spherical shape, does the vibrational energy become appreciably smaller than the intrinsic excitation energy ΩG, as required by the adiabatic condition*. In the absence of pairing interaction this type of vibration vanishes.

The collective motion considered above corresponds to vibrations of the average value of the quadrupole moment. Such a simple physical picture is meaningful only when fluctuations of the quadrupole moment do not exceed the vibrational amplitude. According to (91), the quadratic fluctuation of the qudrupole moment is given by

$$(\delta Q)^2 = \langle \hat{Q}^2 \rangle - \langle \hat{Q} \rangle^2 = \sum_{\nu\nu'} | q_{\nu\nu'} |^2 (U_\nu V_{\nu'} + V_\nu U_{\nu'})^2. \tag{164}$$

For simplicity, we shall consider only the outside nucleons. In a proper representation, when the states ν are eigenstates in the self-consistent field, the matrix element $q_{\nu\nu'}$ is diagonal (cf. (94)) so that we have

$$(\delta Q)^2 = \sum_{\nu} | q_{\nu\nu} |^2 \, 4 \, U_\nu^2 V_\nu^2.$$

For spherical nuclei ($\eta = 0$), one finds $4 U_\nu^2 V_\nu^2 = \Theta_N$ and, after simple calculations, we obtain

$$(\delta Q_\lambda)^2 = \Theta_N \sum_{\nu} | q_{\nu\nu} |^2 = \frac{\Omega}{12} q_0^2 \Theta_N \left(1 - \frac{\xi^2}{3}\right). \tag{165}$$

On the other hand, using the relation (98) between Q_λ and η and substituting for η the amplitude of zero vibrations,

$$\eta^0 = \sqrt{\frac{\hbar}{2 B_\eta \omega_1}} = \left[\frac{h \omega_1}{3 G} \Theta_N \left(1 - \frac{\xi^2}{3}\right)\right]^{-1/2}, \tag{166}$$

we find for the zero-vibration amplitude of the quadrupole moment

$$(Q_\lambda^0)^2 = \frac{\Omega}{12} q_0^2 \Theta_N \left(1 - \frac{\xi^2}{3}\right) \frac{\Omega G}{\hbar \omega_1}. \tag{167}$$

Comparing (165) and (167), we obtain

$$\left(\frac{\delta Q_\lambda}{Q_\lambda^0}\right)^2 = \frac{\hbar \omega_1}{\Omega G} = \sqrt{1 - \frac{\Theta_N}{\Theta_{N_0}}}. \tag{168}$$

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* Here, we are referring to even-even nuclei. In odd nuclei, this adiabatic condition is not fulfilled because of the small excitation energy of the odd particle.

As it is seen from (168), the requirement that this ratio be small coincides with the adiabatic condition.

Consider, now, the second normal vibration ($a_1 = 0$). The closed-shell core participates mainly in this vibration. The outside nucleons are only slightly deformed. The ratio of the amplitudes η and β', in this type of vibrations compared to that in the first type, is given by

$$\left(\frac{\eta}{\beta'}\right)_2 = -\left(\frac{\beta'}{\eta}\right)_1 \frac{B_{\beta'}}{B_\eta} = -\left(\frac{\eta}{\beta'}\right)_1 \left\{\frac{B_{\beta'}}{B_\eta}\left(\frac{\beta'}{\eta}\right)_1^2\right\}. \tag{169}$$

Since $B_{\beta'}$, is of the order of B_{irr} it is seen from (169) that the polarization of the outside nucleons is reduced by the factor $\left(\frac{\beta}{\eta}\right)^2 B_{\mathrm{irr}}/B$ given by (156). The second type of vibration occurs with a high frequency which is determined by the properties of the core and does not depend appreciably on the pairing interaction and on the number of the nucleons in the unfilled shell. Since there is almost no coupling between this vibration and the outside nucleons, the adiabatic condition requires the vibrational energy $h\omega_1$ to be small only compared with the distance between the shells.*

Concluding Remarks

Starting from the basic assumption that a pairing correlation of a "superconducting" type exists between nucleons, we have attempted to investigate consistently the effects of this correlation in different nuclear phenomena.

Although the calculations are based on a rather idealized model, a great number of experimental facts of a different kind are explained in a natural way from a single point of view, viz.,

a) Stability of the spherical shape of nuclei near the closed shells;
b) Sharp transition between spherical and deformed nuclei;
c) Significant reduction of the moment of inertia from the value for rigid rotation;
d) Existence of low-energy vibrations in spherical nuclei near the bound of instability.

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* In the oscillator model, $h\omega_2$ turns out to be two times larger than the distance between the shells; this violates the adiabatic condition$^{18)}$.

The equilibrium deformations, the moment of inertia, the vibrational frequencies, and the inertial parameter obtained from the present model are of the order of magnitude observed, and exhibit a reasonable dependence on the parameters. Besides these collective effects, some particular features of the single-particle spectra are explained (energy gap in even-even nuclei, increased level density just above the gap).

It is outside the scope of this paper to relate the pairing correlation to explicit forms of nucleon-nucleon forces. Here, we are restricting ourselves to a semi-phenomenological description of this correlation*. The matrix element $\langle \nu\nu | G | \nu' \nu' \rangle$ which represents the pairing interaction has been assumed, for simplicity, to be constant and its value G is the only additional parameter introduced in order to describe the pairing correlation. A dependence $\langle \nu\nu | G | \nu' \nu' \rangle$ on ν and ν' might be essential for a more detailed description. For example, the constancy of $\langle \nu\nu | G | \nu' \nu' \rangle$ (and, therefore, Δ_ν) leads in spherical nuclei to the same energy for all quasi-particles $E_\nu = \sqrt{\Delta_\nu^2 + (\varepsilon_\nu - \lambda)^2} = \frac{1}{2}\Omega G$ and, therefore, to a degeneracy of the excited states. A dependence of Δ_ν on ν eliminates this degeneracy. The residual interaction between quasi-particles causes the same effect and may also be important for a detailed analysis of single-particle spectra.

To simplify the problem, we did not distinguish between protons and neutrons. If we do not consider any pairing interaction between neutrons and protons, or if they occupy different shells, then the generalization of the problem is straightforward. The case with some neutron-proton pairing correlation included remains to be investigated.

For spherical nuclei, we have considered the idealized scheme of strongly degenerate levels removed from each other (shells). The validity of the present results for shells with a small number of states, as well as the effect of the splitting of a shell into subshells, will need further analysis.

Finally, it may be added that the pairing correlation may affect also other nuclear phenomena such as quadrupole and magnetic moments, electromagnetic transitions, etc.

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* Only a few qualitative remarks have been made in I. 4 in order to indicate which parts of the nucleon-nucleon forces are responsible for the pairing interaction.

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Appendix A

Here, we write down the expression for $H_{\text{int}} = H_{40} + H_{31} + H_{22}$. For compactness, we rewrite (10) in the following way:

$$b_{\nu\sigma} = U_{\nu\sigma} x_{\nu\sigma} + V_{\nu\sigma} y_{\nu\sigma}^{+}, \tag{A. 1}$$

where

$$\left.\begin{array}{ll} x_{\nu+} = y_{\nu-} = \alpha_{\nu}; & x_{\nu-} = y_{\nu+} = \beta_{\nu} \\ U_{\nu\pm} = U_{\nu}; & V_{\nu\pm} = \pm V_{\nu}. \end{array}\right\} \tag{A. 2}$$

In this notation, H_{int} is given by

$$\left.\begin{array}{l} H_{40} = -\frac{1}{4}\sum \langle 12|G|2'\,1'\rangle U_1 U_2 V_{2'} V_{1'}\, x_1 x_2^{+} y_{2'}^{+} y_{1'}^{+} + \text{conj.} \\[2ex] H_{31} = -\frac{1}{2}\sum \langle 12|G|2'\,1'\rangle (U_1 U_2 V_{2'} U_{1'} - V_1 V_2 U_{2'} V_{1'})\, x_1^{+} x_2^{+} y_{2'}^{+} x_{1'} \\ \hfill + \text{conj.} \\[2ex] H_{22} = -\frac{1}{4}\sum \langle 12|G|2'1'\rangle (U_1 U_2 U_{2'} U_{1'} + V_1 V_2 V_{2'} V_{1'})\, x_1^{+} x_2^{+} x_{2'} x_{1'} \\[2ex] \qquad + \sum \langle 12|G|2'1'\rangle U_1 V_2 V_{2'} U_{1'}\, x_1^{+} y_{2'}^{+} y_2 x_{1'}, \end{array}\right\} \tag{A. 3}$$

where the indices correspond to ν and σ (e.g., $1 \equiv \nu_1 \sigma_1$) and the matrix elements are antisymmetrized

$$\langle 12|G|2'1'\rangle = \langle \nu_1 \sigma_1 \nu_2 \sigma_2 | G | \nu_2' \sigma_2' \nu_1' \sigma_1' \rangle - \langle \nu_1 \sigma_1 \nu_2 \sigma_2 | G | \nu_1' \sigma_1' \nu_2' \sigma_2' \rangle. \tag{A. 4}$$

The matrix elements have the symmetry properties following from the definition of the conjugate states:

$$\langle \nu_1 \sigma_1 \nu_2 \sigma_2 | G | \nu_2' \sigma_2' \nu_1' \sigma_1' \rangle = \langle \nu_1 - \sigma_1 \nu_2 - \sigma_2 | G | \nu_2' - \sigma_2' \nu_1' - \sigma_1' \rangle^* \qquad \text{(A. 5)}$$

from which it follows, in particular, that

$$\langle \nu_1 + \nu_2 - | G | \nu_2' - \nu_1' + \rangle = \langle \nu_2' + \nu_1' - | G | \nu_1 - \nu_2 + \rangle . \qquad \text{(A. 6)}$$

Appendix B

Here, we shall calculate the nuclear energy (104) for small deformations of the self-consistent field. The main point will be to show that the effect of a variation of the single-particle wave functions with deformation may be neglected for the outside nucleons. The following calculations will explicitly exhibit also the procedure of the extraction of an additional self-consistent field and the choice of the new single-particle eigenstates ν, which demonstrate the nature of the first canonical transformation (3).

Let us look for the ground state of the Hamiltonian (101). The single-particle eigenstates ν in a deformed field are determined by the requirement of diagonalization of the single-particle energies $\tilde{\varepsilon}_{\nu\nu'}$, i.e., according to (94), by

$$\varepsilon_{\nu\nu'} - \hat{\mu}\, q_{\nu\nu'} = \sum_k \varepsilon_k^0 \varphi_{k\nu}^* \varphi_{k\nu'} - \tilde{\mu} \sum_{kk'} q_{kk'}^0 \varphi_{k\nu}^* \varphi_{k'\nu'} = \tilde{\varepsilon}_\nu \delta_{\nu\nu'}$$

which can also be rewritten as

$$(\varepsilon_k^0 - \tilde{\varepsilon}_\nu)\, \varphi_{k\nu} = \tilde{\mu} \sum_{k'} q_{kk'}^0 \varphi_{k'\nu}, \qquad \text{(B. 1)}$$

where the states k and the quantities ε_k^0 and $q_{kk'}^0$ correspond to the spherical field. We assume that the states k, corresponding to the same degenerate level, are chosen to make the matrix elements $q_{kk'}^0$ diagonal inside each shell. Assuming that $\varphi_{k\nu} = \delta_{k\nu} + \varphi_{k\nu}^{(1)}$ where the deviations from the spherical symmetry $\varphi_{k\nu}^{(1)}$ are small, we find in the first approximation

$$\varphi_{k\nu}^{(1)} = \frac{\tilde{\mu} q_{k\nu}^0}{\varepsilon_k^0 - \varepsilon_\nu^0} \qquad \text{(B. 2)}$$

and, therefore,

$$\varepsilon_{\nu\nu} = \varepsilon_\nu^0 + \tilde{\mu}^2 \sum_{\nu'} \frac{| q_{\nu\nu'}^0 |^2}{\varepsilon_{\nu'}^0 - \varepsilon_\nu^0} \equiv \varepsilon_\nu^0 + \tilde{\mu}^2 p_\nu^0 \qquad \text{(B. 3)}$$

$$q_{\nu\nu} = q^0_{\nu\nu} + 2\,\tilde{\mu} \sum_{\nu'} \frac{|\,q^0_{\nu\nu'}\,|^2}{\varepsilon^0_{\nu'} - \varepsilon^0_{\nu}} = q^0_{\nu\nu} + 2\,\tilde{\mu}\, p^0_{\nu} \tag{B. 4}$$

$$\tilde{\varepsilon}_{\nu\nu} = \varepsilon_{\nu\nu} - \tilde{\mu}\, q_{\nu\nu} = \varepsilon^0_{\nu} - \tilde{\mu}\, q^0_{\nu\nu} - \tilde{\mu}^2\, p^0_{\nu}. \tag{B. 5}$$

(For the closed shells, $\tilde{\mu} = \mu + \varkappa Q$ must be replaced by $\tilde{\mu}' = \mu' + \varkappa Q$). From (B. 5) it follows that the total splitting of the unfilled shell is given by (cf. (99))

$$\varepsilon'' - \varepsilon' = \tilde{\mu}\, q_0 + \tilde{\mu}^2\, p_0, \tag{B. 6}$$

where

$$p_0 = p^0_{\nu}\,(\varepsilon_{\nu} = \varepsilon') - p^0_{\nu}\,(\varepsilon_{\nu} = \varepsilon''). \tag{B. 7}$$

Using (B. 4), one obtains for the quadrupole moments

$$Q_{cl} = 2\tilde{\mu}' {\sum_{\nu}}'\, 2\, p^0_{\nu} \equiv 2\,\tilde{\mu}'\, P', \quad \Big({\sum_{\nu}}'\, q^0_{\nu\nu} = 0\Big) \tag{B. 8}$$

$$Q_{\lambda} = \sum_{\nu}^{\lambda} q^0_{\nu\nu}\, 2\, V^2_{\nu} + 2\,\tilde{\mu} \sum_{\nu}^{\lambda} p^0_{\nu}\, 2\, V^2_{\nu}. \tag{B. 9}$$

The quantity V^2_{ν} depends on the total splitting of the λ-shell, i.e., on the parameter η. Therefore, we may write

$$\sum_{\nu}^{\lambda} q^0_{\nu\nu}\, 2\, V^2_{\nu} = q_0\, \varLambda\,(\eta) \tag{B. 10}$$

$$\sum_{\nu}^{\lambda} p^0_{\nu} 2\, V^2_{\nu} = p_0\, \varLambda'\,(\eta). \tag{B. 11}$$

The function $\varLambda\,(\eta)$ has been calculated earlier and is given by (100). The function $\varLambda'\,(\eta)$ is of the same order as $\varLambda\,(\eta)$.

The energy of non-interacting particles (the first term in (96)), is, according to (B. 3), given by

$$\sum_{\nu} \varepsilon_{\nu\nu}\, 2\, V^2_{\nu} = \sum_{\nu} \varepsilon^0_{\nu}\, 2\, V^2_{\nu} + \tilde{\mu}'^2 {\sum_{\nu}}'\, 2\, p^0_{\nu} + \tilde{\mu}^2 \sum_{\nu}^{\lambda} p^0_{\nu}\, 2\, V^2_{\nu}. \tag{B. 12}$$

Note that the first term in the right hand side is constant, since

$$\sum_{\nu} \varepsilon^0_{\nu}\, 2\, V^2_{\nu} = {\sum_{\nu}}'\, 2\, \varepsilon^0_{\nu} + \varepsilon_{\lambda}\, N_{\lambda} \equiv W_0.$$

Using (B. 8) and (B. 11), we obtain

$$\sum_{\nu} \varepsilon_{\nu\nu}\, 2\, V^2_{\nu} = W_0 + \frac{1}{4\,P'}\, Q^2_{cl} + \tilde{\mu}^2\, p_0\, \varLambda'\,(\eta). \tag{B. 13}$$

To estimate the expressions obtained above, we asume now that the states k correspond to the oscillator potential. In this model, the quantities q_0 and p_0 are given, in the usual notation, by

$$q_0 = \frac{3\,\hbar n}{m\omega}, \qquad p_0 = \frac{3\,\hbar n}{2\,m^2\,\omega^3}. \tag{B. 14}$$

(n is the principal quantum number). From (B. 14) and (B. 6) it follows that

$$\frac{\tilde{\mu}\, p_0}{q_0} = \tilde{\mu}\, q_0 \frac{p_0}{q_0^2} = \frac{\tilde{\mu}\, q_0}{6\,\hbar\omega n} \approx \frac{\varepsilon'' - \varepsilon'}{6\,\varepsilon_F} \ll 1, \tag{B. 15}$$

where ε_F is the Fermi energy. Within the accuracy of the small factor (B. 15), we may neglect the last terms in (B. 6) and (B. 9); then, these equations coincide with (99) and (98). The last term in (B. 13), which depends on η, is to be compared with other η-dependent terms in (96), say, $-\frac{1}{2}\varkappa Q_\lambda^2$. Then, we find

$$\frac{\tilde{\mu}\, p_0 \Lambda'}{\varkappa Q_\lambda^2} = \frac{\tilde{\mu}\, p_0}{q_0} \cdot \frac{\tilde{\mu}\, \Lambda'}{\varkappa Q_\lambda \Lambda}. \tag{B. 16}$$

Since $\Lambda' \sim \Lambda$ and $\tilde{\mu} \sim \varkappa Q_\lambda$, the ratio (B. 16) is of the order of the small factor (B. 15). Therefore, the last term in (B. 13) may be neglected, and this justifies the equation (103).

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FOUNDATIONS OF THE THEORY OF DYNAMICAL SYSTEMS OF INFINITELY MANY DEGREES OF FREEDOM. I

BY

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CONTENTS

Synopsis

It is shown effectively that, while there are many unitarily inequivalent representations of the canonical Bose-Einstein field variables, the S-matrix can be theoretically specified without using any particular representation. The central idea is that the bounded functions of finite subsets of the canonical variables, together with their limits in a physically meaningful sense, are substantially the same for all representations. On the other hand, convergence questions may depend strongly on the representation; in fact, formal operators fairly typical of divergent interaction Hamiltonians may be rendered hermitian operators in Hilbert space by a suitable choice of representation. Applications are made to the 'clothing' of field kinematics, statistics, and canonical variables, for a theory in which only the transformation properties of single particles under an arbitrary covariance group, and a covariant interaction, need to be specified. The results are mostly of a general character, such as the existence of a physical vacuum, and the possibility of ascribing definite constitutions in terms of primary elementary particles to bound states. It is shown also that the canonical variables and occupation numbers of a field can be described by the so-called 'free-field representation' only if the physical vacuum is invariant under the dynamical development of the system in essentially the interaction representation.

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Introduction

In both classical and quantum mechanics of systems of a finite number of degrees of freedom, one has to do with so-called canonical variables $p_1, p_2, \ldots, p_n$ and $q_1, q_2, \ldots, q_n$, which are now fairly well understood mathematically. The theory of unbounded operators in Hilbert space has provided a foundation for the use of these variables that is made in quantum mechanics. When the number of degrees of freedom is infinite, the situation is different. The canonical variables are relatively most useful in quantum mechanics, and it is here that the greatest mathematical difficulties appear. From the beginning, the success of quantum field theory has been attended by 'infinities' in even the simplest cases. It was assumed that the canonical variables $p_1, p_2, \ldots,$ and $q_1, q_2, \ldots,$ were operators, but the vectors on which they acted had for the most part only hypothetical character, which did not appear to matter substantially for the computational use to which the theory was put, but made it difficult to get at the bottom of the trouble.

This difficulty about 'interacting' systems was nevertheless accompanied by unclouded optimism concerning the mathematical basis for the theory of free systems, which went unexamined for many years. One had the p's and q's satisfying the basic relations $p_j q_k - q_k p_j = -i\delta_{jk}$ $(j, k = 1, 2, \ldots)$, and it was assumed that any two such systems were equivalent, apart from the irrelevant complication of multiplicity, which was generally suppressed by assuming the p's and q's to act irreducibly; upon this informal axiomatic basis the theory rested. Within the past decade these matters have been gone into, and it was found that this central assumption was literally in great error. There were at least continuum many inequivalent such systems; some of the most commonly applied so-called canonical transformations, – even that of multiplying the p's by a positive constant and dividing the q's by the same constant ($\neq 1$) –, led to inequivalent systems; and these facts had a concrete analytical basis, having nothing to do with the 'pathology' of unbounded operators, etc., persisting when the relations were strengthened into the formally equivalent ones due to WEYL, which involved only algebraic operations on bounded operators.

A unique theory of 'free' systems could be salvaged by defining the canonical p's and q's to be the specific ones treated rigorously by COOK, following the basic physical ideas of FOCK, and of BOHR and ROSENFELD. This set of variables proved to be especially well adapted to the program of treating systems in terms of their transformation properties, as well as to the correlation of their wave and particle aspects. Apart from the unpleasantly strong inhibitions on the application of canonical transformations, the mathematical situation in the theory of free systems developed in a satisfactory way, and there seemed little doubt that the Fock-Cook system was at least appropriate in connection with the theoretical idea of a field of completely non-interacting particles, and possibly appropriate for the physically fictitious 'bare' particles. But it was not clear how the latter field and the free physical-particle field (whose 'freedom' is experimental, and not necessarily mathematical, since in all theories the physical particles involve self-interactions) were related, and the precise character of the p's and q's for interacting fields remained a mystery,—which in fact had conceivably to await a new physical idea for its elucidation.

This paper gives a mathematical interpretation of the canonical variables which, from a foundational viewpoint, obviates the uniqueness troubles mentioned, and does so by eliminating from the mathematical formalism features lacking in physically operational significance. While this shows that in spirit the assumption about the essential uniqueness of the canonical variables was in a way partially sound, it also indicates that many tacit assumptions need to be revised,—e. g. it shows that the zero-interaction and the free physical-particle canonical variables cannot be expected to be unitarily equivalent, even in comparatively simple cases. A significant application is to make possible the physically effective quantization of fields of particles whose transformation properties are non-unitary, such as the important type admitting an indefinite invariant inner product. It also narrows slightly, but perhaps illuminatingly, the gap between the mathematical formulations of classical and quantum mechanics, a dynamical transformation in either theory being an automorphism of a certain C^*-algebra, the unitary transformations of quantum mechanics being seen to play an essentially technical role.

In a purely mathematical way, this work relates essentially to an abstract C*-algebra $\mathfrak{A}$ which is invariantly attached to a real topological linear space $\mathfrak{H}$ admitting a Hilbert space structure, and to a representation of the symplectic group on the direct sum of $\mathfrak{H}$ with its dual by automorphisms of this algebra $\mathfrak{A}$. A distinguished automorphism of $\mathfrak{A}$ which commutes with the action on $\mathfrak{A}$ of a distinguished subgroup of the symplectic group plays a fundamental role in the later developments. The canonical variables are in a sense affiliated with $\mathfrak{A}$, which consists essentially of all bounded functions of a finite number of the canonical variables, together with their uniform limits.

When $\mathfrak{H}$ is finite-dimensional, $\mathfrak{A}$ consists of all bounded linear transformations on $L_2(\mathfrak{H})$ (within algebraic isomorphism). The general linear group on $\mathfrak{H}$ induces automorphisms of this algebra through its action on $L_2(\mathfrak{H})$ in an obvious manner, involving normalization in terms of the determinant of the transformation, and this action extends to the symplectic group over the direct sum of $\mathfrak{H}$ with its dual. In the case of present interest in which $\mathfrak{H}$ is infinite-dimensional, the Hilbert space $L_2(\mathfrak{H})$ can be effectively formulated, and an analogous canonical unitary representation on $L_2(\mathfrak{H})$ obtained for the orthogonal group on $\mathfrak{H}$, relative to any admissible Hilbert space structure on $\mathfrak{H}$; but the full general linear group on $\mathfrak{H}$ cannot act on $L_2(\mathfrak{H})$ in any reasonable fashion, one relevant difficulty being the absence of a determinant for such transformations. Nevertheless, it induces an automorphism of $\mathfrak{A}$, which is all that is essential for, or operationally relevant to, kinematical and dynamical purposes, and which determines the corresponding unitary transformation on $L_2(\mathfrak{H})$, when it happens to exist, uniquely within a scalar factor.

This has been stated in terms of a particular representation for the algebra $\mathfrak{A}$ of 'field observables', but it is of crucial importance that the space on which $\mathfrak{A}$ acts can be eliminated, and that essentially only $\mathfrak{A}$ as an abstract algebra is fundamentally necessary or logically relevant. It is more than conceivable that the interacting field p's and q's cannot be represented as operators in the same representation as that in which the free-field p's find q's and operators (a partially heuristic result to this effect for certain fields is due to HAAG), but it is still possible to obtain the interacting ones from the free-field ones essentially by an automorphism of $\mathfrak{A}$, by virtue of its essentially abstract algebraic character. Such an automorphism is just as good as the unitary operator in terms of which it has been conventionally assumed that a dynamical transformation in quantum mechanics is to be mathematically expressed, for it preserves spectral values, expectation values in states, the purity of states, etc.; it has, in fact, a certain advantage, in that it has greater operational meaning (in particular there is no phase ambiguity). Even when, in a particular representation, $\mathfrak{A}$ acts irreducibly, relatively few of its automorphisms will be implementable by unitary transformations, the quotient of its full group of automorphisms by the subgroup of those so implementable being infinite-dimensional in any reasonable sense.

Therefore it is not surprising that the Hamiltonians of the quantum theory of interacting fields do not appear to correspond to operators, for it is only in the comparatively rare event that the corresponding integrated motion is representable by unitary transformations that this will be the case. For this reason and for greater operationalism, we define physical particles substantially in terms of the scattering operator and the field kinematics, without reference to the interacting field Hamiltonian, and the relatively explicit theoretical construction of these particles from the 'pristine' ones (the so-called 'clothing' of the particles) makes it clear that, in general, their canonical operators will not be merely a similarity transform of those of the pristine particles. This difficulty, which is parallel to that circumvented by renormalization in conventional field theory, is here treated in a theoretically effective and mathematically rigorous manner. It appears that renormalizable divergences may well arise in substantial part from the attempt to enforce analytically the logically unnecessary and rigorously absent unitary equivalence between pristine and free physical-particle representations.

It may clarify our results to discuss briefly their character for the very simple case when $\mathfrak{H}$ is finite-dimensional. The central uniqueness theorem is then a variant of the fundamental result on the uniqueness of the Schrödinger operators developed by STONE and VON NEUMANN, whose results are used in the proof of our theorem. On the other hand, in its present formulation, it may also be regarded as a variant of a well-known theorem of PLESSNER, stating that a quasi-invariant regular measure on Euclidean space is equivalent to Lebesgue measure. The relevant unitary ray representation on $L_2(\mathfrak{H})$ of the symplectic group on the direct sum of a finite-dimensional $\mathfrak{H}$ with its dual is, however, not treated in the existing literature known to us.

It may also be helpful to compare our approach with one sketched by von Neumann$^{(10)}$, in which field dynamics is likewise to be expressed more or less in terms of automorphisms of an algebra. Apart from this similarity, there appears to be nothing in common between the approaches. The elegant and somewhat formal idea of von Neumann is that all the measurable field-theoretic variables should be expressible in terms of a 'type II_1' ring, whose automorphisms are expressible by unitary operators, which however are in general outside the ring; it is based technically on a *weakly* closed ring. The present intuitive idea is roughly that the only measurable field-theoretic variables are those that can be expressed in terms of a *finite* number of canonical operators, or *uniformly* approximated by such; the technical basis is a *uniformly* closed ring (more exactly, an abstract C^*-algebra). The crucial difference between the two varieties of approximation arises from the fact that, in general, weak approximation has only analytical significance, while uniform approximation may be defined operationally, two observables being close if the maximum (spectral) value of their difference is small. More technically, weak approximation depends on the particular representation of the canonical operators, and also will be affected by an enlargement of the physical system under consideration, while uniform approximation is independent of the particular representation of the canonical variables, and is unaffected by enlargement of the system. The weak closure in analytically relevant concrete representations (e. g., the zero-interaction representation) of the present algebra of field observables may well consist of all bounded operators, and so have little connection with a ring of type II_1.

The specific formal operators of relativistic field theory and of possible extensions of the theory will be treated on a later occasion, to which we defer also the consideration of more general varieties of statistics and the representation of non-linear transformations on the single-particle space $\mathfrak{H}$ by automorphisms of the algebra $\mathfrak{A}$ of field observables. We may note that significant progress relevant to the latter has been made by LEONARD GROSS(2), while a discussion of general statistics as well as a survey of the physical background of the present work is given in(3).

1. Field Observables

A *single-particle* (state-vector) structure Σ is defined as a system ($\mathfrak{H}$, $\mathfrak{H}'$, B), where $\mathfrak{H}$ and $\mathfrak{H}'$ are real linear spaces, and B is a real non-singular bilinear form on ($\mathfrak{H}$, $\mathfrak{H}'$). Thus, for fixed x in $\mathfrak{H}$ (resp. x' in $\mathfrak{H}'$), $B(x, x')$ is a linear function of x' in $\mathfrak{H}'$ (resp. x in $\mathfrak{H}$), while for any non-vanishing x (resp. x'), there exists an x' (resp. x) such that $B(x, x') \neq 0$.

Example 1.1. Let $\mathfrak{H}$ be a real linear topological space admitting a Hilbert space structure, let $\mathfrak{H}'$ be its dual, and set $B(x, x') = x'(x)$.

Example 1.2. Let $\mathfrak{M}$ be a complex Hilbert space with a distinguished conjugation J. Let $\mathfrak{H}$ be the set of all elements of $\mathfrak{M}$ left invariant by J, as a linear space, and $\mathfrak{H}'$ the set of elements taken by J into their negative. Set $B(x, x') = i(x, x')$, where $(.\,,.)$ denotes the canonical inner product in $\mathfrak{M}$; it is easily seen that B is real-valued. This structure will be called *standard*.

A *canonical system over* Σ is a defined as an (ordered) pair of linear maps $p(.)$ and $q(.)$ from $\mathfrak{H}$ and $\mathfrak{H}'$, respectively, to respective commutative families of self-adjoint operators on a (complex) Hilbert space (called the representation space) such that

$$e^{ip(x)}\, e^{iq(x')} = e^{iB(x,x')}\, e^{iq(x')}\, e^{ip(x)}$$

for arbitrary x in $\mathfrak{H}$ and x' in $\mathfrak{H}'$. Linearity, it should be noted, is with reference to the strong operations on the unbounded linear operators on the representation space. That is, it is required that $p(ax+by)$ be the closure of $ap(x)+bp(y)$ for arbitrary x and y in $\mathfrak{H}$ and real numbers a and b, and similarly in the case of $q(.)$. Further, commutativity of unbounded self-adjoint operators is in the sense that any two spectral projections of the operators commute (in the usual sense). It follows that a linear map $p(.)$ of the type described is precisely one such that $U(x) = e^{ip(x)}$ defines a unitary representation $U(.)$ of the additive group of $\mathfrak{H}$, whose restriction to any finite-dimensional submanifold is continuous in the strong operator topology; and similarly for $q(.)$.

Example 1.3. Assume the $\mathfrak{H}$ in Example 1.2 is countably-dimensional, and let $e_1, e_2, \ldots$ be an orthonormal basis for $\mathfrak{H}$. Define $\mathfrak{H}_0$ as the set of finite linear combinations of the e_k $(k = 1, 2, \ldots)$, $\mathfrak{H}'$ as $i\mathfrak{H}_0$, and B_0 as the restriction of B to $\mathfrak{H}_0' \times \mathfrak{H}_0'$. This yields a single-particle space $\Sigma_0 = (\mathfrak{H}_0, \mathfrak{H}_0', B_0)$.

Now let $p_1, p_2, \ldots$ and $q_1, q_2, \ldots$ be two sequences of self-adjoint operators on a complex Hilbert space K such that any two p_k commute and also any two q_k commute, while $e^{ip_j s}\, e^{iq_k t} = e^{i\delta_{jk} st}\, e^{iq_k t}\, e^{ip_j s}$. It is not difficult to show that there exists a unique canonical system over Σ_0 such that $p(e_k) = p_k$ and $q(ie_k) = q_k$; and that, conversely, every canonical system over Σ_0 arises in this way.

A bounded linear operator T (on the representation space) is said to *depend on submanifolds* $\mathfrak{M}$ of $\mathfrak{H}$ and $\mathfrak{M}'$ of $\mathfrak{H}'$ in case T is in the weak closure of the algebra generated (algebraically) by the $\exp(ip(x))$ and $\exp(iq(x'))$ as x and x' range over $\mathfrak{M}$ and $\mathfrak{M}'$, respectively. The collection of all bounded linear operators dependent on a pair of fixed manifolds $\mathfrak{M}$ and $\mathfrak{M}'$ forms a weakly closed ring $\mathfrak{A}_{\mathfrak{M},\mathfrak{M}'}$, while the union over all finite-dimensional $\mathfrak{M}$ and $\mathfrak{M}'$ of the $\mathfrak{A}_{\mathfrak{M},\mathfrak{M}'}$ forms an algebra $\mathfrak{A}$ whose uniform closure is called the *representation algebra of field observables* (over Σ).

Now the algebra $\mathfrak{A}$ evidently depends not only on Σ, but also on the particular canonical system over Σ involved in its definition. The next theorem establishes the essential point that, as an algebra, – or physically, as regards operationally significant aspects –, $\mathfrak{A}$ is independent of the representation employed. The corresponding abstract algebra uniquely associated with Σ (as a pair of linear spaces with a distinguished bilinear form) may then be referred to as the algebra $\mathfrak{A}(\Sigma)$ *of all (bounded) field observables over* Σ. This is essentially, in conventional physical language, the system of observables of the Bose-Einstein field of particles with wave functions in the direct sum $\mathfrak{H} \oplus \mathfrak{H}'$.

THEOREM 1. *For any two canonical systems over a single-particle space* $\Sigma = (\mathfrak{I}, \mathfrak{H}', B)$, *there exists a unique algebraic isomorphism between the corresponding representation algebras of field observables that exchanges the bounded Baire functions of the canonical* $p(x)$ *and* $q(x')$ *for all* x *in* $\mathfrak{H}$ *and* x' *in* $\mathfrak{H}'$.

That is, denoting the one canonical system as above and the other by the use of the superscript $^{\sim}$, there exists a unique algebraic isomorphism of $\mathfrak{A}$ onto $\mathfrak{A}^{\sim}$ (where among the algebraic operations is included adjunction) that takes $\varphi(p(x))$ and $\varphi(q(x'))$ into $\varphi(p^{\sim}(x))$ and $\varphi(q^{\sim}(x'))$, respectively, for every bounded Baire function φ, and arbitrary $x \varepsilon \mathfrak{H}$ and $x' \varepsilon \mathfrak{H}'$. Actually a stronger result will be established, which implies, e. g., that such an isomorphism exchanges also functions of any finite number of canonical variables.

To prove the theorem, let $\mathfrak{M}$ and $\mathfrak{M}'$ be finite-dimensional subspaces of $\mathfrak{H}$ and $\mathfrak{H}'$, respectively, that are mutually separating, in the sense that the restriction of B to $\mathfrak{M} \times \mathfrak{M}'$ is non-singular. Bases may then be chosen in $\mathfrak{M}$ and $\mathfrak{M}'$ in such a manner that $B(x, x')$ has the form $x_1 x_1' + \ldots + x_r x_r'$ for x and x' in $\mathfrak{M}$ and $\mathfrak{M}'$, respectively, the x_j (resp. x_j') being the coordinates of x (resp. x') relative to the basis in $\mathfrak{M}$ (resp. $\mathfrak{M}'$). We can now employ the uniqueness theorem for canonical systems in the case of finitely many degrees of freedom in the form given in(11). According to this, the most general such system is, within unitary equivalence, a discrete direct sum of copies of the conventional (Schrödinger) representation. In particular, the restrictions $p_{\mathfrak{M}}(.)$ and $q_{\mathfrak{M}}(.)$ of $p(.)$and $q(.)$ to $\mathfrak{M}$ and $\mathfrak{M}'$, respectively, have the forms

$$p(x) = p_0(x) \times I_L \qquad q(x') = q_0(x') \times I_L \ (x \varepsilon \mathfrak{M},\ x' \varepsilon \mathfrak{M}'),$$

where $(p_0(.),\ q_0(.))$ is an irreducible canonical system over $\Sigma_0 = (\mathfrak{M},\ \mathfrak{M}',\ B_0)$, B_0 being the restriction of B to $\mathfrak{M} \times \mathfrak{M}'$, and I_L is the identity operator on a Hilbert space L dependent on $\mathfrak{M}$ and $\mathfrak{M}'$. Furthermore, $(p_0(.),\ q_0(.))$ is unitarily equivalent to the Schrödinger system; the precise form of this will not be needed, but only that any two irreducible canonical systems over a finite-dimensional single-particle space are necessarily unitarily equivalent.

Now the bounded Baire functions of the $p_0(x)$ and of the $q_0(x')$ generate, as x and x' range over $\mathfrak{M}$ and $\mathfrak{M}'$, respectively, a (weakly closed) ring of operators $\mathfrak{B}_{M,M'}$. The map $T \to T \times I_L$ is an algebraic isomorphism of $\mathfrak{B}_{M,M'}$ onto the ring $\mathfrak{A}_{M,M'}$ generated by the bounded Baire functions of the $p(x)$ and $q(x')$, as x and x' range over $\mathfrak{M}$ and $\mathfrak{M}'$ respectively. (Here 'ring' is, as generally when referring to operators on a Hilbert space, a weakly closed self-adjoint ring of bounded linear operators, that contains the identity operator on the space). This is clear from the behaviour of direct products with an identity operator, from which it is also apparent that the isomorphism exchanges the $\varphi(p(x))$ and $\varphi(q(x'))$ with the $\varphi(p_0(x))$ and $\varphi(q_0(x'))$, respectively, for arbitrary x and x' in $\mathfrak{M}$ and $\mathfrak{M}'$, respectively.

It follows that there exists an algebraic isomorphism $\theta_{M,M'}$ of $\mathfrak{A}_{M,M'}$ onto $\mathfrak{A}^{\sim}_{M,M'}$ that exchanges the $\varphi(p(x))$ and $\varphi(q(x'))$ with the $\varphi(p^{\sim}(x))$ and $\varphi(q^{\sim}(x'))$ for all bounded Baire functions φ, and x and x' in $\mathfrak{M}$ and $\mathfrak{M}'$, respectively, inasmuch as a ring $\mathfrak{B}^{\sim}_{M,M'}$ analogous to $\mathfrak{B}^{\sim}_{M,M'}$ would exist, and these two rings, by the uniqueness in the finite-dimensional case, would be algebraically isomorphic in the appropriate manner. Moreover, $\theta_{M,M'}$ is the unique isomorphism with the stated property, for otherwise there would exist a non-trivial automorphism of $\mathfrak{A}_{M,M'}$ leaving fixed the $\varphi(p(x))$ and $\varphi(q(x'))$ for x in $\mathfrak{M}$ and x' in $\mathfrak{M}'$. By virtue of the isomorphism of $\mathfrak{A}_{M,M'}$ there would consequently exist a non-trivial automorphism of $\mathfrak{B}_{M,M'}$ leaving fixed the $\varphi(p_0(x))$ and $\varphi(q_0(x'))$ for x in $\mathfrak{M}$ and x' in $\mathfrak{M}'$. But the irreducibility of the canonical system $(p_0(.),\ q_0(.))$ over Σ_0 implies that $\mathfrak{B}_{M,M'}$ consists of all bounded linear transformations on the representation space of the system. As is well known, every automorphism of this algebra is inner, which implies that an automorphism leaving fixed a set of generators for this ring of operators must be the identity.

Now, if $\mathfrak{N}$ and $\mathfrak{N}'$ are mutually separating subspaces of $\mathfrak{M}$ and $\mathfrak{M}'$, respectively, the restriction of $\theta_{M,M'}$ to $\mathfrak{A}_{N,N'}$ has precisely the properties that characterize $\theta_{N,N'}$, so that $\theta_{M,M'}$ must extend $\theta_{N,N'}$. Therefore there exists an automorphism θ_0 of the algebra $\mathfrak{A}_0$ consisting of the set-theoretic union of the $\mathfrak{A}_{M,M'}$ as $(\mathfrak{M}, \mathfrak{M}')$ varies over the collection of all pairs of finite-dimensional mutually separating subspaces of $\mathfrak{H}$ and $\mathfrak{H}'$, respectively, onto the corresponding subalgebra $\mathfrak{A}_0^{\sim}$ of $\mathfrak{A}^{\sim}$ uniquely determined by the property that $\varphi(p(x))$ and $\varphi(q(x'))$ go into $\varphi(p^{\sim}(x))$ and $\varphi(q^{\sim}(x'))$, respectively, for all x in $\mathfrak{H}$, x' in $\mathfrak{H}'$, and bounded Baire functions φ. In this connection it is relevant to observe that by elementary algebra the foregoing collection forms a directed system under the ordering: $(\mathfrak{M}, \mathfrak{M}') \subset (\mathfrak{N}, \mathfrak{N}')$ in case $\mathfrak{M} \subset \mathfrak{N}$ and $\mathfrak{M}' \subset \mathfrak{N}'$. Now an algebraic isomorphism of one C^*-algebra with another preserves the norm (or operator 'bound'), so that all the $\theta_{M,M'}$ are isometries. Hence so also is θ_0, and it follows by continuity that θ_0 can be uniquely extended to an algebraic isomorphism θ from the closure of $\mathfrak{A}_0$ onto the closure of $\mathfrak{A}_0^{\sim}$, that exchanges the canonical operators in the designated fashion.

Remark 1.1. Theorem 1 shows only the algebraic uniqueness of canonical systems. A system first defined by Fock in a formal manner and given a rigorous analytical interpretation and examination by Cook(1) was shown in (5) to satisfy the Weyl relations, thereby establishing the existence of a canonical system in the present sense. This system has been utilized in heuristic and implicit fashion in much of the literature on field theory. It seems possibly appropriate for the mathematical representation of the partially nebulous idea of a field of 'bare' particles. It is also in extensive although often somewhat unconscious use for the representation of a field of 'free physical' particles. To avoid the tacit assumption,–which will later appear to be an unnecessary and generally incorrect oversimplification,– that the same mathematical representation is appropriate for both the zero-interaction and the free physical-particle canonical operators (which involve the self-interactions of the particles), we shall call the mathematically and physically distinguished representation described the zero-interaction, rather than the more common 'free-field', representation.

Although this representation is irreducible and the representation algebra $\mathfrak{A}^{\sim}$ contains all bounded functions of any finite set of canonical operators, it does not consist of all bounded linear transformations on the representation space. This can be seen from the result(5) that, if $(p(\cdot), q(\cdot))$ denotes the bare-particle system, the systems $(p_\lambda(\cdot), q_\lambda(\cdot))$ defined by the equation

$p_\lambda(.) = \lambda p(.)$, $q_\lambda(.) = \lambda^{-1} q(.)$, are mutually unitarily inequivalent ($0 < \lambda < \infty$). For, by Theorem 1, there must exist an automorphism of $\mathfrak{A}^\sim$ taking the system $(p(.), q(.))$ into the system $(p_\lambda(.), q_\lambda(.))$ for any λ. If $\mathfrak{A}^\sim$ consisted of all bounded linear transformations on the representation space, then every automorphism of it would consist of transformations by a fixed unitary operator; but, by the cited result, no such transformation can actually take the system for $\lambda = 1$ into the system for a different value of λ.

A specific operator in the zero-interaction representation that does not represent an observable is the well-known one called the 'total number of particles', where an unbounded self-adjoint operator on a representation space is said to represent an observable in case every continuous function vanishing outside an interval on the real axis gives, on application to the operator, an element of the representation algebra. (This is in keeping with elementary physical notions; cf. in particular Section 3, below). In purely mathematical terms we may state: *For a standard infinite-dimensional single-particle structure, if N is the self-adjoint operator representing the total number of particles in the zero-interaction system* (cf. below and 8)), *and φ is a bounded Baire function on the reals that is not constant on the non-negative integers, then $\varphi(N)$ is not a field observable (i.e. not in A).*

Consider first the case when $\varphi_1(0) \neq \varphi(1)$. Let $x_1, x_2, \ldots$ be a sequence of orthonormal vectors in $\mathfrak{H}$; then there is no difficulty in verifying that, for any field observable R (element of $\mathfrak{A}$), $\lim_n (Rx_n', x_n') = (Ru, u)$, where x_n' is the vector in the bare-particle respresentation space obtained from x_n by injecting $\mathfrak{H}$ in a canonical fashion into the space of covariant symmetric square-integrable tensors over the complex extension of $\mathfrak{H}$, while u is the unit vector (unique within multiplication by a scalar) in the domain of N that is annihilated by N. On the other hand, it is easily seen that $(\varphi(N) x', x') = \varphi(1)$ for every bounded Baire function φ and vector x in $\mathfrak{H}$ (the prime having the same significance as before), while $(\varphi(N) u, u) = 0$. Now more generally, if $\varphi(k) \neq \varphi(k+1)$, then the same argument applies, with u replaced by the symmetric tensor product of $x_1, x_2, \ldots x_k$, and x_n replaced by the symmetric tensor product of u with the x' ($i \leqslant n$).

Remark 1.2. The preceding work shows that the notion of a function of a finite number of canonical variables is independent of the representation of the canonical system, in keeping with its anticipated observable character.

Because of the non-commutativity of the canonical operators, some delicacy is necessary in the formulation of the relevant notion of functions. To clarify this matter we may make the definition: *A function of a collection of closed densely defined operators* on a Hilbert space is a closed densely defined operator that commutes with all unitary operators that commute with every operator in the collection and their adjoints.

In particular, a function of a single normal operator in the foregoing sense can be shown to be precisely a Baire function of the operator in the usual sense when $\mathfrak{H}$ is countable-dimensional, and in a suitably extended sense for inseparable $\mathfrak{H}$ (cf.(6)). Now in the case of the Schrödinger operators $p_1^{(0)}, p_2^{(0)}, \ldots, p_r^{(0)}$ and $q_1^{(0)}, q_2^{(0)}, \ldots, q_r^{(0)}$, on the space $\mathfrak{H}_0$ of square-integrable functions of r real variables, every bounded linear operator on $\mathfrak{H}_0$ is a function of the p's and q's in the foregoing sense, and may be symbolized by $f(p^{(0)}(.), q^{(0)}(.))$. The proof of Theorem 1 shows that *for any other canonical system* $(p(.), q(.))$ over the same single-particle r-dimensional space $\mathfrak{H}_0$, *there exists a unique corresponding function* $f(p(.), q(.))$, the image under the isomorphism given by Theorem 1 of the representation algebra of observables of the first system into that of the second of the original function. This result could be extended to unbounded functions, as well as to the specific functions of the canonical operators defined by Fourier integrals, but these developments are not needed in the present paper.

Remark 1.3. In the treatment of time reversal and other reversal operations, an extension of Theorem 1 to the case of conjugate-linear ring isomorphisms is needed. It may be stated as

COROLLARY 1.1. *For any two canonical systems over the single-particle spaces* $(\mathfrak{H}, \mathfrak{H}', B)$ and $(\mathfrak{H}, \mathfrak{H}', -B)$, *respectively, there exists a unique conjugate-linear ring-isomorphism between the corresponding representation algebras of field observables that exchanges the bounded Baire functions of the canonical* $p(x)$ *and* $q(x')$ *for all* x *in* $\mathfrak{H}$ *and* x' *in* $\mathfrak{H}'$.

Consider first the situation in a finite number of dimensions. As before, a basis may be chosen so that $B(x, y)$ has the form $\Sigma_k x_k y_k$, and the uniqueness theorem in the finite dimensional case reduces the question to that of showing the existence of an appropriate isomorphism for the algebra of the Schrödinger representation. It is easily seen that ordinary complex conjugation in the representation space effects (via the corresponding similarity transformation) the required isomorphism. This isomorphism is unique because the product of any two such conjugate-linear ring isomorphisms is a full algebraic isomorphism leaving fixed the $p(x)$ and $q(x')$, and so the identity. Now in the case of an infinite number of dimensions, the proof given for Theorem 1 applies with obvious changes to the present situation, making use of the foregoing finite-dimensional result.

2. Transformation Properties of the Field Observables

It is axiomatic that a suitable displacement of the single-particle structure should give rise to a corresponding displacement of the field. For example, if L is any Lorentz transformation, it is generally postulated that there is an associated unitary operator $U(L)$ on the state vector space of the field, and that these operators give (within scalar factors at least) a representation of the Lorentz group. This means essentially that any change of frame in ordinary physical space gives a corresponding transformation on the field states. The present section is devoted to the mathematical formulation of this correspondence, i. e., the field kinematics, and to a generalization of it which permits the treatment of field statistics along parallel lines.

We are concerned here with those transformations on the direct sum $\mathfrak{H} \oplus \mathfrak{H}'$ of the real linear space associated with a single-particle structure $(\mathfrak{H}, \mathfrak{H}', B)$, that leave invariant within sign the skew form $[u, v] = B(x, y') - B(y, x')$, where $u = x \oplus x'$ and $v = y \oplus y'$. A transformation leaving the form strictly invariant will be called *symplectic*, while one that reverses its sign will be called *anti-symplectic*.

Theorem 2 establishes, in physical terminology, that any symplectic transformation group (unitary or not) gives a corresponding group of transformations of the associated Bose-Einstein observables. On the other hand, it should be noted that the state vectors, in a particular representation of the field observables, need not be correspondingly transformable. In other terms, if L is any single-particle transformation, then there will exist in a purely formal way a symbolic transformation $U(L)$ on the state vectors, special cases of this correspondence being treated in the field theory literature; but in general, $U(L)$ will not exist in a rigorous analytical sense; and it is here shown that, if T is a function of a finite number of canonical operators (or a uniform limit of such), then nevertheless $U(L)TU(L)^{-1}$ can be given satisfactory mathematical meaning. This gives then a rigorous and covariant scheme for 'quantizing' any given single-particle species in accordance with Bose-Einstein statistics, which uses only the transformation properties of the single particle, and is sufficiently general to be applicable to cases where there exists no invariant positive definite inner product for single-particle wave functions. There is no need for the single-particle space $\mathfrak{H} \oplus \mathfrak{H}'$ to be irreducible under the action of the 'covariance' group, in fact it may decompose continuously, making it possible to quantize simultaneously a continuum of distinct single-particle types.

In particular, whether or not the 'free-field' Hamiltonian H exists as a bona fide operator, the motion $X \rightarrow e^{itH} X e^{-itH}$ always exists; the question of the existence of H as an operator has meaning only within a particular representation of the field observables, and can be dealt with by techniques given in(4). (Conceivably one could ask, independently of the representation, for an H that 'represents an observable' in the sense defined in the last section, but this requirement is so strong that all non-trivial single-particle types are apparently eliminated thereby). The zero-interaction representation has the distinguished feature that any unitary single-particle displacement can be represented by a unitary transformation on the representation space. From this it can be inferred that, if the single-particle Hamiltonian is diagonalizable, then there exists a representation for the field observables in which the corresponding field Hamiltonian has rigorous existence as a self-adjoint operator.

THEOREM 2. *Let* $\Sigma = (\mathfrak{H}, \mathfrak{H}', B)$ *be a single-particle structure. For any symplectic (resp. anti-symplectic) transformation* T *on the direct sum* $\mathfrak{H} \oplus \mathfrak{H}'$, *there is a unique automorphism (resp. conjugate-linear automorphism)* $\theta(T)$ *of the algebra of field observables over* Σ *that takes* $P(z)$ *into* $P(Tz)$ *for all* z *in* $\mathfrak{H} \oplus \mathfrak{H}'$, *where* $P(z)$ *is the self-adjoint generator of the one-parameter unitary group defined by the equation*

$$U(t) = \exp[itp(x)] \exp[itq(x')] \exp[-\tfrac{1}{2} i t^2 B(x,x')] \quad (z = x \oplus x'; -\infty < t < \infty).$$

There is no difficulty in showing that $U(\,.\,)$ is strongly continuous, and in deriving from the Weyl relations that $U(t+t') = U(t)\,U(t')$ for arbitrary real t and t', so that $P(z)$ is well-defined. As before, the terminology that $P(z)$ is taken into $P(Tz)$ by an automorphism θ is used to mean that $\theta\,[\varphi(P(z)] = \varphi[P(Tz)]$ for all bounded Baire functions φ and for all canonical systems of operators. It is clear from the definition of $P(z)$ and the spectral theorem (or alternatively, from the irreducibility of the Schrödinger canonical system) that the $\varphi(P(z))$ are actually in the representation algebra $\mathfrak{A}^{\sim}$ of field observables (in every representation).

Next, note the formula

$$\exp[iP(z)]\exp[iP(z')] = \exp[\tfrac{1}{2}i(f'(x)-f(x'))]\exp[iP(z+z')]$$

for arbitrary $z = x \oplus f$ and $z' = x' \oplus f'$ in $\mathfrak{H} \oplus \mathfrak{H}'$, which follows directly from the definition of the $P(z)$ together with the Weyl relations. Conversely, from this formula the original Weyl relations follow on substituting the relevant values for z and z', since $P(.)$ extends both $p(.)$ and $q(.)$. Thus there is a one-to-one correspondence between canonical systems as originally defined and maps $P(.)$ from $\mathfrak{H} \oplus \mathfrak{H}'$ to the self-adjoint operators on a Hilbert space that satisfy the condition given by the preceding formula. Now if $P(.)$ is such a map, and if T is any symplectic transformation on $\mathfrak{H} \oplus \mathfrak{H}'$, it is immediate that the map $P'(.)$, where $P'(z) = P(Tz)$ is of the same type, and so defines a canonical system. The existence and uniqueness of the stated automorphism follow now from Theorem 1. The case of an anti-symplectic transformation follows similarly from Corollary 1.1.

It may be noted that it follows directly from the preceding formula that $P(z) + P(z') \subset P(z+z')$, but the linearity properties of $P(.)$ will not be used in this paper.

Remark 2.1. In the special case of a single-particle structure such as that described in Example 2 of Section 1, creation and annihilation operators such as are often used conventionally may be introduced. While they are not at all essential for foundational purposes, they are helpful in computational questions, their primary advantage being their invariance under complex scalars (that of the canonical variables being restricted to real scalars).

COROLLARY 2.1. *Let Σ be a standard single-particle structure and let $P(.)$ be the map defined in Theorem 2. Then the operator $P(z) - iP(iz)$ has a closure $C(z)$ for all z in $\mathfrak{H} \oplus \mathfrak{H}'$ and $C(\lambda z) = \lambda C(z)$ for all non-vanishing complex numbers λ.*

The formula established in the proof of Theorem 2 shows that the one-parameter groups generated by $P(z)$ and $P(iz)$ satisfy the Weyl relations (unless $z = 0$, in which case the conclusion of the Corollary is trivial). It follows by an argument used in the proof of Theorem 1 that the representation space can be represented as a direct product of two Hilbert spaces in such a manner that $P(z)$ and $P(iz)$ are represented as the direct products of canonical operators over a one-dimensional space with identity operators, on a Hilbert space of possibly infinite dimension. From this it is readily deduced that it suffices, in connection with the existence of the closure, to establish the existence of a closure for $P_1 + ia\, Q_1$, where (P_1, Q_1) is a canonical pair in the Schrödinger representation, and a is real; and this result is well known. To show the homogeneity of $C(.)$ under complex scalars it suffices, because of the obvious homogeneity of $P(.)$ under real non-vanishing scalars, to treat the case when $\lambda = i$, and the result then is immediate.

Other familiar elementary facts about the creation and annihilation operators can similarly be deduced by reduction to the one-dimensional case.

3. The Representation Structure Determined by a State of the Field

The field statistics arise only when additional structure, in the form of a distinguished state of the field,—representing in physical terms the underlying vacuum state, without reference to which the occupation numbers are not fully defined,—is given. The same is true of the field energy as a well-defined operator, rather than as a generator of a transformation on the dynamical variables. The occupation numbers could equally well be defined as such generators, although they do not play this role in as physically natural a way as the energy and momenta. Finally, 'clothing' of the canonical variables arises from the imposition of a definite state.

To deal with these matters, observe that any state E of the algebra $\mathfrak{A}$ of field observables over $(\mathfrak{H}, \mathfrak{H}', B)$ induces a topology on the group of non-singular symplectic or anti-symplectic linear transformations on the single-particle space $\mathfrak{H} \oplus \mathfrak{H}'$, defined as the weakest one for any element A of $E\,(A^{\theta(T)})$ is a continuous function of the transformation T, where $\theta(T)$ is as in Th. 2, and we use, as in the following, exponential notation for automorphisms. An *E-regular transformation* on $\mathfrak{H} \oplus \mathfrak{H}'$ is defined as a non-singular symplectic or anti-symplectic transformation T such that

$$E\,[(A^*A)^{\theta(T)}] \leq c(T)\, E\,[A^*A],$$

where $c(T)$ is a number that is independent of A. A *regular state* E on $\mathfrak{A}$ is one such that $E(Ae^{iP(z)}B)$ is a continuous function of z, relative to any finite-dimensional subspace of $\mathfrak{H} \oplus \mathfrak{H}'$ (in the conventional topology in this subspace, – i. e. the unique one in which it is a real linear topological space), for all pairs of elements A and B of $\mathfrak{A}$. It may be noted that, in case the representation space associated with E is separable, the foregoing functions are automatically continuous if they are Baire functions, as follows from the proof of Theorem 3 together with the fact due to von Neumann that a measurable one-parameter group of unitary transformations in a separable Hilbert space is automatically continuous.

THEOREM 3. *For any state E of the algebra $\mathfrak{A}$ of field observables over a single-particle structure $\Sigma = (\mathfrak{H}, \mathfrak{H}', B)$ there is a corresponding representation structure $(\mathfrak{K}, \varphi, \lambda, \Gamma)$, unique within unitary transformation of the complex Hilbert space $\mathfrak{K}$, such that:* 1) *φ is a homomorphism of $\mathfrak{A}$ into the algebra of all bounded linear operators on $\mathfrak{K}$;* 2) *λ is a continuous linear map of $\mathfrak{A}$ into a dense subspace of $\mathfrak{K}$;* 3)

$$[(\varphi(A)\lambda(B), \lambda(C)) = E(C^*AB)]$$

for arbitrary A, B, and C in $\mathfrak{A}$; 4) *Γ is a representation of the group $\mathfrak{F}$ of all E-regular transformations on $\mathfrak{H} \oplus \mathfrak{H}'$ by continuous linear or conjugate-linear transformations on $\mathfrak{K}$, such that $\Gamma(T)\lambda(A) = \lambda(A^{\theta(T)})$ for all A in $\mathfrak{A}$ and T in $\mathfrak{F}$.*

In case E is regular, there exists also a concrete canonical system $(p^{\sim}(.), q^{\sim}(.))$ over Σ with representation space $\mathfrak{K}$, uniquely determined by the condition that, for every bounded Baire function f, the image under φ of the (abstract) field observables $f(p(x))$ and $f(q(x'))$ is $f(p^{\sim}(x))$ and $f(q^{\sim}(x'))$, for all x and x' in $\mathfrak{H}$ and $\mathfrak{H}'$, respectively. For any E-regular transformation T,

$$\Gamma(T)P^{\sim}(z)\,\Gamma(T)^{-1} = P^{\sim}(Tz),$$

where $P^{\sim}(.)$ is defined on $\mathfrak{H} \oplus \mathfrak{H}'$ as in Th. 2. In case K is separable, $\Gamma(.)$ has a continuous restriction to any Lie subgroup.

It is well known that with any state of a C^*-algebra is associated the representation structure defined by $(\mathfrak{K}, \varphi, \lambda)$, and that this structure is unique within unitary equivalence (cf.$^{(9)}$). It may be noted for future use that, automatically, $\varphi(A)\lambda(B) = \lambda(AB)$. To obtain the representation Γ, a representation Γ_0 of $\mathfrak{F}$ on the image $\mathfrak{K}_0$ of $\mathfrak{A}$ under λ may be defined by the equation $\Gamma_0(T)\lambda(A) = \lambda(A^{\theta(T)})$ for all A in $\mathfrak{A}$ and T in $\mathfrak{F}$; that $\Gamma_0(T)$ is thereby well-defined follows directly from the inequality that asserts the E-regularity of T. This regularity shows further that $\Gamma_0(T)$ is a bounded linear transformation on the dense subspace $\mathfrak{K}_0$ of $\mathfrak{K}$, and so may be uniquely extended to a continuous linear transformation $\Gamma(T)$ on all of $\mathfrak{K}$. There is no difficulty in verifying that $\Gamma_0(.)$ is a representation, and in concluding from this that $\Gamma(.)$ is also a representation.

Now let $A(z)$ denote the element of $\mathfrak{A}$, $e^{iP(z)}$, and put $\varphi(A(z))=A^\sim(z)$. It is clear from the fact that φ is a homomorphism and that $A(z)$ satisfies the equation derived in the proof of Th. 2 that

$$A^\sim(z)\,A^\sim(z')=\exp\,[(i/2)\,[z,z']]\,A\,(z+z').$$

It is readily deduced that the $A^\sim(z)$ are unitary. The regularity condition on E means precisely that the inner products $(A^\sim(z)\,f,g)$ are continuous functions of z relative to any finite-dimensional subspace of $\mathfrak{H}\oplus\mathfrak{H}'$, for arbitrary fixed f and g in the dense subset $\mathfrak{K}_0$ of $\mathfrak{K}$, which implies, making use of the unitary character of the $A^\sim(z)$, that the same is true for all f and g in $\mathfrak{K}$. In particular, $(A^\sim(tz)\,f,\,g)$ is for arbitrary fixed f and g in $\mathfrak{K}$ and fixed z in $\mathfrak{H}\oplus\mathfrak{H}'$ a continuous function of t. Thus $[A^\sim(tz);\ -\infty<t<\infty]$ is a continuous one-parameter group of unitary operators. It follows that the group has a self-adjoint generator, which will be designated $P^\sim(z)$. It is immediate that $P^\sim(.)$ satisfies the equation derived in the proof of Th. 2, and so determines a concrete canonical system over Σ with representation space $\mathfrak{K}$, and having the stated property.

Now it is not difficult to show that

$$\Gamma(T)\,\varphi(X)\,\Gamma(T)^{-1}=\varphi(X^{\theta(T)}),$$

making use of 3) and 4). In particular, if $X=f(P(z))$ for some z in $\mathfrak{H}\oplus\mathfrak{H}'$, then it follows that

$$f(P^\sim(Tz))=\Gamma(T)\,f(P^\sim(z))\,\Gamma(T)^{-1}.$$

To extend this to the case when f is the unbounded function $f(t)=t$, it suffices to show that W is a bounded linear transformation in a Hilbert space having an inverse of the same type, and if $Wf(A)\,W^{-1}=f(B)$ for two self-adjoint transformations A and B and arbitrary bounded Baire functions f, then $WAW^{-1}=B$. This is equivalent to showing that $WA=BW$. Now B and BW are closed transformations, and taking f to be the characteristic function of the interval $(-n,\,n)$, and letting $n\to\infty$, it is easy to conclude that $WA \subset BW$. By symmetry, $W^{-1}B \subset AW^{-1}$, and transforming by W gives the reverse inclusion, thereby completing the proof of the stated transformation properties.

In dealing with the last assertion of the theorem, "Lie subgroup" may be taken in the rather general sense of a subgroup in the algebraic sense, bearing a distinguished Lie group structure, together with a continuous algebraic isomorphism of it into the group of E-regular transformations. To prove the assertion, note first that for any vector u in $\mathfrak{K}$ of the form $\lambda(A)$, for some A in $\mathfrak{A}$, $|\Gamma(T)u|$ is a continuous function of the E-regular transformation T, since its square is $E[(A^*A)^{\theta(T)}]$, which is continuous by definition of the topology on $\mathfrak{F}$. By the density of $\lambda(\mathfrak{A})$ in $\mathfrak{K}$, together with the separability of $\mathfrak{K}$, $|\Gamma(T)|$ is the least upper bound of a sequence of these continuous functions, and so is a Baire function. A result due to Hille and Phillips (see the proof of Theorem 9.3.1 in [2A]) shows that the restriction of $\Gamma(.)$ to any continuous one-parameter subgroup is continuous. Using canonical coordinates in a neighbourhood of the identity in the Lie group, the continuity for a Lie group follows from that for the case of a one-parameter group.

Example 3.1. Let Σ be the single-particle structure described in Example 1.2. It is easily seen that every unitary transformation on M is symplectic. Therefore, by Theorem 2, there exists for any unitary transformation U on $\mathfrak{M}$ a (unique) automorphism of the algebra of field observables over $\mathfrak{M}$ taking $P(z)$ into $P(Uz)$, for arbitrary z in $\mathfrak{M}$. The *zero-interaction vacuum* is given by

COROLLARY 3.1. *There exists a unique regular state of the algebra of field observables over Σ that is invariant under the field action of every unitary transformation on the single-particle space $\mathfrak{M}$.*

The existence of at least one such state is clear from the form of the Fock-Cook representation, or alternatively, from the theory of the normal distribution in Hilbert space (cf.$^{(5)}$). To prove its uniqueness, let E denote any other such state. Applying Theorem 3 and the von Neumann structure theorem for canonical systems over a finite-dimensional space, there exists for any finite-dimensional subspace $\mathfrak{N}$ of $\mathfrak{M}$, a non-negative operator D of absolutely convergent trace, on the representation space $\mathfrak{K}$ of a Schrödinger representation F of the algebra $\mathfrak{A}'$ of field observables over $\mathfrak{N}$, such that

$$E(A) = tr(F(A)D),\ A \text{ in } \mathfrak{A}'.$$

The invariance of E and the known decomposition of $\mathfrak{K}$ under the induced action of the unitary operators on $\mathfrak{N}$ (cf. loc. cit.) imply that D has the form

$$D = \Sigma_{k=0}^{\infty} \, a_k(n) \, P_k(\mathfrak{N}),$$

where $P_k(N)$ is the projection of $\mathfrak{A}$ onto the k-particle subspace, and the $a_k(n)$ are non-negative constants which by unitary invariance depend only on the dimension n of $\mathfrak{N}$. In the case of the standard state first described, all of the $a_k(n)$ vanish except when $k = 0$, so that by forming an appropriate linear combination it may be assumed that, for the given state E, $a_0(1) = 0$. Now since E is determined by its values on the $\mathfrak{A}'$ for large $\mathfrak{N}$, $a_k(n)$ must be non-vanishing for some $k > 0$ and $n > 1$. But this gives rise to a contradiction to the vanishing of $a_0(0)$ in the following way.

The $a_k(n)$ determine the $a_k(n-1)$ in an explicit fashion, since if $\mathfrak{N}_0$ is an $(n-1)$-dimensional subspace of $\mathfrak{N}$, then the field observables over $\mathfrak{N}_0$ form a subalgebra of those over $\mathfrak{N}$; it is clear in fact that the $a_k(n-1)$ may be expressed as positive linear combinations of the $a_k(n)$. By direct computation it is found that, if for some fixed n, $a_k(n) = \delta_{kk'}$, then $a_0(n-1) \neq 0$. Hence $a_0(n-1) \neq 0$ whenever $a_k(n) \neq 0$ for some k, and in particular $a_0(1)$ cannot vanish.

4. Covariant Single-Particle Structures

The previous definition of single-particle structure covers phenomenological aspects, but not the kinematical ones, which are naturally essential in treating field kinematics and covariant dynamics, as well as the origin of the state labels used in statistics. Therefore, before treating the clothing of field statistics and kinematics, it is necessary to be explicit concerning the single-particle kinematics and statistics. It is appropriate to define a single-particle structure with distinguished transformation properties, or for short a *covariant particle* (genus) as a single-particle structure $\Sigma = (\mathfrak{H}, \mathfrak{H}', B)$, together with a given *symmetry group* G, and a linear representation of G by symplectic or anti-symplectic transformations on $\mathfrak{H} \oplus \mathfrak{H}'$. On this basis, Th. 2 gives directly the kinematics of the Bose-Einstein field *observables* for a covariant particle; the kinematics of the *states*, which is well-defined only relative to a distinguished vacuum state, will be treated in the next section.

The statistics are somewhat more involved. In an elementary-particle field theory, a distinguished maximal commuting set of diagonalizable single-particle operators play an essential part as state labels for single particles. In a covariant theory these operators are of group-theoretic origin. This may be formalized by defining a 'quantum number algebra' for a covariant particle Σ as a maximal commutative algebra $\mathfrak{C}$ of simultaneously diagonalizable linear transformations on $\mathfrak{H} \oplus \mathfrak{H}'$, contained in the enveloping algebra $\mathfrak{R}$ of the representation U. (For present purposes the topology, if any, in which algebras are closed is irrelevant; for a standard single-particle structure, the weak operator topology may be used, but all that is essential is that the weak closure of $\mathfrak{C}$ be maximal Abelian in that of $\mathfrak{R}$). In the case of the conventional scalar particle of mass m, e.g., Example 2 applies, with $\mathfrak{M}$ taken as the usual space of normalizable wave functions, J as complex conjugation in momentum space; and then $\mathfrak{R}$ consists of all bounded linear and conjugate-linear operators on $\mathfrak{M}$ (if G is the full improper inhomogeneous Lorentz group; if G is the orthochronous group, then the conjugate-linear operations do not arise), while a suitable $\mathfrak{C}$ consists of all multiplications by bounded measureable functions of the momentum-energy (for either G). This choice of $\mathfrak{C}$ corresponds to the conventional usage of momentum-energy as quantum numbers for scalar particles, a particle of definite momentum-energy corresponding to a minimal projection in $\mathfrak{C}$, the non-existence of this in a rigorous mathematical sense (see below, however) corresponding to the fact that physical particles consist of wave packets, and do not have sharp energy-momentum.

It is important to note that all operational aspects of the particle are determined by the algebra $\mathfrak{R}$ and its commutative subalgebra $\mathfrak{C}$, as abstract algebras, independently of their representation by operators in linear spaces, together with the mapping $U(.)$ of G into $\mathfrak{R}$. In conventional theory of the standard relativistic particles, there is available, – and naturally in use, as it maximizes computational facility, – a concrete representation in which $U(.)$ is an irreducible unitary representation in a complex Hilbert space; but such a representation is not always possible, and in any event the final physical results may be obtained without its use. For foundational purposes, a better formulation of a manifold of particles than as a linear subspace of a vector space is as a projection in $\mathfrak{R}$. The particles that the theory contemplates as really observed correspond to the minimal projections in the subring $\mathfrak{C}$, a particle packet corresponding to a non-minimal projection. While minimal projections in the algebraic sense do not always exist (e.g., in standard relativistic theory they do not), effective minimal projections can be introduced mathematically by using the fact that an algebra such as $\mathfrak{C}$ is isomorphic to the bounded measurable functions on a measure space, the point of which play the role of representatives for particles with sharply defined quantum numbers. On the other hand, this particle-phase space is not needed operationally or logically, but only for clarification and interpretation of the concepts of the theory. The commutativity of the projections in $\mathfrak{C}$ implies that the occupation numbers for them will commute, so the corresponding particles may be simultaneously observed.

To give some relevant examples, as well as for correlation with standard relativistic theory and for their intrinsic interest, we now describe some special single-particle structures analogous to those of the conventional theoretical meson and photon. The examples will be based on the action of a Lie group G on a homogeneous space M; the 'relativistic case' refers to that in which G is the improper inhomogeneous Lorentz group, and M is relativistic in space-time.

4.1. Let $\mathfrak{H}$ be the space of real-valued continuous functions f on M that vanish outside compact sets, and let $\mathfrak{H}'$ be the space of real continuous differential forms of maximal dimension on M, and set $B(f, w) = \int_M fw$. Let G act as usual on $\mathfrak{H}$ and $\mathfrak{H}'$. This is a covariant single-particle structure which may be described as the *genus of all scalar particles on* $\mathfrak{M}$ *relative to the covariance group* G; in the relativistic case, it can be identified with the genus of all scalar particles, in the usual sense, of arbitrary mass.

4.2. Suppose M admits an invariant regular measure under G. The actions of G on $\mathfrak{H}$ and $\mathfrak{H}'$ are then equivalent, and a physically equivalent particle structure is obtained by redefining $\mathfrak{H}$ and $\mathfrak{H}'$ as the spaces of real square-integrable functions on M relative to the invariant measure m, and $B(f, g) = \int_M fg$ dm. Since $\mathfrak{H} = \mathfrak{H}'$, it is possible in this case, as in standard relativistic theory, to use only one space.

4.3. The space $\mathfrak{H}$ of the preceding section admitted only real scalars. The action of complex scalars on $\mathfrak{H}$ comes about in the following way. Suppose there exists a transformation W on $L_2(M)$ that preserves B commutes or anti-commutes with all the $U(g)$, and has the property that $W^2 = -\mathrm{I}$. In the relativistic case, there is an essentially unique such W on the subspace of wave functions of real mass, i. e., those whose Fourier transforms vanish outside the duals of the light-cones, namely the Hilbert transform relative to the time variable. A complex structure is introduced into $\mathfrak{H}$ by defining multiplication by i as W. A complex Hilbert space structure arises when there is given, in addition, a transformation J on $\mathfrak{H}$, having distinguished commutation relations with the $U(g)$, (i. e., $JU(g)J^{-1} = U(g')$, where the transformation $g \rightarrow g'$ is multiplicative), and such that $J^2 = 1$, $WJ = -JW$, and $B(Jf, Jg) = B(g, f,)$. In the relativistic case, it is natural to take J as the operation representing time-reversal. It is easily seen that every element z of $\mathfrak{H}$ can be written uniquely in the form $x + iy$, where x and y are elements left fixed by J, and that $\mathfrak{H}$ attains a complex Hilbert space structure when the inner product is defined as

$$[z', z] = B(x, x') + B(y, y') + i(B(x, y') - B(x', y)),$$

relative to which the $U(g)$ are unitary or antiunitary.

4.4. The elementary-particle species of which a given genus is composed are essentially in one-to-one correspondence with the minimal projections in the center of $\mathfrak{R}$. This center may have no rigorously minimal projections, but by means of the direct integral techniques originated by von Neumann, $\mathfrak{R}$ may always be decomposed as a continuous direct sum of factors $\mathfrak{R}_M$ dependent on a parameter m, and into which G has representations U_M. Taking Example 4.3 in the relativistic case, it is not difficult to show that m can be taken as the mass, and that the elementary constituents are identical (operationally) with the conventional scalar relativistic particles of a given (real or pure imaginary) mass. There is an analytical difference, in that the state vectors of Example 3, and (essentially) also these of the elementary constituents when 'function' is suitably generalized, are real (suitably generalized) functions on M, while the conventional formalism employs positive frequency functions on the dual of M ('momentum space'), but these give abstractly identical representations of the Lorentz group, i. e., they differ only in the labels attached to the particular elementary particles; cf. Section 3 of [9A].

4.5. Let G be the group of real projective 3-space, and M the (four-dimensional) manifold of all projective lines, and let G act as usual on M. There is then no invariant measure on M under G, so that the formulation of Example 1 must be used. If one used the apparently simpler and more conventional type of space, that of all complex-valued continuous functions on M, the action of G would be complex-linear, but would not be symplectic in any natural way, so that no field kinematics would result.

4.6. Let W be a finite-dimensional irreducible representation of G on a real linear space $\mathfrak{L}$, and let $W^{\sim}$ denote the contragredient representation in the dual space $\mathfrak{L}^{\sim}$. In the situation of Example 1, the genus of all particles on M of spin type W may be defined as the covariant particle $(\mathfrak{H} \times \mathfrak{L}, \mathfrak{H}' \times \mathfrak{L}^{\sim}, B \times F; G, U \times (W + W^{\sim}))$, where $F(x, f) = f(x)$ for $x \varepsilon \mathfrak{L}$ and $f \varepsilon \mathfrak{L}^{\sim}$. In case there exists a non-singular bilinear form on $\mathfrak{L}$ that is invariant under W, there is a corresponding canonical correspondence of $\mathfrak{L}$ with $\mathfrak{L}^{\sim}$ which combines with Example 4.2 to make possible the use of only one space as in that example. If the form on $\mathfrak{L}$ is symmetric, the single-particle space will admit an invariant non-singular symmetric, but in general indefinite form. This, e.g., is the situation for the relativistic vector particles, W being here the conventional representation of G on four-vectors. Theorem 2 assures the existence of a convergent and effective field kinematics irrespective of whether there exists an invariant positive-definite inner product.

7. Somewhat more generally than Example 4.6, suppose that for a covariant particle in which $\mathfrak{H}'$ is dual to the topological linear space of Hilbert space structure $\mathfrak{H}$ and G acts contragrediently on $\mathfrak{H}'$ to its action on $\mathfrak{H}$, and in which $B(x, f) = f(x)$ for $x \varepsilon \mathfrak{H}$ and $x' \varepsilon \mathfrak{H}'$, that $\mathfrak{H}$ admits a real symmetric continuous invariant non-singular bilinear form B'. In this event, $\mathfrak{H} \oplus \mathfrak{H}'$ admits a distinguished complex structure and hermitian form; a transformation that is unitary relative to these is symplectic; and the transformations on $\mathfrak{H}$ that leave invariant the given form are represented by complex-linear transformations on $\mathfrak{H} \oplus \mathfrak{H}'$. To see this, let θ denote the map $y \rightarrow f$ of $\mathfrak{H}$ onto $\mathfrak{H}'$, where $f(x) = B(x, y)$, it is readily verified that θ is continuous and linear. Now define $i(x+f) = -\theta^{-1} f + \theta x$; then $i^2 = -1$, justifying the notation. If U is a linear transformation on $\mathfrak{H}$ leaving B invariant, and V is the corresponding symplectic transformation

$$x + f \rightarrow Ux + U^{*-1} f$$

on $\mathfrak{H} \oplus \mathfrak{H}'$, it is straightforward to verify that $iV = Vi$, so that V is complex-linear relative to the structure derived from i. Defining for $z = x + iy$ and $z' = x' + iy'$ a form

$$[z, z'] = B(x, x') + B(y, y) + i\left\{ B(x, y') - B(x', y) \right\},$$

there is no difficulty in verifying that this is a hermitian form and that the symplectic transformations are precisely those preserving its imaginary part. It may also be noted that the V's commute with the canonical conjugation $x + iy \rightarrow x - iy$, which may be described in physical terms as a type of particle-antiparticle conjugation.

8. In case $\Sigma = (\mathfrak{H}, \mathfrak{H}', B)$ is as in Example 1.2, and in case the action $U(.)$ of the covariance group G is given by unitary or anti-unitary transformations on $\mathfrak{M} = \mathfrak{H} \oplus \mathfrak{H}'$, the particle genus may be called *standard*; the conventional relativistic particles are of this type.

5. Clothed Kinematics and Statistics

It will be convenient to refer to the structure obtained from the algebra of field observables over a particle genus by adding to the system a distinguished state, as 'clothed'. In so doing, we do not wish to suggest that the distinguished state must be the 'physical vacuum', which can only be defined when the dynamics is specified, nor, in general, that the clothed structure has any operational physical meaning. The present discussion is purely mathematical. However, in the special case of the physical vacuum, the 'clothing' can be said to represent the effect of the interaction, and consists, so-to-speak, of a 'cloud' of particles around the original 'bare' one created by self-interactions, in a manner that will be made more explicit in this and the following sections.

The clothed canonical variables were defined and treated in Section 2. The effect of the clothing was to make the elements of the abstract algebra into concrete operators, substantially. This section pursues a similar effect on the kinematics and statistics, and deals in particular with the construction of definite operators in Hilbert space that represent the clothed energy-momenta and occupation numbers of the field.

COROLLARY 3.2. *Let $\Sigma = (\mathfrak{H}, \mathfrak{H}', B;\ G, U(.))$ be a covariant particle genus, let E be a state of the algebra of field observables over Σ, and suppose that $U(.)$ is a continuous representation of the Lie group G by E-regular transformations. Then with the notation of Th. 3, and assuming the separability* of $\mathfrak{K}$,

$$g \to \Gamma(U(g))$$

is a continuous linear representation of G on $\mathfrak{K}$; is unitary on the subgroup G_0 of G consisting of elements leaving E invariant, $E(X^{\theta(U(g))}) = E(X)$ for all X in $\mathfrak{A}$; and for any element L of the Lie algebra of G_0, there is a unique self-adjoint operator $L^{\sim}$ on $\mathfrak{K}$, determined by the property that

$$\Gamma(U(\exp(tL))) = e^{itL^{\sim}}.$$

The proof is somewhat similar to that for the existence of clothed canonical variables, and will be omitted.

Remark 5.1. In practice, G_0 will include translation in time, whose generator L is transformed by $U(.)$ (or rather the infinitesimal transformation it induces) into the single-particle energy; and $L^{\sim}$ is then the field energy which is clothed in the sense of being a definite self-adjoint operator arising from the interaction. A variety of elementary and commonly used properties, e. g., the annihilation by $L^{\sim}$ of the vacuum state representative $\lambda(I)$, can be read off immediately from the foregoing results.

To deal with the statistics, it is necessary to use diagonalizable rather than self-adjoint operators, where a *diagonalizable operator* in a complex Hilbert space $\mathfrak{K}$ is an operator T for which there exists a non-singular operator W (both W and W^{-1} being bounded and everywhere defined) such that WTW^{-1} is normal. A collection of such operators is *simultaneously diagonalizable* in case the same W is effective for each of them. If T is diagonalizable and f is a Baire function over the complex numbers, then $f(T)$ is defined as $Wf(T)\,W^{-1}$; it follows readily from the polar decomposition for non-singular operators that this definition is unique, i. e., $f(T)$ is independent of the transformation W used to effect the diagonalization. The spectrum of T is defined as that of WTW^{-1}, and is similarly unique.

Now the occupation number of a single-particle state is the special case of the notion of occupation number of a linear manifold in which the manifold is the one-dimensional one spanned by the state; and any linear manifold may be correlated with an operator whose range is the manifold, under conditions valid in all interesting concrete cases. As indicated in the preceding section, this operator plays a more fundamental role than does the manifold itself. Therefore it is appropriate to show how suitable occupation numbers may be associated with a given such operator P on the single-particle space. When this space admits a suitable complex structure, e. g., in case the single-particle structure is 'standard', it is appropriate to require that $P^2 = P$, but to cover the more general case in which there is or may not be such a complex structure, it may be assumed that $P^3 = -P$. For reasons indicated in the preceding section, such an operation may be called a *particle manifold,* two such manifolds P_1 and P_2 being *simultaneously observable* in case they commute.

COROLLARY 3.3. *Let P be a particle manifold for the particle genus Σ, and suppose that $F(t) = I + P\sin t + (1-\cos t)\,P^2$ is E-regular and depends continuously on t $(-\infty < t < \infty)$, and that K is separable. The one-parameter* *group* $\Gamma(F(t))$ *then has a densely defined diagonalizable generator* N_P*, whose proper values are integral, and annihilates the vacuum state representative* $\lambda(I)$*. The 'occupation numbers'* N_P *of any finite set of simultaneously observable particle manifolds* P *are simultaneously diagonalizable.*

By definition, the generator of the group $[\Gamma(F(t)); -\infty < t < \infty]$ has a domain consisting of all vectors u in $\mathfrak{K}$ such that $\lim_{t \to 0} (it)^{-1} [\Gamma(F(t)) - I] u$ exists, and transforms u into this limit. Now the mapping $t \to \Gamma(F(t)) = V(t)$, say, is continuous, by virtue of the assumed continuity of $F(.)$, and the continuity of the restriction of $\Gamma(.)$ to any Lie subgroup, when $\mathfrak{K}$ is separable. It is evident that $V(.)$ is a representation of the additive group of the reals by continuous linear transformations on $\mathfrak{K}$. Now $(V 2\pi) = I$, so the map $e^{i\theta} \to V(\theta)$ defines a continuous representation of the group of all complex numbers of absolute value one, in the usual topology, on $\mathfrak{K}$. Since this is a compact group, a well-known result due to von Neumann implies that the latter representation is similar, via a non-singular continuous linear transformation of $\mathfrak{K}$ onto $\mathfrak{K}$, to a unitary representation. The existence of a diagonalizable generator N_P now follows from Stone's theorem concerning one-parameter groups of unitary operators. That N_P has in its domain the vacuum state representative $\lambda(I)$ and annihilates it, is clear from the fact that the $V(t)$ leave invariant $\lambda(I)$.

That the proper values of N_P are integral is clear from the same fact for any generator of a continuous unitary representation of the circle group (which can be read off from Stone's theorem). Now let $P_1, \ldots, P_r$ be a finite set of simultaneously observable single-particle manifolds. The map $(e^{i}\,\theta_1, \ldots, e^{i\theta}r) \to \Pi_k \Gamma(F_k(\theta_k))$, where the subscript k on F indicates the replacement of P by P_k, is a continuous representation of a torus group on $\mathfrak{K}$, and as this group is again compact, the same argument as above shows diagonalizability.

Remark 5.2. There is no difficulty in verifying that, in the case of a standard single-particle structure and the zero-interaction vacuum, the present definition of occupation number gives the same as the conventional definition, according to which the number of particles with wave function x in the field is $C(x)^* C(x)$, where $C(x)$ is the creation operator for an x-particle as defined above. The relevant projection is that on the one-dimensional manifold spanned by x, the P used above being of course the multiple of this projection by i. However, for general states, the conventional definition is physically inappropriate, irrespective of the single-particle definition. This can be seen by comparison with the main physical desiderata for occupation numbers, which are: 1) they should have integral proper values; 2) they should annihilate the vacuum state representative; 3) the total field energy or momentum (etc.) should be (at least formally) representable as the sum of the products of the spectral values of the corresponding single-particle observable with the occupation numbers of the corresponding manifolds; 4) if the vacuum state representative v is in the domain of the clothed creation operator $C^{\sim}(x)$ (here we deal only with the standard single-particle structure case), then the vector $C^{\sim}(x)v$ should represent a state in which exactly one x-particle is present and no y-particle, for any y orthogonal to x.

Condition 1) is satisfied by both definitions. Condition 2) is easily seen to be satisfied by the present definition, but there is no apparent reason why it should be satisfied by the conventional definition, in fact this need not make sense, for in general v need not be in the domain of the $C(x)^*C(x)$. Formally at least, this is the case if and only if $C(x)^*C(x)$ has finite expectation value, and there is no difficulty in establishing that states exist in which $C(x)^*C(x)$ has infinite expectation value in the sense that l.u.b. $[E(T^*T)\colon T \varepsilon \mathfrak{A},\ T^*T \leqslant C(x)^*C(x)] = +\infty$. Condition 3) is easily validated in a formal way for the present definition (this suffices, as the condition is needed only for identification of concepts, and not for any analytical purposes) by taking the case when the single-particle operator H (Hamiltonian, say) is of the form $\Sigma_k \lambda_k P_k$, where the λ_k are real and the P_k as above (thus in the standard case, this H is i times the usual one; this formulation allows the same argument to be applied to both the standard and non-standard cases), then the infinitesimal generator of $[\Gamma(\exp(tH));\ -\infty < t < \infty]$ as a one-parameter group (the corresponding field Hamiltonian) should be $\Sigma_k \lambda_k N_{P_k}$. This is virtually immediate from the fact that $\Gamma(.)$ is a representation. Now if $H = \int \lambda dE_\lambda$ is the spectral resolution of H (the E_λ now being such that $E_\lambda^3 = -E_\lambda$), the integral can be regarded as a generalized sum, and in a formal way it follows that the corresponding field operator is $\int \lambda dN_\lambda$, where N_λ is the number of particles in the manifold E_λ, which is precisely what condition 3) requires. On the other hand, with the conventional definition, no such formal equality holds.

Now consider condition 4), assuming the single-particle structure to be standard. Let P_x denote the projection on the single-particle space whose range is the one-dimensional manifold spanned by x. We proceed quite formally, making no attempt at analytical justification. The vacuum state v is $\lambda(I)$, and is taken by the clothed creation operator $C^{\sim}(x)$ into $\lambda(C(x))$. Now a state vector u in $\mathfrak{K}$ represents a state containing one x-particle provided $\Gamma(e^{itP_x})u = e^{it}u$, and one containing no y-particle in case

$$\Gamma(e^{itP_y})\,u = u.$$

Taking now

$$u = \lambda(C(x)),\ \Gamma(e^{itP_x})\,u = \lambda(C(e^{itP_x}x)) = \lambda(C(e^{it}x)) = e^{it}\lambda(C(x))$$

[by the homogeneity of λ and $C(.)$ under complex scalars] $= e^{it}u$. On the other hand,

$$\Gamma(e^{itP_y})\,u = \lambda(C(e^{itP_y}x)) = \lambda(C(x)) = u.$$

With the conventional definition, no such formal development is possible. On the other hand, there may well be no $x \neq 0$ such that v is in the domain of $P(x)$.

The question arises as to whether an interpretation of the $C(x)^*C(x)$ as particle numbers in some sense is possible. In terms of (physically fictitious, but conceptually graphic) ‘pristine’ particles, by which we mean the particles constituting the field, in their original state of zero interaction, before the physically real interaction is ‘switched on’, such an interpretation can be given. These pristine particles are devoid of self-fields and have a certain resemblance to the ‘bare’ particles introduced in a variety of current theories, but in view of the great analytic complexity and lack of uniformity in these treatments, we shall not attempt a precise comparison between the ‘pristine’ and ‘bare’ particles. The ‘switching on’ of the interaction changes the vacuum state of the field from the zero-interaction vacuum, relative to which the pristine particles proceed independently of each other in accordance with their respective single-particle kinematics, to an equilibrium state for the given interaction, representing the ‘physical vacuum’. In this state, no ‘physical’ particles are present, in the sense that the vacuum representative is annihilated by the occupation numbers as just defined; but a large, possibly infinite, number of pristine particles may be present. The total number of pristine particles will be represented by $\Sigma_k C(e_k)^*C(e_k)$, where the e_k constitute a complete orthonormal set in the single-particle space; this operator will generally have no more than formal existence, i. e., be identically infinite from a physical viewpoint. The total number of physical particles, on the other hand, is the generator of the one-parameter group $\Gamma(e^{itI})$,

$-\infty < t < \infty$ (where I is the identity operator in the single-particle space, assumed standard), which will exist as a finite diagonalizable operator under the stated relatively weak regularity conditions.

Remark 5.3. 'Physical particle' as used here is not the same as the conventional theoretical concept, which is tied to the use of the zero-interaction representation for the incoming and outgoing fields. An 'empirical' physical particle, —a theoretical counterpart to that observed in reality,— may be defined as one whose wave function is in the subspace of $\mathfrak{K}$ in which the total number of particles is unity. There need be no natural way to build up $\mathfrak{K}$ from these empirical particles (if indeed they exist in substantial numbers), and in fact the existence of bound states is a contra-indication for this. The present physical particles may be designated as 'primary' in distinction from the 'empirical' ones, since they evidently constitute the theoretically basic concept. Either type of particle may be defined as 'elementary' in case the transforms of its wave functions under the covariance group span an irreducible subspace (under the group). There is no mathematical reason why the elementary empirical particles should in general transform equivalently to the elementary primary ones which are given independently of the interaction. A heuristic argument suggests that, when the scattering automorphism depends continuously on a coupling constant, the empirical particles should have the same discrete quantum numbers (spin, etc.) as corresponding primary particles (correspondence being in the sense that the empirical particle wave function is in the closure of the image under λ of the subalgebra of bounded functions of the canonical variables for the primary particle), but may well differ in continuous quantum numbers (= the mass, in standard relativistic theory). In principle such mass differences are computable, but it should be noted that there need be no empirical particle corresponding to a given primary particle, as the entire corresponding subspace of $\mathfrak{K}$ may consist of states composed from at least two primary particles, and even when it contains a single-particle state there is no theoretical assurance of uniqueness.

Another point of difference between the representation structure obtained above, and the zero-interaction structure commonly used for the representation of free physical fields, is that,—apart from a heuristic continuity argument,—conceivably, the occupation numbers of a maximal simultaneously observable set of single-particle manifolds do not generate a maximal commuting set of operators in $\mathfrak{K}$. Since $\mathfrak{K}$ is spanned by the transforms of v under the bounded functions of the clothed canonical operators, $\mathfrak{K}$ is spanned by states each of which is built up from a finite number of primary particles. Lack of maximality would mean that distinct states could have identical constitutions in terms of elementary primary particles. This would suggest the existence of a certain type of bound state, i. e., an r-particle state whose transforms under the covariance group span a subspace not transforming according to the direct product of r elementary-particle types. The circumstance cited in the preceding paragraph seems, however, more likely to account for the physical existence of bound states.

It is noteworthy also that, although any *finite* set of occupation numbers of commuting projections is simultaneously diagonalizable, this need not always be the case for all occupation numbers of a maximal simultaneously observable set of single-particle manifolds. The elementary physical interpretation is thereby not materially affected, since virtually any experiment can be interpreted in terms of a large finite set of states, and since, if the physical system under consideration is 'enclosed in a large box', simultaneous diagonalization can be effected under reasonable regularity conditions, despite the infinity of the number of single-particle states, due to the discreteness of the single-particle manifolds which then ensues, together with the compactness of the group of all unitary operators in a maximal Abelian algebra of operators on Hilbert space that is generated by its minimal projections, which renders applicable the argument given above. Nevertheless it is possible that this complication may be significant in relation to convergence questions in a fully covariant theory.

For similar reasons, it is no essential loss of generality, in dealing with a finite set of states, to assume that the clothed particle operators are in the zero-interaction representation; but materially wrong or self-contradictory results may then ensue if it is further assumed that the occupation-number operators may be defined in the conventional way. While this may appear to be a plausible simplifying assumption, its cogent character is indicated by Corollary 3.1, which implies that the only field in which the clothed canonical variables and occupation numbers are unitarily equivalent to those of the zero-interaction theory is the trivial one without interaction. In fact, it asserts even more strongly that the occupation numbers are self-adjoint in the intrinsic Hilbert space metric in $\mathfrak{K}$ (in which the clothed canonical variables are self-adjoint) only if there is no interaction; i. e., roughly speaking, the 'wave' and the 'particle' operators cannot be made simultaneously self-adjoint.

6. Collision Dynamics

In the light of the foregoing and the literature on the relation of abstract C^*-algebras to quantum mechanics, it is clear that the appropriate definition of a dynamical transformation is as an automorphism of the algebra of field observables. This is physically more operational as well as mathematically more natural than the conventional assumption that a dynamical transformation is represented by a unitary operator. In fact, it makes little sense in itself to ask whether a given automorphism is inducible by a unitary transformation, as it may be so induced in certain representations but not in others.

Thus a conventional-type dynamics would be given by the assignment to each ordered pair s, s' of 'space-like' surfaces with s' later than s of an automorphism $a_{s,s'}$, of the algebra of field observables, this automorphism being interpreted as the transformation of a dynamical variable on s into the corresponding variable on s', which interpretation requires the mathematical assumption that $a_{s,s'} \, a_{s',s''} = a_{s,s''}$. Such a dynamics would be (Lorentz-) covariant in case $\theta(g) \, a_{s,s'} \, \theta(g)^{-1} = a_{g(s), g(s')}$ for every transformation g of the Lorentz group, where $\theta(g)$ is the automorphism of the algebra of field observables that corresponds to g in accordance with Theorem 2, while $g(s)$ denotes the space-like surface into which s is carried by g. For a collision dynamics, corresponding to the partial simplification of the foregoing in which only the limit of $a_{s,s'}$, as s and s' tend to the infinite past and future respectively, there is a single automorphism a, and the dynamics is covariant when a commutes with all the $\theta(g)$. In the following, we restrict attention to the analogue of this type of dynamics, which may quite possibly be all that is observable physically, and in any event plays a fundamental theoretical role.

In principle, the specification of a completely determines the collision dynamics. Given any 'incoming' state E of the algebra of field observables, the corresponding 'outgoing' state is E^a, where for any field observable X, $E^a(X) = E(X^a)$, the action of a and other automorphisms being written exponentially when convenient. But to make any connection with what is physically observed, it is evident that the states must be 'labeled' in identifiable terms, and here the essential and material complication arises that, roughly speaking, it is not the absolute state E that is observed, but rather its deviation in a certain sense from the 'physical' vacuum state.

Conventionally, the physical vacuum state and the related notion of physical particle are introduced, through the use of the total field Hamiltonian, in a fashion that leads rapidly to divergences. In addition to the low mathematical viability of this approach, it is relatively unoperational. A simpler and more direct approach involves rather the definition of the vacuum from the 'scattering' automorphism a, a basic desideratum being invariance under a. In addition in a covariant (e. g. relativistic) theory, it should also be invariant under the covariance group (e. g. the Lorentz group), or at least under the associated transformations used to label the single-particle states (e. g., translations in space-time, whose generators give the energy-momentum operators). Physically these requirements may be expected to determine essentially uniquely the physical vacuum for the automorphisms describing real interactions, as otherwise there should be a hitherto unobserved selection rule.

The next result is to the effect that, for any given covariant automorphism, a physical vacuum exists, together with an associated analytical structure adequate for the fundamental physical interpretations. To fix the ideas, this distinguished automorphism will be called the 'scattering' automorphism. A state invariant under this automorphism and under a distinguished subgroup G_0 of the covariance group, which is not a non-trivial convex linear combination of two other such states, is called a 'physical vacuum' relative to G_0 and the automorphism.

THEOREM 4. *For any covariant scattering automorphism of the algebra* $\mathfrak{A}$ *of field observables over a covariant particle genus, and any maximal Abelian subgroup* G_0 *of the covariance group* G*, there exists a physical vacuum state. The corresponding representation space* $\mathfrak{K}$ *is irreducible under the joint action of the clothed field observables, the scattering automorphism, and the clothed unitary representation of* G_0. *In case the single-particle structure is standard, or more generally if there exists a state of* $\mathfrak{A}$ *invariant under all of* G*, then a physical vacuum relative to all of* G *exists.*

The states of $\mathfrak{A}$ form a compact convex subset Δ of the dual, in its weak topology relative to $\mathfrak{A}$. The scattering automorphism a and the Abelian subgroup G_0 act on the dual to $\mathfrak{A}$ continuously and in such a fashion as to leave invariant Δ. A well-known variant of a fixed-point theorem due originally to Birkhoff and Kellogg allows the conclusion to be drawn that the subcollection of states invariant under a and G_0 is non-empty. It is easily seen that this subcollection is again compact and convex, and so by the Krein-

Milman theorem contains an extreme point, which is a physical vacuum state as defined above. The irreducibility of the joint action on $\mathfrak{K}$ of $\varphi(\mathfrak{A})$, G_0 (via $\Gamma(.)$), and the unitary operator S determined uniquely by the condition $S\lambda(X) = \lambda(X^a)$, for all X in $\mathfrak{A}$, follows by a trivial variation of the proof of Th. 5.3 in [7].

Now suppose there exists a state E_0 of $\mathfrak{A}$ that is invariant under the action of all of G,—such as the zero-interaction vacuum in the case of a standard single-particle structure. Varying the foregoing proof by replacing Δ by the subset consisting of the least convex closed subset of Δ containing E_0 and all of its transforms by positive and negative powers of a, one still obtains a closed convex set of states, each of which is invariant under G, and the totality of which is invariant under a. By the same fixed-point theorem, there exist elements of this subset that are invariant under a. The sub-collection of all such elements is again a compact convex set, and so by the Krein-Milman theorem contains an extreme point, which is then a physical-vacuum state relative to all of G and the given scattering automorphism.

Remark 6.1. By this result, the main burden of obtaining a convergent dynamics is shifted onto the problem of setting up the scattering automorphism for the physical system under consideration. The material simplification brought about by the use of an automorphism rather than a unitary operator is that its form and existence are independent of the employment of special representations, while the S-operator itself will be unitary in general only in one particular representation, which it is part of the theoretical problem* to determine. To illustrate this point, consider a purely hypothetical theory in which S is given in a purely formal manner as $\exp[ig\,\Sigma_k\, Q_k^2]$, where the single-particle structure is assumed standard, and $Q_k = q(e_k)$; $e_1, e_2, \ldots$ being a complete orthonormal set in the single-particle space. There is no doubt that $\Sigma_k Q_k^2$ fails to exist as an operator in the zero-interaction representation, nor is there any other apparent canonical system over a single-particle Hilbert space in which this formal expression would appear to define an operator. Nevertheless a corresponding automorphism can be set up fairly briefly, and it follows that S can be represented by a bona fide unitary operator in a certain Hilbert space.

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* As here formulated. In certain other current approaches (e.g. those of HAAG, KÄLLEN and WIGHTMAN, and of LEHMANN et al.) it is essentially part of the postulates of the theory that the S-operator is unitary in the zero-interaction representation. This is a substantial implicit restriction on the interaction, and in fact no example of such a theory with real particle creation has yet been constructed.

Remark 6.2. The situation is particularly simple in the case of the single-particle structure of Example 3, Section 1, which is often used in approximate non-covariant theories. The typical interaction Hamiltonian in these theories is a linear form in the P_n and Q_n whose coefficients are bona fide operators in Hilbert space. In certain cases the coefficients of the P_n vanish (or do so after a suitable transformation), and the transformation $Q_n \to a_n Q_n$, $P_n \to a_n^{-1} P_n$, with $a_n \to 0$ sufficiently rapidly will generally convert a divergent such hamiltonian into a hermitian (densely-defined) operator in a Hilbert space. As the time-ordered exponential of the interaction Hamiltonians (in the interaction representation), the formal S-operator induces a (scattering) automorphism which is a Stieltjes product integral of automorphisms generated by such Hamiltonians, and the crucial point in its existence has always been the finiteness of the generator, which follows as indicated. In particular, when the coefficients are operators in Hilbert space such that each is bounded, a transformation of the indicated type exists.

Remark 6.3. For the validity of Theorem 4 and its physical interpretation, it is not essential that the scattering automorphism a be onto. The only difference is that if a is merely into, the emergent S-operator will be merely isometric, and not necessarily unitary. This corresponds to a type of dissipative process for which there is no indication in elementary-particle physics, but which could conceivably be applicable in thermodynamical situations.

It is not even altogether essential that a be into; it would suffice substantially for it to be given as a homomorphism of the algebra $\mathfrak{A}$ of field observables in a concrete representation, into the bounded operators on the representation space. The physical vacuum state E is then defined as satisfying $E(X) = E(X^a)$ in case the field observable X is such that X^a is in $\mathfrak{A}$, together with invariance under G_0 and ergodicity as before, and its existence follows from an extension of the fixed-point theorem mentioned to mappings from points to convex sets (cf. [1 A]). The mapping in question takes a state E_0 invariant under G_0 into the set of all states E_1 of $\mathfrak{A}$ such that $E_1(X) = E_0(X^a)$ whenever X^a is in $\mathfrak{A}$. As an illustration, consider the purely hypothetical theory with standard single-particle structure in which S is given in a formal way as $\exp[i\Sigma_k b_k Q_k^{2r}]$, where $b_1, b_2, \ldots$ is a bounded sequence of real numbers, and r is a positive integer. This is a quite divergent and generally intractable expression, but it may be shown without particular difficulty that, in the zero-interaction representation, it can be formulated as a homomorphism of $\mathfrak{A}$ into the bounded operators. It then follows that there exists a representation in which a may be represented by an isometric transformation S defined in a certain subspace of $\mathfrak{K}$, in the sense that $\lambda(A^a) = S\lambda(A)$ whenever A and A^a are both in $\mathfrak{A}$. Actually, it is plausible that the image under the homomorphism described is $\mathfrak{A}$ itself, in which case S would be unitary and defined on all of $\mathfrak{K}$, but the verification of this would be technically tedious and is not required for the existence of a physical vacuum in the foregoing sense.

Remark 6.4. We are not in a position to treat the uniqueness and the regularity of the physical vacuum, but both seem very plausible for the case of a theoretical description of real particles, and considerably more far-reaching assumptions are commonly made. One such assumption, which we are unable to substantiate theoretically, is that the clothed canonical variables act irreducibly on $\mathfrak{K}$. The justification is that, in a formal way, S and the clothed kinematics are given as functions of the canonical variables, so that from the irreducibility under the action of all of these, as stated in Theorem 4, it is reasonable to conclude the irreducibility under the canonical variables alone. It may well be true that, whenever a and the action of G_0 on the field observables are limits in some suitable sense of inner automorphisms,—which is a way of formulating the plausible requirement that the theory be obtainable as a limit of cut-off theories,—then this irreducibility follows. However, not enough is known at present concerning the approximation of the scattering automorphism by inner ones either to make this line of attack effective, or to demonstrate its insufficiency.

Remark 6.5. It should be noted that even when the physical vacuum state is not invariant under all of G (this is state in the sense of expectation value; the corresponding state vector in $\mathfrak{K}$ is always invariant under all of G), the physical results of the theory, i. e., the S-matrix elements between finite-particle states labeled by the given maximal Abelian family of quantum numbers, are nevertheless fully invariant. For although a transformation g of G will in general change the physicel vacuum state E into a new state E^g, defined by the equation $E^g(X) = E(X^{\theta(U(g))})$, a similarity transformation on the quantum numbers, by $U(g)$, is required, resulting in a new maximal Abelian Algebra conjugate to the original one; and due to the covariance of the scattering automorphism, the two effects cancel.

Remark 6.6. It may be noted that there are a variety of algebras similar to the algebra of field observables as defined above that could be used in place of it without any essential change in the foregoing. Theorems 1—4 would be substantially unaffected if $\mathfrak{A}$ were replaced by the C^*-algebras generated by all bounded Baire (or continuous, or uniformly continuous) functions of the canonical variables; and would be valid in modified form for the C^*-algebra generated by the continuous functions vanishing at infinity of the canonical variables. Which of these algebras to use would appear to be mainly a matter of technical convenience. On physical grounds, it may be expected that the resulting representation spaces relative to the physical vacuum (and accompanying structures) would be identical; this is quite parallel to the circumstance that the L_2-completions of the Baire functions, continuous functions, and polynomials in [0,1] are identical. There is no difficulty in formulating in precise mathematical terms the relatively weak regularity assumptions on the physical vacuum under which the S-matrix finally obtained will be independent of the type of algebra employed. It is important to note also that the foregoing work applies to the still more general formulation of dynamics in terms of transformation of the linear forms that define expectation values in states (in mathematical terms, only the dual of the scattering automorphism is really needed). In this situation, the unitary *S-operator* would have to be replaced by a bilinear form on $\mathfrak{K}$ (the *S-matrix*), but otherwise Theorems 3 and 4 are substantially unaffected. A dynamics of this type is essentially completely determined by the knowledge of the vacuum expectation values $E_{vac}[e^{iP}(out)^{(z)}\, e^{iP}(in)^{(z')}]$ as a function of the two single-particle wave functions z and z'.

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COULOMB DEFLECTION EFFECTS ON IONIZATION AND PAIR-PRODUCTION PHENOMENA

BY

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CONTENTS

Synopsis

The process of K-ionization of atoms by heavy, charged particles is analysed by a semi-classical, time-dependent perturbation method. Non-relativistic wave functions are used for the atomic electrons. The deflection of the bombarding particle in the Coulomb field of the target nucleus is shown to play an important part in the calculation of cross sections in the low-energy region of the projectile. Numerical calculations of K-ionization cross sections for protons turn out to be in good agreement with recent light-target experiments. An estimate is made of the effect of using relativistic electron wave functions in the present perturbation treatment. The method developed is further applied to the pair-production process caused by slow protons impinging on a heavy target element.

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1. Introduction

The ejection of atomic electrons by impingement of heavy, charged particles (protons, deuterons, α-particles) is followed by the emission of the characteristic x-radiation of the target. Recent measurements have given more accurate information about this effect$^{(1-4)}$. The experimental cross sections turned out to deviate greatly from the values given by the existing theory.

The theory of the excitation of atoms by slow, heavy, charged particles has been considered by Mott$^{(5)}$, Bethe$^{(6)}$ and Henneberg$^{(7)}$. The last-mentioned author has performed extensive calculations of the K-shell ionization cross sections. He used the Born approximation, i. e. plane waves for the incoming particles and Coulomb wave functions with respect to the nucleus for the electrons, treating the interaction between the projectile and the electron to first order. A partial justification for this procedure was given by Henneberg$^{(7)}$, and also by Mott along somewhat different lines$^{(5)}$. This question will be treated in detail in sections 2 and 3.

If we accept the above assumption of Henneberg, the differential cross section for ejection of a K-electron with the final energy E_f is given by

$$\frac{d\sigma_K}{dE_f} = \frac{4\,\pi}{\hbar^2} Z_1^2 e^4 \frac{M_1}{E_1} \int_{q_0}^{\infty} \frac{dq}{q^3}\, J \tag{1.1}$$

$$J = \sum_f \left| \int e^{i\underline{q}\,\underline{r}}\, \psi_i(\underline{r})\, \psi_f^*(\underline{r})\, d\underline{r} \right|^2. \tag{1.2}$$

Here, Z_1, M_1 and E_1 are the charge, mass and energy of the bombarding particle; q is the momentum change of the projectile, q_0 its minimum value. The electron wave functions are denoted by ψ. The summation in (1.2) is extended over all final electron states.

Henneberg used non-relativistic Coulomb wave functions in (1.2). As it became clear that there was considerable discrepancy between the theory and the experiments, Jamnik and Zupančič(8) repeated the calculations with relativistic wave functions for the electron. The relativistic increase of the electron density near the origin resulted in an enlargement of the cross section for heavy elements. For elements in the middle of the periodic table, however, the relativistic corrections were small[1].

The deviations mentioned above may be due in part to the fact that the approximation of Henneberg does not take into account the Coulomb repulsion between the impinging particle and the nucleus. The most recent observations seem to support this idea(2, 3, 4). The repulsion prevents particles of low energy from getting close to the nucleus and may thus be expected to give rise to a cross section smaller than predicted by the above-mentioned theory. It is the purpose of the present work to investigate the energy region where this repulsion effect can be expected to be of importance.

Later in the work it will be shown that the decisive parameter in this connection is $\xi = dq_0$, where d is half the distance of closest approach in a head-on collison and q_0 is, as before, the minimum momentum transfer of the bombarding particle. For values $\xi \gtrsim 1$, ionization cross sections much smaller than the predictions of the earlier calculations may be expected. Only in the limit $\xi \ll 1$ can the Coulomb repulsion be neglected and the plane-wave procedure be considered valid.

It is just in the low-energy region, where the great divergences from the earlier calculations are found, that a classical treatment of the projectile is justified. The condition for such a treatment is (cf. § 1.3 of ref. 10)

$$\varkappa = \frac{2 Z_1 Z_2 e^2}{\hbar v_1} \gg 1, \tag{1.3}$$

where Z_2 is the charge of the target nucleus and v_1 the velocity of the incoming particle. This enables us to take the Coulomb repulsion into account by choosing an appropriate path for the projectile.

Stephens and Staub(11, 12) recently reported measurements of the cross section for pair production by slow protons impinging on a tantalum target. They found values smaller by a factor of over a hundred than the predictions of first-order Born-approximation calculations(13). This too may be due to the deflection of the proton in the Coulomb field of the nucleus. The phenomenon is briefly considered in the last section of this work.

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[1] A summary of both the experimental and the theoretical aspects of x-ray production by heavy, charged particles is given by Merzbacher and Lewis in Handbuch der Physik **34** (1958) 166.

2. Approximations Used in the Treatment of *K*-ionization by Heavy Particles

The character of the process of *K*-ionization by heavy, charged particles depends on the relations between the four inverse lengths k, α, $\frac{1}{d}$, and q_0. Here, $\hbar k$ is the momentum of the ejected electron and $\alpha = \frac{Z_2 e^2 m}{\hbar^2}$ the inverse *K*-shell radius. The parameter $1/d$ is the inverse of half the distance of closest approach in a head-on collision, $d = \frac{Z_1 Z_2 e^2}{2 E_1}$ (cf. sec. 1). For the minimum momentum transfer q_0 of the bombarding particle we have, provided $\frac{\Delta E}{E_1} \ll 1$,

$$\left.\begin{aligned} q_0 &= \frac{\Delta E}{\hbar v_1} \\ \Delta E &= E_f + E_B \end{aligned}\right\}, \tag{2.1}$$

where E_f is the kinetic energy of the ejected electron and $|E_B| = \frac{Z_2^2 e^4 m}{2 \hbar^2}$ is the binding energy of the *K*-electron.

It is of interest to notice that the relative values of d^{-1}, q_0, and α are largely determined by the parameter $\varkappa$. Thus, if we define ξ_0 as the value of $\xi = d q_0$ for $\Delta E = E_B$, we have

$$d\alpha = \frac{1}{4 Z_1} \frac{m}{M_1} \varkappa^2, \tag{2.2}$$

$$\xi_0 = \left(\frac{1}{4 Z_1}\right)^2 \frac{m}{M_1} \varkappa^3 \tag{2.3}$$

and

$$\frac{d\alpha}{\xi_0} = \left(\frac{\alpha}{q_0}\right)_{\max} = \frac{4 Z_1}{\varkappa}. \tag{2.4}$$

For the above-mentioned quantities one has the following four possibilities–corresponding, in the order mentioned, to increasing energy of the projectile–:

1) $$\frac{1}{q_0} < \frac{1}{\alpha} < d, \quad \varkappa > 2 \sqrt{\frac{M_1}{m} Z_1} \quad . \tag{2.5}$$

This corresponds to a projectile which is unable to force its way into the K-shell. If $\frac{Z_1}{\alpha} < d$, we even get $\Delta E > E_1$, so that ionization is impossible.

2) $$\frac{1}{q_0} < d < \frac{1}{\alpha}, \quad 2\sqrt{\frac{M_1}{m}Z_1} > \varkappa > 4Z_1; \ (\xi > 1). \tag{2.6}$$

For such energies the projectile is able to penetrate the K-shell, but the ionization probability is very strongly affected by the Coulomb deflection.

3) $$d < \frac{1}{q_0} < \frac{1}{\alpha}, \quad \varkappa > 4Z_1; \ (\xi < 1). \tag{2.7}$$

In this domain the Coulomb deflection still plays a part. (It is shown in the present work that the earlier calculations (cf. refs. 7 and 18) are in principle correct for $\xi \to 0$.)

4) $$d < \frac{1}{\alpha} < \frac{1}{q_0}, \quad \varkappa \ll 4Z_1. \tag{2.8}$$

Here the ionization process cannot be handled by semi-classical methods. The relevant treatment is the one given by BETHE in his article on the passage of heavy, charged particles through matter, cf. ref. 6.

In the present treatment we consider especially the energy domains 2) and 3). We shall therefore assume in the following that

$$\frac{\alpha}{q_0} \ll 1. \tag{2.9}$$

As will be seen later, the calculations are considerably simplified when

$$\frac{k}{q_0} \ll 1. \tag{2.10}$$

The condition for this inequality to hold true is nearly the same as the condition for (2.9) (cf. eqs. (2.5), (2.6) and (2.7)), namely

$$\varkappa \gg 4Z_1, \tag{2.11}$$

which is seen from the inequality

$$\frac{k}{q_0} = \frac{2\,mkv_1}{\hbar\,(\alpha^2 + k^2)} < \frac{2\,mkv_1}{\hbar\,2\,\alpha k} = \frac{2\,Z_1}{\varkappa}. \tag{2.12}$$

Later it is shown that the majority of the secondary electrons are ejected with energies much smaller than the K binding energy, i. e.

$$k \ll \alpha. \tag{2.13}$$

TABLE 2.1

Element	Z_2	E_1 (keV)	$\varkappa$	ξ_0	$d\alpha$
Fe	25.	140[3]	21.8	0.28	0.051
		1300[3]	7.2	0.0094	0.0052
Mo	42.	240[3]	26.8	0.56	0.084
		1600[2]	10.5	0.033	0.013
		2400[1]	8.6	0.018	0.0083
Pb	82.	1920[1]	18.6	0.21	0.046

[1] See ref. 1. [2] See ref. 2. [3] See ref. 4.

Besides, it should be noted that for the following perturbation treatment to be valid it is a necessary condition that the charge of the projectile is much smaller than that of the target nucleus, i.e. $Z_1 \ll Z_2$.

Table 2.1 shows the various parameter values for some of the cases experimentally investigated by proton bombardment.

3. First-order, Time-dependent Perturbation Treatment of the K-ionization

We want to deal with the ionization process in such a way that the Coulomb deflection can be taken into account. This may be done by a semi-classical perturbation treatment. We express the problem in impact

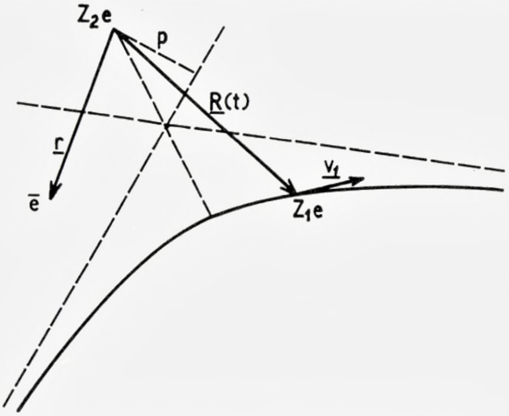

Fig. 3.1. Classical picture of the impact process.

parameter form and treat the interaction between the projectile and the electron as the perturbation.

The differential cross section for the ejection of an atomic electron with the final energy E_f is given by the general expression

$$\frac{d\sigma}{dE_f} = \frac{2\pi}{\hbar^2}\int_0^\infty p\,dp \left| \int_{-\infty}^{\infty} dt e^{i\omega t} \langle f | V(r, t) | i \rangle \right|^2 . \tag{3.1}$$

Here, p is the impact parameter and $\omega = \Delta E/\hbar$. In the following we shall consider interactions of the Coulomb type

$$V = \frac{Z_1 e^2}{|\underline{r} - \underline{R}(t)|}; \tag{3.2}$$

$\underline{r}$ is here the position vector of the electron and $\underline{R}(t)$ that of the incoming particle.

a. The cross section for straight-line paths of the incoming particles

(i) *A general theorem*

We first consider the case where the projectiles follow straight-line paths, that is, we disregard the Coulomb repulsion of the bombarding particles by the nucleus. The cross sections thus obtained are exactly the same as those

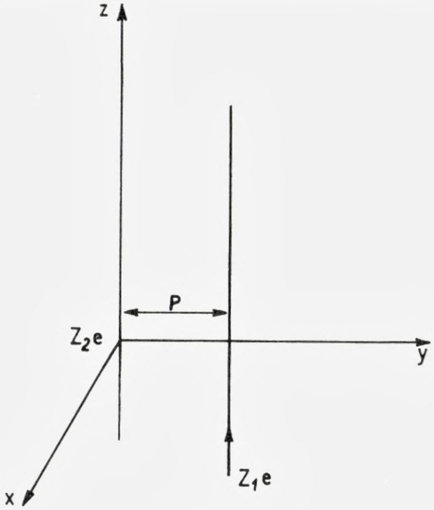

Fig. 3.2.

found if one employs the previously mentioned plane-wave method, disregarding the deflection of the bombarding particles by collision with the electrons (cf. also ref. 14). This is shown mathematically in Appendix I, but can also be seen from the fact that the cross section (1.1) for a bombarding particle with a given velocity v_1 is independent of its mass. The mass may therefore be infinitely great, and thus the particle may be treated in a classical way.

We place our coordinate system with its origin at the nuclear centre of mass and its z-axis in the direction of the incoming particle. This particle moves in the y–z plane as illustrated in fig. 3.2. As shown in Appendix I, the cross section is then given by

$$\left.\begin{aligned} \frac{d\sigma}{dE_f} &= 4\pi Z_1^2 \frac{M_1}{E_1}\frac{e^4}{\hbar^2}\int_0^\infty p\,dp\,|\mathrm{M}_p|^2 \\ \mathrm{M}_p &= \int d\tau\,\psi_i\psi_f^*\,e^{iq_0z}\,K_0(q_0\varrho). \end{aligned}\right\} \qquad (3.3)$$

K_0 is the modified Bessel function of the third kind and zeroth order, and

$$\varrho^2 = x^2+(p-y)^2. \qquad (3.4)$$

(ii) *The matrix element for emission of K-electrons*

From eqs. (3.3) we are now able to derive the cross section for K-electron emission for a fixed value of the impact parameter, $(d\sigma_K/dE_f)_p$. For the electrons we use non-relativistic Coulomb eigenfunctions in the form given by Alder and Winther$^{(15)}$.

The details of the evaluation of this matrix element are given in Appendix II, b. By a rather lengthy procedure one reaches the following result:

$$\left.\begin{aligned} \mathrm{M}_p(l,m) &= i^{-m}\frac{\Gamma(2l+3)}{\Gamma\left(l+\frac{3}{2}\right)}\left[(2l+1)\frac{(l-m)!}{(l+m)!}\right]^{1/2} \\ &\quad\times\frac{\pi}{2}N_iN_f^{l,k}k^l\int_0^\infty dt\,t^{m+1}J_m(pt)\,s^{l-m-2}\,C_{l-m}^{m+\frac{1}{2}}\left(\frac{q_0}{s}\right) \\ &\quad\times(\alpha+i(s-k))^{-(2l+3)}\,F_2\{\,\}. \end{aligned}\right\} \qquad (3.5)$$

In (3.5), N_i and $N_f^{l,k}$ are energy normalization constants; l and m denote the angular momentum quantum numbers of the final state in the continuum; s is defined by

$$s^2 = q_0^2 + t^2; \; 0 \leq t \langle \infty ,$$

and $C_{l-m}^{m+\frac{1}{2}}$ is a Gegenbauer polynomial.

$$F_2\{\,\} = F_2\left\{2\,l+3,\; l+1,\, l+1+i\eta,\; 2\,l+2,\; 2\,l+2;\; \frac{2\,is}{\alpha + i\,(s-k)},\; \frac{-2\,ik}{\alpha + i\,(s-k)}\right\} \tag{3.6}$$

is an Appell function, which is a hypergeometric function of two variables. In sub-section (ii) of Appendix II, b it is shown that

$$\left.\begin{aligned} F_2\{\,\} &= \frac{1}{l+1}\left(\frac{\alpha - i\,(s+k)}{\alpha + i\,(s-k)}\right)^{-(l+1)}\left(\frac{\alpha + i\,(s+k)}{\alpha + i\,(s-k)}\right)^{-(l+1+i\eta)} \\ &\times \frac{1}{\alpha - i\,(s+k)}\left\{(-i\eta)\,(\alpha - ik)\;{}_2F_1\left(l+1,\; l+1+i\eta,\;\; 2\,l+2;\; \frac{4\,sk}{\alpha^2 + (s+k)^2}\right)\right. \\ &\left. + (l+1+i\eta)\,\alpha\,\frac{\alpha + i\,(s-k)}{\alpha + i\,(s+k)}\;{}_2F_1\left(l+1,\; l+2+i\eta,\;\; 2\,l+2;\; \frac{4\,sk}{\alpha^2 + (s+k)^2}\right)\right\}. \end{aligned}\right\} \tag{3.7}$$

Here, $\eta = -\dfrac{Z_2 e^2}{\hbar v} = -\dfrac{\alpha}{k}$ (minus sign because we are dealing with negatrons); v is the final electron velocity, and ${}_2F_1\;(\;)$ are ordinary hypergeometric functions.

Up to this point in the development no approximations have been introduced.

In the following we shall restrict ourselves to cases where the inequalities (2.9) and (2.10) are fulfilled. Under these conditions, the contributions to the matrix element $\mathrm{M}_p\,(l,\, m)$ in eq. (3.5) from l-values larger than zero become negligible. The $F_2\{\,\}$ function is then considerably simplified. As sketched in sub-section (ii) of Appendix II, b, we arrive at the result

$$\left.\begin{aligned} G\,(k) &\equiv (\alpha + i\,(s-k))^{-3}\, F_2\{\,\} \\ &= \frac{i}{2\,s}\, Im\left\{\frac{(\alpha + i\,(s-k))^{i\eta - 1}}{(\alpha + i\,(s+k))^{i\eta + 1}}\right\}. \end{aligned}\right\} \tag{3.8}$$

An expansion of G in powers of k/s and α/s gives

$$G = \frac{1}{s^3}\left\{\frac{\alpha}{s}\left(1 - \frac{\eta\,k}{\alpha}\right) + \left(\frac{\alpha}{s}\right)^3 \frac{2}{3}\left(-19 + 5\,\frac{k^2}{\alpha^2}\right) + - - - \right\}. \tag{3.9}$$

Since

$$\int_0^\infty t^{m+1} J_m\,(p\,t)\,(t^2 + q_0^2)^{-\mu-1} = \frac{p^\mu\, q_0^{m-\mu}\, 2^{-\mu}}{\Gamma\,(\mu+1)}\, K_{m-\mu}\,(p\,q_0) \tag{3.10}$$

(see ref. 16, 7.14.2, eq. (59), hereafter quoted as H. T. F.), we have from eqs. (3.5) and (3.9)

$$\mathrm{M}_p(0,0) \simeq \frac{\alpha}{2} N_i N_f^{0,k} \frac{1}{q_0^4} (p q_0)^2 K_2(p q_0) \tag{3.11}$$

and consequently

$$\left(\frac{d\sigma_K}{dE_f}\right)_p = Z_1^2 \frac{M_1}{E_1} \frac{e^4}{\hbar^2} \frac{Z_2^2}{2\, a_0^2} \left| N_i \right|^2 \left| N_f^{0,k} \right|^2 \frac{1}{q_0^8} (p q_0)^4 (K_2(p q_0))^2, \tag{3.12}$$

where a_0 is the Bohr radius.

Fig. 3.3 shows the variation of $\left|\mathrm{M}_p(0,0)\right|^2$ with the impact parameter. The greatest contributions to the ionization probability are seen to come from impact parameters for which $p \sim \frac{1}{q_0}$.

The expression (3.12) contains only the leading term in a development in powers of $\frac{\alpha}{q_0}$. From (3.10) it may be shown, however, that also higher terms in the cross section (corresponding for instance to higher terms in (3.9) or to higher l-values) exhibit a similar dependence on p.

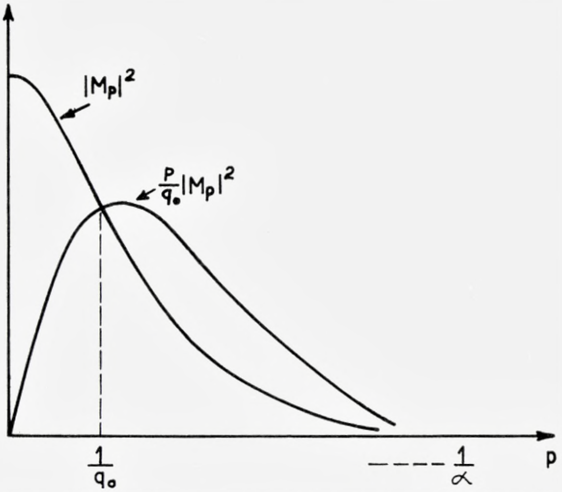

Fig. 3.3. The probability of ejection of a K-electron as a function of the impact parameter p for straight-line orbits. The area under the curve $\frac{p}{q_0} |\mathrm{M}_p|^2$ shows the contributions to the total cross section from the various p-values. It is assumed that $\frac{1}{q_0} \ll \frac{1}{\alpha}$. The calculations are valid only for $p \ll \frac{1}{\alpha}$.

Since the Coulomb deflection becomes large for impact parameters of the order of or smaller than the distance of closest approach $d\left(=\frac{Z_1 Z_2 e^2}{2 E_1}\right)$, this deflection must be expected to be of importance when d is not very much smaller than $\frac{1}{q_0}$.

Up till now we have assumed $\alpha \ll q_0$, corresponding to the cases considered in eqs. (2.6) and (2.7). In the opposite case of $q_0 \lesssim \alpha$, the expansions employed above are no longer valid, and, moreover, the semi-classical methods break down, cf. eqs. (2.8). The velocity of the projectile is in this case larger than that of the K-electron; therefore we may apply considerations from the stopping-power calculations extensively treated by Bethe in ref. 6.

The total cross section for emission of K-electrons with the final energy E_f is given by

$$\left(\frac{d\sigma_K}{dE_f}\right)_{\text{str. } l.} = 2\pi \int_0^\infty p\, dp \left(\frac{d\sigma_K}{dE_f}\right)_p .$$

Using an integral formula given by Lommel (cf. ref. 17, p. 136), we deduce

$$\left(\frac{d\sigma_K}{dE_f}\right)_{\text{str. } l.} = \frac{2^5}{5}\pi Z_1^2 \frac{M_1}{E_1}\frac{e^4}{\hbar^2}\frac{Z_2^2}{a_0^2} \,|N_i|^2\, |N_f^{0,\,k}|^2 \frac{1}{q_0^{10}}. \tag{3.13}$$

This is exactly the same formula as the one derived by Huus et al.$^{(18)}$ by means of the Born approximation.

Eq. (3.12) also enables us to calculate the cross section for K-ionization by particles scattered through a small angle, $\theta \ll 1$, since this cross section is expected to be the same as that for a straight-line path with corresponding impact parameter. (See fig. 3.5 and the explanatory text to that figure.) We have

$$\left(\frac{d\sigma_K}{d\Omega}\right)_{\text{str. } l.} = \frac{d\sigma_R}{d\Omega}\left(\frac{d\sigma_K}{dE_f}\right)_p = f_1 \frac{\left(\xi \operatorname{cotg}\frac{\theta}{2}\right)^4}{\sin^4\frac{\theta}{2}}\left(K_2\left(\xi \operatorname{cotg}\frac{\theta}{2}\right)\right)^2; \tag{3.14}$$

$d\sigma_R/d\Omega$ is the differential cross section for Rutherford scattering, and

$$f_1 = \frac{d^2}{4} Z_1^2 \frac{M_1}{E_1}\frac{e^4}{\hbar^2}\frac{Z_2^2}{2\,a_0} \,|N_i|^2\, |N_f^{o,\,k}|^2 \frac{1}{q_0^8}. \tag{3.15}$$

The cross sections (3.13) and (3.14) have been labelled with the index str. *l.* because they are derived on the basis of a straight-line calculation. The expressions are expected to be valid in the limit $\xi \to 0$.

In fig. 3.5, $\left(\frac{d\sigma_K}{d\Omega}\right)_{\mathrm{str.}\,l.}$ is given for $\xi = 0.2$. In the same figure it is shown how the angular dependence is influenced by the Coulomb deflection, as calculated below.

b. Cross sections for hyperbolic paths

(i) *General procedure*

In the following we shall calculate the cross section for emission of secondary K-electrons, taking into account the deflection of the projectile. We shall confine ourselves to the monopole term in the potential, assuming that term to be the dominating one for $\alpha \ll q_0$ as in the case of the straight-line integrals. We then have

$$\left.\begin{aligned} \frac{d\sigma_K}{dE_f} &= \frac{2\pi}{\hbar^2} d^2 Z_1^2 e^4 \int_1^\infty \varepsilon\, d\varepsilon \\ &\times \left| \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \psi_f | \begin{Bmatrix} \dfrac{1}{R(t)}, & r < R \\ \dfrac{1}{r}, & r > R \end{Bmatrix} | \psi_s \rangle \right|^2, \end{aligned}\right\} \quad (3.16)$$

where ε is the eccentricity of the hyperbolic path of the incoming particle. For this path we use a parametric representation previously employed by, among others, TER-MARTIROSYAN$^{(19)}$:

$$\left.\begin{aligned} x &= d\,(\cosh w + \varepsilon) \\ y &= d\sqrt{\varepsilon^2 - 1}\ \sinh w \\ z &= 0 \\ R &= d\,(\varepsilon \cosh w + 1) \\ t &= \frac{d}{v_1}(\varepsilon \sin h w + w). \end{aligned}\right\} \quad (3.17)$$

Inserting for the electronic wave functions in eq. (3.16) the integral representations given by ALDER and WINTHER$^{(15)}$, we get

$$\left.\begin{aligned} \frac{d\sigma_K}{dE_f} &= \frac{2\pi}{\hbar^2} d^2 Z_1^2 e^4 \left| N_i \right|^2 \left| N_f^{0,\,k} \right|^2 \int_1^\infty \varepsilon\, d\varepsilon \\ &\times \left| \int_{-\infty}^{\infty} dt\, e^{i\omega t} \left\{ \frac{1}{\Gamma(1-i\eta)\,\Gamma(1+i\eta)} \int_0^1 du \left(\frac{u}{1-u}\right)^{i\eta} \right.\right. \\ &\times \left.\left. \left[\int_0^R \frac{dr}{R} r^2 e^{-rb} + \int_R^\infty dr\, r\, e^{-rb} \right] \right\} \right|^2 . \end{aligned}\right\} \quad (3.18)$$

Here,

$$b = \alpha - ik + 2\, iku. \quad (3.19)$$

The integration over r is easily carried out, yielding for the factor in square brackets in (3.18)

$$I_R = \frac{2}{Rb^3} - \frac{e^{-bR}}{b^2}\left(1 + \frac{2}{Rb}\right). \quad (3.20)$$

The integration over time is more complicated. Using (3.17), we have

$$\left.\begin{aligned} I_b = v_1 \int_{-\infty}^{\infty} dt\, e^{i\omega t} I_R = \int_{-\infty}^{\infty} dw \left\{ \frac{2}{b^3} - \frac{e^{-bd(\varepsilon \cosh w + 1)}}{b^2} \left(d(\varepsilon \cosh w + 1) + \frac{2}{b} \right) \right\} \\ \times e^{i\xi(\varepsilon \sinh w + w)}. \end{aligned}\right\} \quad (3.21)$$

As shown in Appendix II, c, the integration leads to

$$\left.\begin{aligned} I_b = 4\, b^{-3} e^{-\frac{\pi}{2}\xi} K_{i\xi}(\varepsilon\xi) - 2\, b^{-2}(d + 2\, b^{-1})\, e^{-bd} \left(\frac{bd+i\xi}{bd-i\xi}\right)^{\frac{i\xi}{2}} \\ \times K_{i\xi}\left(\varepsilon\sqrt{b^2 d^2 + \xi^2}\right) - d\, b^{-2} e^{-bd} \varepsilon \left\{ \left(\frac{bd+i\xi}{bd-i\xi}\right)^{\frac{i\xi+1}{2}} K_{i\xi+1}\left(\varepsilon\sqrt{b^2 d^2 + \xi^2}\right) \right. \\ \left. + \left(\frac{bd+i\xi}{bd-i\xi}\right)^{\frac{i\xi-1}{2}} K_{i\xi-1}\left(\varepsilon\sqrt{b^2 d^2 + \xi^2}\right) \right\} \end{aligned}\right\} \quad (3.22)$$

or

$$\left.\begin{aligned} I_b = 2\, b^{-3} \left\{ 2\, e^{-\frac{\pi}{2}\xi} K_{i\xi}(\varepsilon\xi) - e^{-bd} \left(\frac{bd+i\xi}{bd-i\xi}\right)^{\frac{i\xi}{2}} \right. \\ \left. \times \left[\left(2 + \frac{b^2 d^2}{bd - i\xi}\right) K_{i\xi}\left(\varepsilon\sqrt{b^2 d^2 + \xi^2}\right) + \frac{\varepsilon\, b^2 d^2}{\sqrt{b^2 d^2 + \xi^2}} K_{i\xi-1}\left(\varepsilon\sqrt{b^2 d^2 + \xi^2}\right) \right] \right\}. \end{aligned}\right\} \quad (3.23)$$

Up to this point the development is exact.

According to a multiplication theorem for the Bessel functions (H.T.F. 7.15, eq. (19) we have

$$\frac{K_\nu\left(\varepsilon\sqrt{b^2 d^2+\xi^2}\right)}{\left(\sqrt{b^2 d^2+\xi^2}\right)^\nu} = \sum_{n=0}^{\infty}\left(-\frac{\varepsilon b^2 d^2}{2}\right)^n \frac{1}{\xi^{\nu+n}}\,\frac{K_{\nu+n}(\varepsilon\xi)}{n!}. \tag{3.24}$$

As

$$\frac{|b|\,d}{\xi} \simeq \frac{\alpha}{q_0}$$

and

$$|b|d \simeq d\alpha,$$

this expansion is fast converging, provided the inequality (2.9) is fulfilled.

Applying (3.24) to (3.23), we deduce

$$\left.\begin{aligned} I_b = 2\,e^{-\frac{\pi}{2}\xi}\, b^{-3}\Big\{ & 2\,K_{i\xi}(\varepsilon\,\xi) - e^{-bd}\left(1-\frac{bd}{i\xi}\right)^{-i\xi} \\ \times\Big[& \left(2+\frac{b^2 d^2}{bd-i\xi}\right)K_{i\xi}(\varepsilon\,\xi) - \frac{b^4 d^4}{bd-i\xi}\,\frac{\varepsilon}{2\xi}\,K_{-i\xi+1}(\varepsilon\,\xi) \\ + & \left(-2+\frac{b^2 d^2}{bd-i\xi}\right)b^4 d^4\,\frac{\varepsilon^2}{8\,\xi^2}\,K_{-i\xi+2}(\varepsilon\,\xi) + - - - - \Big]\Big\}, \end{aligned}\right\} \tag{3.25}$$

where we have written explicitly terms arising from the expansion (3.24) with $n \leq 2$.

Since

$$\left(1-\frac{bd}{i\xi}\right)^{-i\xi} = e^{-i\xi\, ln\left(1-\frac{bd}{i\xi}\right)}$$

$$\simeq e^{bd}\left\{1+\frac{i\xi}{2}\left(\frac{bd}{i\xi}\right)^2+\frac{i\xi}{3}\left(\frac{bd}{i\xi}\right)^3+\left(\frac{i\xi}{4}-\frac{\xi^2}{8}\right)\left(\frac{bd}{i\xi}\right)^4+ - - - - \right\},$$

we obtain by inserting this expression into (3.25) and taking into account that $|b|\,d \simeq d\alpha \ll 1$

$$b^3\cdot I_b \simeq 2\,e^{-\frac{\pi}{2}\xi}\sum_{n=0}^{\infty} k_n'\,\varepsilon^n\,K_{-i\xi+n}(\varepsilon\,\xi), \tag{3.26}$$

where

$$\left.\begin{aligned}
k_0' &= -\frac{b^3\,d^3}{3\,\xi^2} + \frac{b^4\,d^4}{\xi^2}\left(\frac{i}{2\,\xi} - \frac{1}{4}\right) \\
k_1' &= i\,\frac{b^4\,d^4}{2\,\xi^2} \\
k_2' &= \frac{b^4\,d^4}{4\,\xi^2} \\
k_3' &= -\frac{b^6\,d^6}{12\,\xi^3} \\
&\text{— — — — — —} \\
k_n' &= \frac{n-1}{2^{n-1}\,n\,!}\left(-\frac{b^2\,d^2}{\xi}\right)^n \quad \text{(valid for } n \geq 2).
\end{aligned}\right\} \tag{3.26, a}$$

We can now carry out the u-integration (see eq. (3.18)) by using an integral representation of the ordinary hypergeometric function (H.T.F. 2.12, eq. (1)). In the general case the result of the u-integration is given by

$$\int_0^1 \left(\frac{u}{1-u}\right)^{i\eta} b^n\,du = (\alpha - ik)^n\;{}_2F_1\left(3-2\,n,\;1+i\eta,\;2;\;\frac{2\,ik}{ik-\alpha}\right);\;(n \geq 2). \tag{3.27}$$

For the majority of the ejected electrons, $k \ll \alpha$ (cf. eq. (3.13)). This enables us to perform a confluence, thus getting

$$I_\varepsilon = 2\,e^{-\frac{\pi}{2}\xi}\sum_{n=0}^{\infty} k_n\,\varepsilon^n\,K_{-i\xi+n}(\varepsilon\,\xi) \tag{3.28}$$

with

$$\left.\begin{aligned}
k_0 &= \left(-\frac{d^3}{\xi^2}\right)\left(\left(\frac{1}{3} + \frac{d\alpha}{2}\right) - i\,\frac{d\alpha}{\xi}\right) \\
k_1 &= i\,\alpha\,\frac{d^4}{\xi^2} \\
k_2 &= \frac{\alpha}{2}\,\frac{d^4}{\xi^2} \\
k_3 &= -\frac{1}{36}\,\frac{d^6}{\xi^3}\,19\,\alpha^3 \\
&\text{— — — — — — — — —} \\
k_n &= \frac{1}{\alpha^3}\,\frac{n-1}{2^{n-1}\,n\,!}\,\Phi\,(3-2\,n,\;2;\;-2)\left(-\frac{d^2\,\alpha^2}{\xi}\right)^n;\;\; n \geq 2.
\end{aligned}\right\} \tag{3.28, a}$$

Φ is here the confluent hypergeometric function.

As $\frac{d\alpha}{\xi_0} = \frac{4\,Z_1}{\varkappa}$, we see that for sufficiently high values of $\varkappa$, (3.28) may to a good approximation be written as

$$I_\varepsilon = 2\,e^{-\frac{\pi}{2}\xi}\left\{\left[-\frac{d^3}{3\,\xi^2}+\alpha\frac{d^4}{\xi^2}\left(\frac{i}{\xi}+\frac{\varepsilon^2-1}{2}\right)\right]K_{i\,\xi}(\varepsilon\,\xi)+\alpha\frac{d^4}{\xi^3}\varepsilon\,K_{-i\,\xi+1}(\varepsilon\,\xi)\right\}. \tag{3.29}$$

This equation will be useful in the following discussion of the angular distribution.

(ii) *Angular distributions of the scattered projectiles after ionization*

Equations (3.28) and (3.29) for I_ε give a direct expression for the dependence of the cross section on ε, i.e. on the deflection of the incident particle.

First we let the hyperbolic path of the incoming particle degenerate into a straight line, i.e. we put $\varepsilon \gg 1$ in eqs. (3.17), which corresponds to keeping the impact parameter fixed, but letting $d \to 0$. Eq. (3.28) is then replaced by

$$I_{\mathrm{str.}\,l.} = 2\sum_{n=2}^{\infty} k_n\,\varepsilon^n K_n(\varepsilon\,\xi), \tag{3.30}$$

where $k_2, k_3, \ldots.$ are given by (3.28, a). This result is obtained in a straightforward manner by application of the integral formulae given in Appendix II, c. The terms in (3.30) correspond exactly to the terms in the straight-line monopole expansion, the first of which is given by (3.11), since for $\varepsilon \gg 1$ we have $\varepsilon\xi \simeq p\,q_0$.

It is also useful to consider the opposite extreme case $\varepsilon = \varepsilon_c \simeq 1$. This corresponds to ionization by particles scattered in the backward direction. Putting

$$K_{-i\,\xi+1}(\varepsilon\xi) = -\frac{i}{\varepsilon}K_{i\,\xi}(\varepsilon\xi) - K'_{i\,\xi}(\varepsilon\xi)$$

in (3.29), we have

$$I_\varepsilon = 2\,e^{-\frac{\pi}{2}\xi}\frac{d^3}{\xi^2}\left\{\left(-\frac{1}{3}\right)K_{i\xi}(\varepsilon\xi) - \varepsilon\frac{d\alpha}{\xi}K'_{i\xi}(\varepsilon\xi)\right\}. \tag{3.31}$$

We shall furthermore evaluate (3.31) for the case of $\xi \ll 1$. Here we may use the approximate expressions

$$\left.\begin{aligned} K_{i\,\xi}(\varepsilon_c\,\xi) &\simeq -\ln(\varepsilon_c\,\xi) \\ K'_{i\,\xi}(\varepsilon_c\,\xi) &\simeq -\frac{1}{\varepsilon_c\,\xi}. \end{aligned}\right\} \tag{3.32}$$

From (3.31) we then obtain

$$\left.\begin{aligned} I_\varepsilon &\simeq 2\, e^{-\frac{\pi}{2}\xi} \frac{d^2}{\xi^2}\left\{\frac{d}{3}\ln(\varepsilon_c\,\xi) + \frac{d^2\alpha}{\xi^2}\right\} \\ &= 2\, e^{-\frac{\pi}{2}\xi} \frac{1}{q_0^2}\left\{\frac{\alpha}{q_0^2} + \frac{d}{3}\ln(\varepsilon_c\,\xi)\right\}. \end{aligned}\right\} \tag{3.33}$$

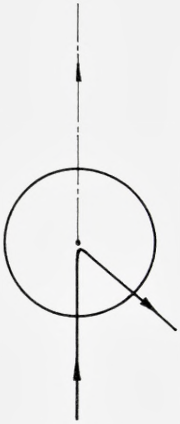

Fig. 3.4.

The dominating term in this formula corresponds to the main term in the matrix element for a particle moving on a straight-line path with the impact parameter zero. This is immediately seen from eq. (3.12), considering that

$$\lim_{pq_0\to 0}\left((pq_0)^2 K_2(pq_0)\right) = 2.$$

From a physical point of view this was to be expected since the monopole effect considered does not depend on the direction of the outgoing particle. Moreover, for $\xi \ll 1$ the region of deflection ($\sim d$) is small compared with q_0^{-1}, the quantity characterizing the interaction with the electron. Thus, the approach to the straight-line excitation probability, for $\xi \ll 1$, is to be expected not only for backward scattering but for any scattering angle.

Quite generally we define

$$y = \frac{I_\varepsilon}{e^{-\frac{\pi}{2}\xi}\cdot I_{\mathrm{str.}\,l.}} \tag{3.34}$$

since, in many cases, the main deflection effect is contained in the factor $\exp\left\{-\frac{\pi}{2}\xi\right\}$. For particles scattered in the backward direction ($\varepsilon = \varepsilon_c \simeq 1$) with sufficiently large $\varkappa$ and $\xi \ll 1$ it is easily seen from (3.33) that

$$\left.\begin{aligned} y &= 1 + \frac{4}{3} Z_1 \frac{M_1}{m}\left(\frac{\xi}{\varkappa}\right)^2 \ln(\varepsilon_c\,\xi) \\ \text{or}\qquad y &= 1 + \frac{1}{12} Z_1 \frac{M_1}{m}\left(\frac{\Delta E}{E_1}\right)^2 \ln(\varepsilon_c\,\xi). \end{aligned}\right\} \tag{3.35}$$

For $\varepsilon \gg 1$ and $\xi \gtrsim 1$ we have

$$y \simeq \frac{K_{-i\xi+2}(\varepsilon\,\xi)}{K_2(\varepsilon\,\xi)} \simeq 1 - \frac{\xi}{2\,\varepsilon} \tag{3.36}$$

(see p. 204 of ref. 20).

The case $\xi \gg 1$, $\varepsilon \simeq 1$ may in principle also be handled by the aid of asymptotic formulae for $K_{i\xi}(\xi)$, $\xi \gg 1$. Such formulae are found in Chapter 8 of ref. 17. We stress the fact that these considerations are valid only for sufficiently high values of $\varkappa$. For smaller $\varkappa$, more terms in (3.28) must be taken into account. The results of the above analysis may be used to modify the angular distribution found from the straight-line approach in (3, a, (ii)). Choosing $\xi = 0.2$ and a $\varkappa$-value of 25, we obtain for α-particles a result which in fig. 3.5 is compared with the corresponding curve for $(d\sigma_K/d\Omega)_{\mathrm{str.}\, l.}$

(iii) *Total cross sections*

The total cross section for emission of a K-electron with definite energy can be obtained from (3.28) by an integration over the eccentricity. Using one of LOMMEL's integral formulae (ref. 17, Chapter 5), one obtains after an elementary but rather tedious integration

$$\left.\begin{aligned} I &= \int_1^\infty d\varepsilon \cdot \varepsilon \, |I_\varepsilon|^2 \\ &= 4\, e^{-\pi\xi} \left(\frac{d^3}{\xi^2}\right)^2 \left\{ A\,(K_{i\xi}(\xi))^2 + B\,\xi\, K_{i\xi}(\xi)\, K'_{i\xi}(\xi) + C\,(K'_{i\xi}(\xi))^2 \right\}. \end{aligned}\right\} \quad (3.37)$$

A, B, and C are polynomials whose number of terms depends on the number included in (3.28).

The convergence of the expressions for A, B, and C depends, as seen from (3.28), on the parameters $d\alpha$ and ξ, which in their turn may be expressed in terms of $\varkappa$ (cf. eqs. (2.2) and (2.3)). For sufficiently large $\varkappa$ ($\varkappa \gtrsim 30$ for protons) a rather good approximation may be obtained if one neglects terms in (3.28) of higher order than $n = 2$. For the coefficients A, B, and C one then finds

$$\left.\begin{aligned} A &= -\frac{4}{9}\frac{d\alpha}{\xi^2} + \frac{8}{5}\left(\frac{d\alpha}{\xi^2}\right)^2 \\ B &= \frac{1}{9}\frac{d\alpha}{\xi^2} - \frac{8}{5}\left(\frac{d\alpha}{\xi^2}\right)^2 \\ C &= \frac{1}{18} - \frac{4}{9}\frac{d\alpha}{\xi^2} + \frac{8}{5}\left(\frac{d\alpha}{\xi^2}\right)^2 \\ &\left(\frac{d\alpha}{\xi_0^2} = 64\, Z_1^3 \frac{M_1}{m}\frac{1}{\varkappa^4}\right). \end{aligned}\right\} \quad (3.38)$$

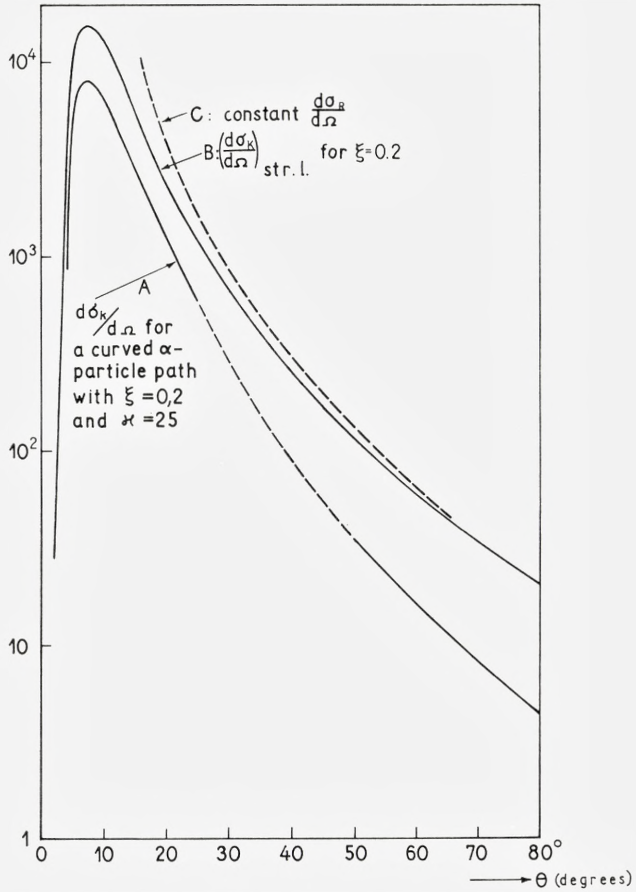

Fig. 3.5. The angular distribution, $\frac{d\sigma_K}{d\Omega}$, of α-particles after K-ionization (curve A) compared with the corresponding curve for straight-line orbits, $\left(\frac{d\sigma_K}{d\Omega}\right)_{\text{str. } l.}$ (curve B). The ordinate is in arbitrary units.

The angles for the straight-line curve are determined from the relation $\varepsilon^2 = 1 + \frac{p^2}{d^2}$ between the eccentricity $\varepsilon = \frac{1}{\sin\frac{\theta}{2}}$ and the impact parameter p. Thus, $pq_0 = \xi \operatorname{cotg}\frac{\theta}{2}$.

The dotted curve C is proportional to the Rutherford-scattering cross section $\frac{d\sigma_R}{d\Omega} = \frac{\varepsilon^4}{4} d^2$ and has been normalized so as to approach $\left(\frac{d\sigma_K}{d\Omega}\right)_{\text{str. } l.}$ for small p.

The curve denoted $d\sigma_K/d\Omega$ includes Coulomb-deflection effects (cf. the text). Consequently, the ratio between the curves A and B in the region of small angles is given by the factor $e^{-\pi\xi}$.

The dotted part of curve A represents the region in which the approximation formulae for the Hankel functions break down.

For smaller values of $\varkappa$, higher terms in (3.28) may have a significant effect. However, for $\varkappa \leq 30$ one may utilize the fact that the third term in eq. (3.37) (the one including C) is greatly dominating. For A and B the approximation (3.38) is then sufficient, but for C one must take into account terms in (3.28) in which $n > 2$. The general expression for C is given by

$$\left.\begin{aligned} C &= \frac{1}{18} - \frac{4}{9}\frac{d\alpha}{\xi^2} + \frac{1}{\xi^2}\sideset{}{'}\sum_{m=0}^{\infty} a_m \left(\frac{d^2\alpha^2}{\xi^2}\right)^{m+1} \\ \text{with}\qquad a_m &= \frac{(-1)^m}{2(m+5)} \sideset{}{'}\sum_{i+j=m} 2(i+1)\,2(j+1) \\ &\times \Phi(-1-2i, 2; -2)\,\Phi(-1-2j, 2; -2). \end{aligned}\right\} \tag{3.39}$$

Thus,

$$a_0 = \frac{8}{5},\quad a_1 = -\frac{152}{9},\quad a_2 = \frac{8}{5}\frac{4061}{63},\quad \dots . \tag{3.39, a}$$

It should be noted that the term $\frac{8}{5}\left(\frac{d\alpha}{\xi^2}\right)^2$ in C (eqs. (3.38) and (3.39)) corresponds to the dominating term obtained from the straight-line calculations (cf. eq. (3.13)), provided we use the approximate expressions (3.32) for the Bessel functions in (3.37).

The general expression for the cross section for ejection of K-electrons is given by

$$\frac{d\sigma_K}{dE_f} = \frac{2\pi}{\hbar^2} d^2 Z_1^2 e^4 \,|N_i|^2\, |N_f^{0,k}|^2 \frac{1}{v_1^2} I, \tag{3.40}$$

which can also be written in the form

$$\frac{d\sigma_K}{dE_f} = e^{-\pi\xi} (d\sigma_K/dE_f)_{\mathrm{str.}\,l.} (1 - f(\varkappa, \xi)), \tag{3.41}$$

where $(d\sigma_K/dE_f)_{\mathrm{str.}\,l.}$ is the dominating term in the cross section for straight-line paths given by eq. (3.13). The correction factor $f(\varkappa, \xi)$ can then be found from (3.38) and (3.39).

As the coefficients k_n in (3.28) are calculated under the condition $k \ll \alpha$, the most consistent procedure is to use $f(\varkappa, \xi_0)$ when calculations are made on the basis of (3.41).

However, in the cases considered, the difference between $f(\varkappa, \xi_0)$ and $f(\varkappa, \xi)$ is of no importance. In the domain of large $\varkappa$-values the main correction to the cross section arises from the factor $e^{-\pi\xi}$, in which one should insert the value of ξ appropriate to the electron energy considered.

c. Symmetrization of the cross sections

The above semi-classical treatment of the K-ionization process depends on the condition $\varkappa \gg 4 Z_1$ and in addition requires $\Delta E < E_1$. If the value of $\Delta E/E_1$ is not very small compared with unity, one may obtain a significant improvement of the semi-classical expressions by choosing symmetrized values for the parameters d and ξ which enter in these expressions.

The problem is analogous to the one considered in the case of Coulomb excitation of nuclei, and the symmetrizing procedure may be justified in the same way as for that process, cf. ref. 21, sec. II, B6.

The symmetrized parameters d and ξ are given by

$$d^S = \frac{Z_1 Z_2 e^2}{M_1 v_1 v_2} \tag{3.42}$$

$$\xi^S = \frac{Z_1 Z_2 e^2}{\hbar}\left(\frac{1}{v_2} - \frac{1}{v_1}\right) \tag{3.43}$$

or

$$d^S = d\left(1 - \frac{\Delta E}{E_1}\right)^{-\frac{1}{2}} \tag{3.44}$$

$$\xi^S = \xi \frac{2 E_1}{\Delta E}\left(\left(1 - \frac{\Delta E}{E_1}\right)^{-\frac{1}{2}} - 1\right). \tag{3.45}$$

Here, v_2 is the velocity of the projectile after the impact. We also define ξ_0^S and d_0^S by putting $\Delta E = E_B$ in the symmetrized equations.

d. The effects of screening and finite nuclear size

The screening of the Coulomb field of the nucleus by the atomic electrons may interfere in two different manners.

a) The incoming particle is moving in a screened Coulomb field rather than an unscreened one. The orbit described in (3.17) is therefore not quite correct. On the other hand, we are only concerned with those energies of the incoming particles for which $d \ll {}^1/_\alpha$. This means that the motion in the region of considerable screening is already nearly unperturbed by the field of the nucleus. The screening effect is thus negligible.

b) The electron–in the bound as well as in the free state–is moving in the screened Coulomb field. This case is treated in the following ways:

1) The electron gets additional energy from the repulsion by the other electrons. Although this energy is relatively small as compared with the K binding energy, it is of some significance owing to the great dependence of the cross section on ξ. However, we may take this effect into account by using the experimental ionization energies in the expression for $\Delta E = E_B + E_f$ rather than the theoretical, unscreened ones.

2) The change of the wave functions by the screening potential falls into two parts:

α) The so-called internal screening effect is taken into account by the use of the screened nuclear charge $Z_2^{\mathrm{eff}} \simeq Z_2 - 0.3$ rather than Z_2 in the expressions for $d\sigma_K/dE_f$. This is obviously a small correction.

β) The effect of the outer part of the screening is a rather smooth change of the potential, appreciable only for distances larger than $\frac{a_0}{2Z_2^{1/3}}$ (see Chapter 2 of ref. 22). Clearly, such a change is rather negligible for the initial states, where the wave functions extend only to distances of about $\frac{a_0}{Z_2}$.

For the final-state wave functions we may again argue that in the inner region, which determines the transition matrix element, the wave function is approximately equal to that for a free Coulomb field, except for the normalization factor. However, to the extent to which the penetration through the screened part of the field can be treated in the WKB approximation, the normalization in the inner region is determined directly from that chosen in the asymptotic region and does not depend on the potential in the intermediate region. Thus, the use of pure Coulomb wave functions for the continuous states seems to be rather well justified. From such an argument, one expects the normalization factor to be affected by a factor of the order of $\theta^{\frac{1}{4}}$, where θ is the ratio of the observed to the unscreened binding energy. However, since this correction is rather small compared with that arising from the change in ξ, it is neglected here.

Finally, we consider the effect of the finite nuclear size. This effect influences the electronic S wave functions in the neighbourhood of the nucleus. However, the effect on the matrix elements for ionization is very small since the characteristic distances in the radial integrals are of the order of the larger of the two quantities $\frac{1}{q_0}$ and d. Under the conditions here considered, the characteristic distance is many times larger than the nuclear radius, and therefore the change in the electronic wave functions caused by the finite nuclear size is small. Moreover, this change vanishes in the non-relativistic approximation.

e. Discussion and comparison with experimental cross sections

The present treatment of the ionization process has one feature in common with those of HENNEBERG(7) and of JAMNIK and ZUPANČIČ(8). In all three treatments the cross sections are obtained as series developments in the quantity α/q_0. Accordingly, the evaluated formulae can only be applied to experiments where the inequality (1.3) is fulfilled, i.e. where the energy of the incident particle is so small that α/q_0 is less than unity. The other approximations involved in the three methods are such, however, that they may be said to have somewhat different regions of application.

The relativistic effects in the electron wave functions, which are important in the heavier elements (see below), are dealt with in the work of JAMNIK and ZUPANČIČ only.

The advantage of Henneberg's calculations is that he succeeds in transforming the expressions for the cross section so as to give a rather fast convergence up to $\alpha/q_0 \simeq 1$.

The present method is evidently most favourably applied to the region of small energies, where the Coulomb deflection is of importance.

For bombarding energies so great that α is close to q_0, one thus expects Henneberg's formula to represent the best approximation, but with decreasing energy the Coulomb deflections rather soon become significant (for $\varkappa \gtrsim 12\, Z_1$). In the transition region where these effects begin to play a part and where α/q_0 is still not very small, none of the available treatments are very reliable, since as yet no estimate has been made of the deflection effects for the higher multipole transitions.

The relativistic effects have so far been considered only for straight-line orbits (8), for which it is found that correction terms of the relative order of $(Z_2 \zeta)^2 \frac{q_0}{\alpha}$ arise in the monopole matrix element $\left(\zeta = \frac{e^2}{c\hbar}\right.$ is the fine-structure $\left.\text{constant}\right)$. An extension of this treatment to the case of curved orbits leads to integrals which are difficult to evaluate, but it seems reasonable to expect a similar correction. Thus, a rough approximation to the relativistic straight-line cross section may be obtained by evaluation of the expression (11) of Jamnik and Zupančič(8) for the monopole excitations to lowest order in α/q_0*; one finds that in this case their integral I is proportional to

$$\left.\begin{aligned} &\left(\frac{\alpha}{q_0}\right)^{2(\gamma+1)}\left(1+\delta(1-\gamma)\frac{q_0}{\alpha}\right), \\ \text{where} \qquad &\gamma=\sqrt{1-(\zeta Z_2)^2} \\ &\delta=\frac{2(3+2\gamma)}{5+4\gamma}\frac{\pi}{4} \end{aligned}\right\} \qquad (3.46)$$

($\gamma = 1$ corresponds to the nonrelativistic case).

By multiplying the cross section deduced from (3.46) by the appropriate curvature factors found by the non-relativistic methods (cf. (3.41)) one expects to obtain an approximate value for the cross section also in the case of heavier target elements.

In figs. 3.6, 3.7, 3.8, and 3.9 the calculated cross sections are compared with the experimental data. From (3.41) we obtain the differential cross section, from which the total cross section for K-ionization is found by graphical integration, allowance being made for the fact that there are two electrons in the K-shell. Moreover, the formula (3.41) is modified so as to take the screening into account in accordance with the prescriptions given in sec. 3, *d*.

For the lighter elements, the theoretical values agree rather well with the experiments and are seen to represent a considerable improvement on those for straight-line orbits. The agreement appears to extend to $\varkappa$-values as low as about 12, for which the α/q_0 corrections are rather large and for which the accuracy of the present theory is therefore questionable.

For the heavier elements (Mo and Ag) the experimental values appear to be significantly in excess of the theoretical estimates, but it seems likely that the deviation is to be attributed mainly to relativistic corrections, which are expected to enlarge the cross sections for these elements appreciably. A simple estimate of these corrections, obtained in the manner described

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* In eqs. (14) of ref. 8, which must be used for this purpose, there is a misprint. In the equation for q_m the numerator in the coefficient of the second confluent hypergeometric function should be $4m+2$ instead of $4m$.

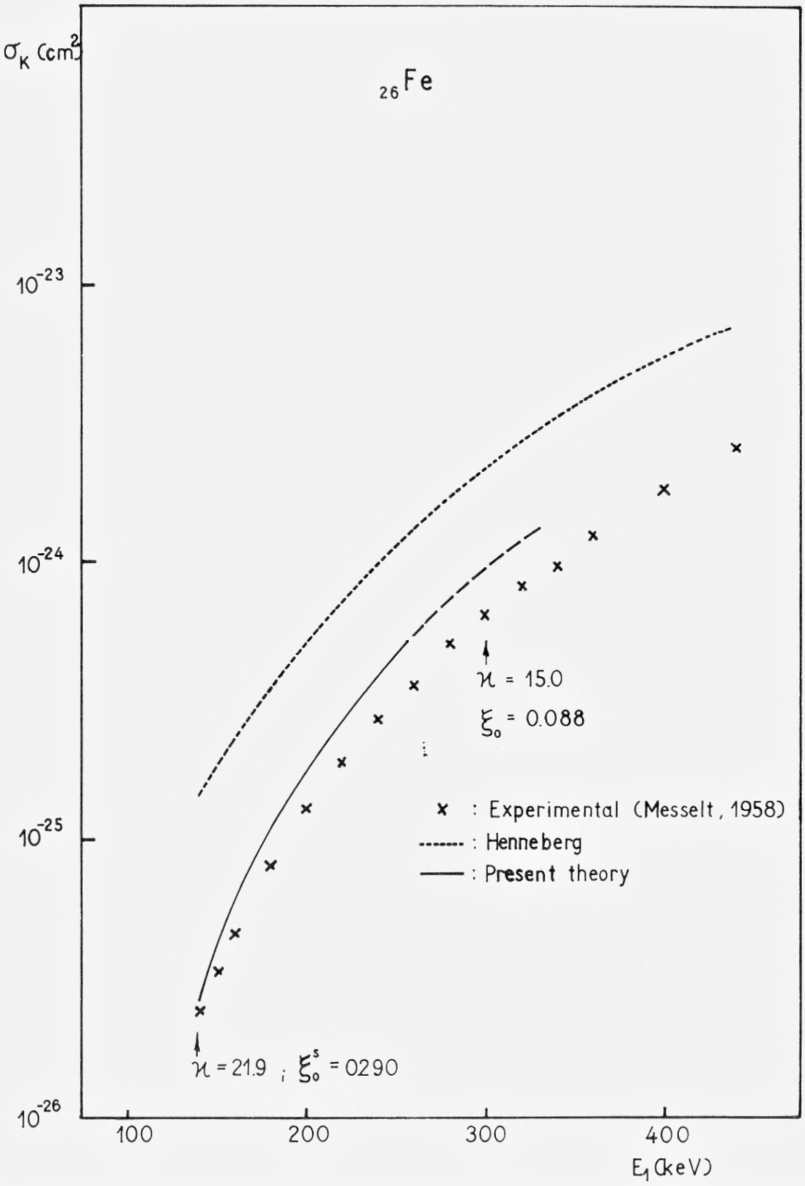

Fig. 3.6. *K*-ionization cross section for an iron target as a function of the proton energy. In this and the following calculations, five terms in the series development (3.39) have been taken into account. The dotting of the theoretical curve indicates the energy region in which the convergence of the series becomes slow and in which higher multipoles in the interaction may begin to contribute significantly.

For comparison, the values obtained from Henneberg's expression (as evaluated by Messelt$^{(4)}$) are shown.

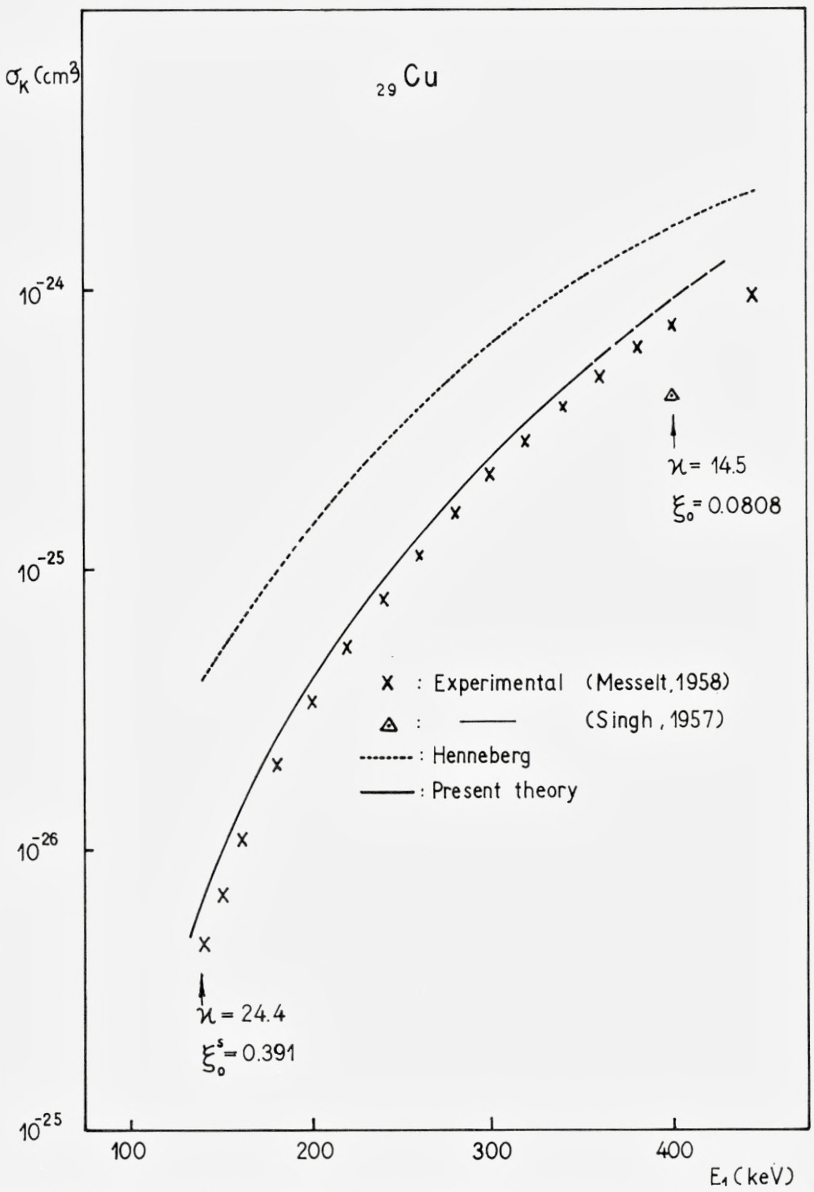

Fig. 3.7. *K*-ionization cross section for a copper target as a function of the proton energy. For further details see the text of fig. 3.6.

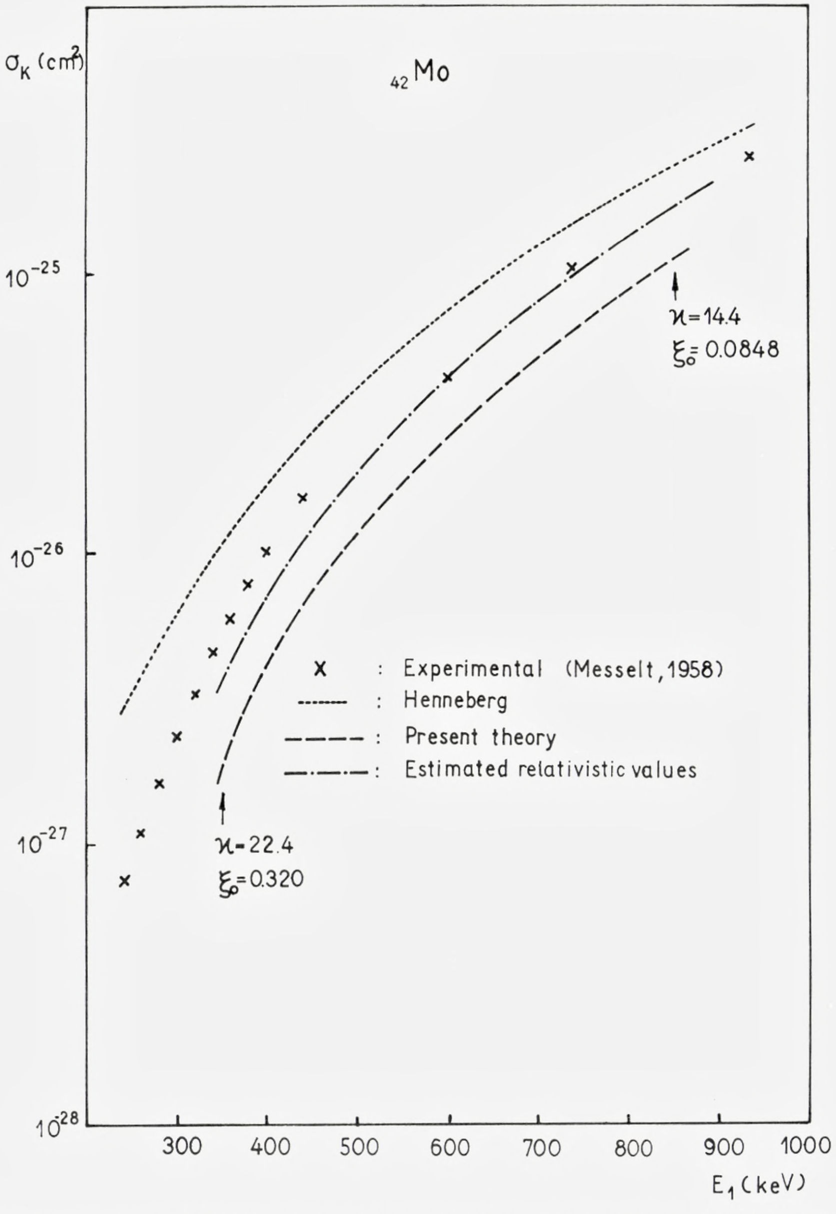

Fig. 3.8. σ_K for a molybdenum target as a function of the proton energy E_1. The non-relativistic theory is incapable of explaining the observed data. The dot-and-dash curve shows the approximate relativistic values obtained on multiplication of the dominating terms in Jamnik and Zupančič's formula$^{(8)}$ by the curvature factors found by the non-relativistic methods.

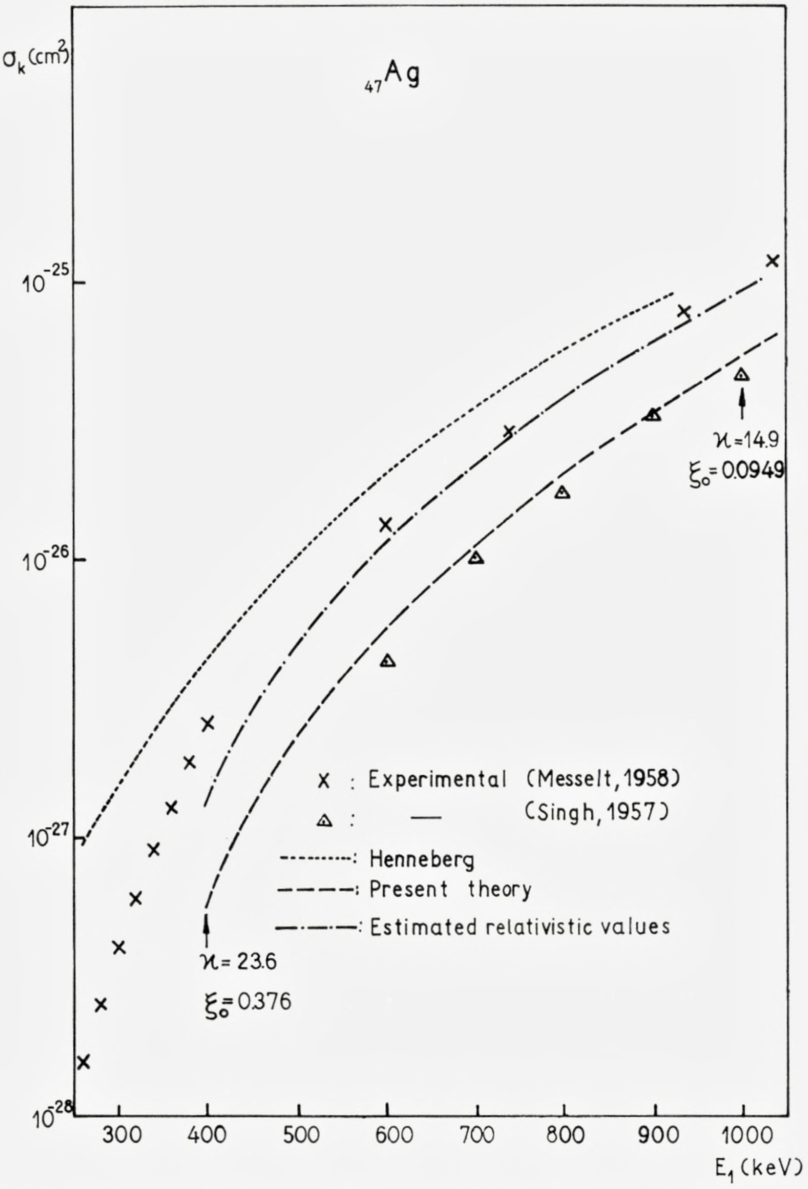

Fig. 3.9. σ_K for a silver target as a function of the proton energy. The relativistic effects are here more pronounced than for molybdenum.

above, is seen in the figures; it appears to improve the agreement with experiments considerably.

In consequence of the domination of the monopole terms, the angular distribution of the ejected electrons should be approximately isotropic.

For higher bombarding energies $\left(\frac{\alpha}{q_0} > 1\right)$ the angular distribution of the ejected electrons should in principle be evaluated by the methods of Massey and Mohr (cf. ref. 23)*.

4. Pair Production by Slow Protons

The cross section for pair production by protons impinging on tantalum was recently investigated by Stephens and Staub(11, 12). Their proton energy was $E_1 = 1.5$ MeV. The cross section was found to be less than $2 \cdot 10^{-32}$ cm² and thus smaller by a factor of a hundred or more than the value predicted by Born-approximation calculations as made by Heitler and Nordheim(13).

One observes that the $\varkappa$ and ξ_0 values corresponding to this process are about 19 and 3 respectively. The use of methods analogous to the one applied to the K-ionization should therefore be justified.

In the present energy region we may carry through the calculations by taking into account only the electrostatic interactions between the particles (see ref. 13).

Considerations analogous to those in 3, b, (i) lead to the conclusion that only contributions from S-states play a part in the calculation of cross sections. This is due to the smallness of the parameter k/q_0, where k is now any of the electron momenta. One has for sufficiently small values of E_1

$$k/q_0 \leq \frac{\sqrt{4\, E_1 \frac{m}{M_1} (\varDelta E - 2\, mc^2)}}{\varDelta E} < \sqrt{\frac{4\, m}{M_1}\left(1 - \frac{2\, mc^2}{E_1}\right)} \ll 1. \quad \Bigg\} \qquad (4.1)$$

The cross section for pair production is then given by a formula completely analogous to eq. (3.16). Following simple hole-theory arguments,

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* Note the misprints in this reference.

one inserts for the final and initial states the Coulomb wave functions for an electron and a hole in the continuum. By using integral representations of these functions(15) one gets

$$\left.\begin{aligned} \frac{d\sigma}{d(E^+E^-)} &= \frac{2\pi}{\hbar^2} d^2 e^4 \,|\, N_+ \,|^2 \,|\, N_- \,|^2 \int_1^\infty \varepsilon \, d\varepsilon \\ &\times \left| \int_{-\infty}^{+\infty} dt e^{\mathrm{i}\omega \mathrm{t}} \left\{ \frac{1}{\Gamma(1-i\eta_-)\,\Gamma(1+i\eta_-)\,\Gamma(1-i\eta_+)\,\Gamma(1+i\eta_+)} \right.\right. \\ &\times \left.\left. \int_0^1 du \left(\frac{u}{1-u}\right)^{i\eta_-} \int_0^1 dv \left(\frac{v}{1-v}\right)^{i\eta_+} \left[\int_0^R \frac{dr}{R} r^2 e^{-rb} + \int_R^\infty dr\, r\, e^{-rb} \right] \right\} \right|^2, \end{aligned}\right\} \tag{4.2}$$

where

$$\omega = \frac{\Delta E}{\hbar}$$

and

$$\left.\begin{aligned} b = &- ik_- + 2\, ik_- u \\ &- ik_+ + 2\, ik_+ v. \end{aligned}\right\} \tag{4.3}$$

Following the procedure given in 3, b, (i), we obtain a formula identical with (3.23). This formula is valid on conditions similar to (2.9) and (2.10). As, in the cases of interest, ξ is of the order of magnitude one or larger, only small values of ε will contribute to the cross section. In the case considered here

$$\left.\begin{aligned} |\, b \,|\, d &\simeq \frac{kZ_1 Z_2 e^2}{2 E_1} = \frac{kZ_1 Z_2 e^2}{2\Delta E} \frac{\Delta E}{E_1} \\ &< \frac{k Z_1 Z_2 e^2}{2 \cdot 2\, mc^2} \frac{\Delta E}{E_1} = \frac{1}{4} \zeta\, Z_1 Z_2 \beta_{el} \frac{\Delta E}{E_1} << 1 \\ &\left(\zeta \simeq \frac{1}{137},\ \beta_{el} = v/c\right). \end{aligned}\right\} \tag{4.4}$$

Because of this inequality only the first term of k_0' in the equation corresponding to (3.26, a) will be of importance. The u and v integrations are then trivial. (In the case of the general term b^{2n}, an F_2-function will enter.) The ε integration is now easily carried out, giving

$$\frac{d\sigma}{d(E_+ E_-)} = \frac{2\pi}{\hbar^2} \frac{d^2 e^4}{v_1^2} \,|\, N_+ \,|^2 \,|\, N_- \,|^2 \frac{2\, e^{-\pi\xi}}{9} \frac{d^6}{\xi^4} \,|\, K'_{i\xi}(\xi) \,|^2. \tag{4.5}$$

The expression (4.5) as a function of ξ shows that the important contributing electron energies are confined to values much smaller than the K binding energy of the target. Thus the inequality

$$|\eta_\pm| > 1 \tag{4.6}$$

is well fulfilled.

An approximate formula for $K'_{i\xi}(\xi)$ can be found from ref. 17, sec. 8.42. Then

$$\frac{d\sigma}{d(E^+E^-)} = C_1 \frac{Z_2^{10}}{E_1^9} S \frac{e^{-2\pi\xi}}{\xi^{16/3}} \tag{4.7}$$

Here

$$C_1 = \left(\frac{2}{3}\right)^4 \pi \left(\frac{\pi\, 6^{\frac{2}{3}}}{\Gamma\left(\frac{1}{3}\right)}\right)^2 \left(\frac{e^2}{2\, a_0}\right)^7 \frac{M_1}{m}\, a_0^2$$

and

$$S = \frac{1}{\left(1 - e^{-2\pi\frac{\alpha}{k_-}}\right)\left(e^{2\pi\frac{\alpha}{k_+}} - 1\right)} \tag{4.8}$$

(a_0 is the Bohr radius).

In order to obtain the total σ we must perform the integrations over E^+ and E^-. Because of the inequality (4.6) we have

$$\sigma = C_1 \frac{Z_2^{10}}{E_1^9} \int_0^{E^+_{\max}} dE^+\, e^{-2\pi\frac{\alpha}{k_+}} \int_0^{E^-_{\max}} dE^-\, f(E^+, E^-) \tag{4.9}$$

with

$$\left.\begin{aligned} f &= \frac{e^{-2\pi\mu(2\,mc^2 + E^+ + E^-)}}{(\mu\,(2\,mc^2 + E^+ + E^-))^{16/3}} \\ u &= \frac{Z_2 \cdot \zeta}{2\, E_1\, \beta} \\ &\left(\beta = \frac{v_1}{c}\right). \end{aligned}\right\} \tag{4.10}$$

Expanding the function f around $E^+ + E^- = 0$ and introducing the notation

$$\gamma_1 = 2\,\mu\, mc^2 = Z_2 \cdot \zeta \frac{mc^2}{\beta E_1}, \tag{4.11}$$

we obtain

$$\left.\begin{aligned} f &\simeq \frac{e^{-2\pi\gamma_1}}{\gamma_1^{16/3}}\left(1-\delta_1\left(E^+ + E^-\right)\right) \\ \text{with}\qquad \delta_1 &= \frac{2\,\mu}{\gamma_1}\left(\pi\gamma_1+\frac{8}{3}\right). \end{aligned}\right\}\quad (4.12)$$

Consistently with (4.12) we introduce the following values for the maximum electron energies:

$$\left.\begin{aligned} E^-_{\max} &= \frac{1-\delta_1 E^+}{\delta_1} \\ E^+_{\max} &= \frac{1}{\delta_1}. \end{aligned}\right\}\quad (4.13)$$

Although the expansion in $E^+ + E^-$ may not always be very accurate, the errors involved are not serious for our present purpose of obtaining an estimate of the order of magnitude of the cross section.

The double integration can now easily be carried out, leading to

$$\left.\begin{aligned} \sigma &= 4\,\pi^2\,\frac{e^2}{2\,a_0}\,C_1\,\frac{Z_2^{12}}{E_1^9}\,\frac{e^{-2\pi\gamma_1}}{\delta_1\gamma_1^{16/3}} \\ &\times\left\{I_1-\delta_1 W I_2+\left(\frac{\delta_1 W}{2}\right)^2 I_3\right\} \end{aligned}\right\}\quad (4.14)$$

with

$$\left.\begin{aligned} I_{i\,(=1,2,3)} &= \int_t^\infty \frac{e^{-x}}{x^{2i+1}}\,dx;\; t=\frac{2\,\pi\,\alpha\,\hbar}{\sqrt{2\,m E^+_{\max}}} \\ W &= 8\,\pi^2 Z_2^2\,\frac{e^2}{2\,a_0}. \end{aligned}\right\}\quad (4.14,\ \mathrm{a})$$

A numerical evaluation by means of this formula gives $\sigma \simeq 10^{-48}\ \mathrm{cm}^2 \simeq 10^{-13}\,\sigma_{\mathrm{Born}}$. This result is indeed consistent with the experimental results of STEPHENS and STAUB. The direct curvature effects, $e^{-2\pi\xi}$, give rise to a factor of about 10^{-10} in the cross section. In addition comes the factor $e^{-2\pi\eta_+}$ resulting from the use of Coulomb wave functions for the positrons. Because of the inequality (4.6) this factor, together with the possible errors introduced through the evaluation of the integrals in (4.9), accounts well for the remaining divergence from the earlier calculations. Hence, the conclusion is that, in the low-energy region, the Coulomb repulsion very greatly reduces the cross sections for pair production by heavy, charged particles.

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Appendix I

The Equivalence Between First-order, Time-dependent Perturbation Theory and the Born Approximation at High Energies

1. Let the physical situation be as in fig. 3.2. It is then easily shown (cf. eqs. (3.1), (3.2) and (3.4)) that

$$\left.\begin{aligned}\int_{-\infty}^{\infty} \frac{e^{i\omega t}}{|\underline{r}-\underline{R}(t)|}\,dt &= \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{\sqrt{x^2+(p-y)^2+(v_1 t-z)^2}}\,dt \\ &= \frac{2}{v_1}\,e^{i\frac{\omega}{v_1}z}\,K_0\left(\frac{\omega}{v_1}\varrho\right)\end{aligned}\right\} \quad (\text{A I, } 1)$$

(see ref. 17, p. 172).

Introducing the energy and mass of the projectile, we find

$$\left.\begin{aligned}\frac{d\sigma}{dE_f} = 4\pi Z_1^2 \frac{M_1}{E_1}\frac{e^4}{\hbar^2} &\int d\tau\,\psi_f^*(\underline{r})\,\psi_i(\underline{r}) \int d\tau'\,\psi_f(\underline{r}')\,\psi_i^*(\underline{r}') \\ &\times e^{i\frac{\omega}{v_1}(z-z')} \int_0^{\infty} p\,dp\,K_0\left(\frac{\omega}{v_1}\varrho\right) K_0\left(\frac{\omega}{v_1}\varrho'\right).\end{aligned}\right\} \quad (\text{A I, } 2)$$

In Appendix II, a it is shown that

$$\int_0^\infty p\,dp\, K_0(q_0\varrho)\, K_0(q_0\varrho') = \frac{r_1 K_1(q_0 r_1)}{2\, q_0}, \qquad \text{(A I, 3)}$$

where

$$r_1^2 = (x-x')^2 + (y-y')^2.$$

The cross section may thus be written as

$$\frac{d\sigma}{dE_f} = 2\pi Z_1^2 \frac{M_1}{E_1}\frac{e^4}{\hbar^2}\frac{1}{q_0}\int d\tau\, \psi_f^* \psi_i \int d\tau'\, \psi_f \psi_i^*\, e^{iq_0(z-z')}\, r_1 K_1(q_0 r_1). \qquad \text{(A I, 4)}$$

2. Within the range of validity of the first Born approximation the above cross section is given by

$$\left.\begin{aligned} \frac{d\sigma}{dE_f} &= \frac{1}{4\pi^2} Z_1^2 M_1^2 \frac{e^4}{\hbar^4}\frac{k_f}{k_i}\int d\Omega \\ \times &\left|\iint \exp\left\{ i(k_f\underline{n}_1 - k_i\underline{n}_0)\underline{R}_c\right\}\psi_i(\underline{r})\,\psi_f^*(\underline{r})\, d\tau_c\, d\tau \frac{1}{|\underline{R}_c - \underline{r}|}\right|^2 \end{aligned}\right\} \qquad \text{(A I, 5)}$$

(see ref. 24, Chapters 11 and 12); $k_i \cdot \hbar \cdot \underline{n}_0$ and $k_f \cdot \hbar \cdot \underline{n}_1$ are the initial and final momentum vectors of the colliding particle. $\underline{R}_c$ is its position vector and $d\tau_c$ the volume element in the bombarding-particle space.

By a theorem given by Bethe⁽⁶⁾ this may be written as

$$\left.\begin{aligned} \frac{d\sigma}{dE_f} &= 4 Z_1^2 M_1^2 \frac{e^4}{\hbar^4}\frac{k_f}{k_i}\int d\tau\, \psi_i \psi_f^* \int d\tau'\, \psi_i^*\, \psi_f \\ \times &\int d\varphi\, d\theta_e \sin\theta_e \frac{\exp\left\{ i(k_f\underline{n}_1 - k_i\underline{n}_0)(\underline{r}' - \underline{r})\right\}}{|k_f\underline{n}_1 - k_i\underline{n}_0|^4}. \end{aligned}\right\} \qquad \text{(A I, 6)}$$

We choose the axis of the polar coordinate system in the direction of the incoming particle.

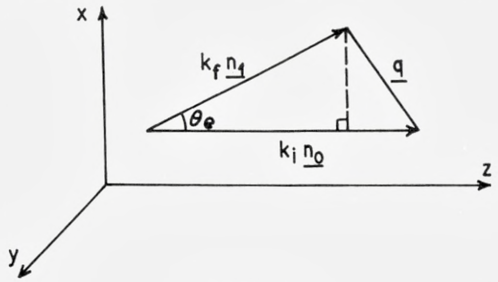

Fig. A I, 1.

Then

$$\left.\begin{aligned} |\,k_f \underline{n}_1 - k_i \underline{n}_0\,|^2 &= k_f^2 + k_i^2 - 2\,k_i k_f \cos\theta_e \\ &= q_0^2 + 2\,k_i k_f (1-\cos\theta_e) \\ q_0 &= k_i - k_f. \end{aligned}\right\} \quad (\mathrm{A\,I},\ 7)$$

We define

$$\left.\begin{aligned} \underline{R}_1 &= \underline{r} - \underline{r}' \\ \underline{R}_1 &= (x-x',\ y-y',\ z-z'). \end{aligned}\right\} \quad (\mathrm{A\,I},\ 8)$$

Consequently,

$$\left.\begin{aligned} (k_f \underline{n}_1 - k_i \underline{n}_0)(-\underline{R}_1) &= -(x-x')\,k_f \sin\theta_e \sin\varphi \\ -(y-y')\,k_f \sin\theta_e \cos\varphi - (z-z')\,k_f&(\cos\theta_e - 1) + (z-z')\,q_0, \end{aligned}\right\} \quad (\mathrm{A\,I},\ 9)$$

and hence

$$\left.\begin{aligned} I &= \int d\varphi \sin\theta_e\, d\theta_e \frac{\exp\{i(k_f \underline{n}_1 - k_i \underline{n}_0)(\underline{r}' - \underline{r})\}}{|\,k_f \underline{n}_1 - k_i \underline{n}_0\,|^4} \\ &= e^{iq_0(z-z')} \int d\varphi \sin\theta_e\, d\theta_e \\ &\times \frac{\exp\{\,i\,[-k_f \sin\theta_e((x-x')\sin\varphi + (y-y')\cos\varphi) - k_f(z-z')(\cos\theta_e - 1)]\,\}}{(q_0^2 + 2\,k_i k_f (1-\cos\theta_e))^2}. \end{aligned}\right\} \quad (\mathrm{A\,I},10)$$

From simple geometrical considerations this may be written as

$$\left.\begin{aligned} I &= \frac{e^{iq_0(z-z')}}{q_0^4} \int d\varphi_1 \sin\theta_e\, d\theta_e \frac{\exp\{i[-k_f r_1 \cos\varphi_1 \sin\theta_e - k_f(z-z')(\cos\theta_e - 1)]\}}{\left(1 + \dfrac{2\,k_i k_f}{q_0^2}(1-\cos\theta_e)\right)^2} \\ r_1^2 &= (x-x')^2 + (y-y')^2. \end{aligned}\right\} \quad (\mathrm{A\,I},11)$$

As

$$\int_0^{2\pi} d\varphi_1 \exp\left\{-ik_f r_1 \sin\theta_e \cos\varphi_1\right\} = 2\,\pi\, J_0(k_f r_1 \sin\theta_e), \quad (\mathrm{A\,I},\ 12)$$

we have

$$I = 2\,\pi \frac{e^{iq_0(z-z')}}{q_0^4} \int_0^{\pi} \sin\theta_e\, d\theta_e \frac{J_0(k_f r_1 \sin\theta_e)\exp\{-ik_f(z-z')(\cos\theta_e - 1)\}}{\left(1 + \dfrac{2\,k_i k_f}{q_0^2}(1-\cos\theta_e)\right)^2}. \quad (\mathrm{A\,I},\ 13)$$

The incoming particle is supposed to suffer little momentum change in the collision:

$$q_0^2 \ll k_i k_f. \quad (\mathrm{A\,I},\ 14)$$

Putting in the denominator

$$1 - \cos\theta_e \approx \frac{\theta_e^2}{2}$$

and in the numerator

$$\cos\theta_e - 1 \approx 0,$$

we deduce the approximate relation

$$I \approx 2\pi \frac{e^{iq_0(z-z')}}{q_0^4} \int_0^{\pi} \theta_e d\theta_e \frac{J_0(k_f r_1 \theta_e)}{\left(1 + \frac{k_i k_f}{q_0^2}\theta_e^2\right)^2}. \qquad \text{(A I, 15)}$$

Using an integral formula given by WATSON (ref. 17, p. 425), we find the following expression

$$I \approx \frac{2\pi e^{iq_0(z-z')}}{q_0^4} \frac{q_0^2}{k_i k_f} \int_0^{\infty} \frac{y dy J_0(q_0 r_1 y)}{(1+y^2)^2} = \frac{\pi e^{iq_0(z-z')}}{q_0 k_i k_f} r_1 K_1(q_0 r_1). \qquad \text{(A I, 16)}$$

Together with (A I, 6) this gives

$$\frac{d\sigma}{dE_f} = 4\pi Z_1^2 M_1^2 \frac{e^4}{\hbar^4} \frac{k_f}{k_i} \int d\tau \, \psi_i \psi_f^* \int d\tau' \psi_i^* \psi_f \frac{e^{iq_0(z-z')}}{q_0 k_i k_f} r_1 K_1(q_0 r_1). \qquad \text{(A I, 17)}$$

Introducing the kinetic energy of the bombarding particle, we finally get

$$\frac{d\sigma}{dE_f} = 2\pi Z_1^2 \frac{M_1}{E_1} \frac{e^4}{\hbar^2} \frac{1}{q_0} \int d\tau \, \psi_i \psi_f^* \int d\tau' \, \psi_i^* \psi_f e^{iq_0(z-z')} r_1 K_1(q_0 r_1), \qquad \text{(A I, 18)}$$

which is identical with the expression (A I, 4).

A proof similar to this one was given by FRAME as early as 1931(14). However, he did not calculate the probability of ionization as a function of the impact parameter.

Appendix II

Mathematical Details of the Calculations

a. An integral formula involving two modified Bessel functions of the third kind and of zeroth order

The integral in eq. (A I, 3) can be written

$$I_1 = \int_0^\infty p dp \, K_0(q_0 \varrho) \, K_0(q_0 \varrho') = \frac{1}{2\pi} \int d\underline{p} \, K_0(q_0 p) \, K_0(q_0 |\underline{r}_1 - \underline{p}|). \qquad \text{(A II, 1)}$$

The last integration is performed in the (p, φ) – plane, where φ is the angle $(\underline{p}, \underline{r}_1)$.

Using the relation

$$2\pi K_0(q_0 r_1) \, I_0(q_0 p) = \int_{-\pi}^{\pi} K_0(q_0 |\underline{r}_1 - \underline{p}|) \, d\varphi, \; r_1 > p \qquad \text{(A II, 2)}$$

and the corresponding one for $r_1 < p$ (see H.T.F. 2, Chapter 7), we get

$$I_1 = K_0(q_0 r_1) \int_0^{r_1} p dp \, I_0(q_0 p) \, K_0(q_0 p) + I_0(q_0 r_1) \int_{r_1}^\infty p dp \, K_0^2(q_0 p) = A + B. \qquad \text{(A II, 3)}$$

It is easily shown by application of well-known integral formulae that

$$\left.\begin{aligned} A &= K_0(q_0 r_1) \frac{r_1^2}{2} \left(K_0(q_0 r_1) \, I_0(q_0 r_1) + K_1(q_0 r_1) \, I_1(q_0 r_1)\right) \\ B &= I_0(q_0 r_1) \frac{r_1^2}{2} \left(K_1^2(q_0 r_1) - K_0^2(q_0 r_1)\right) \end{aligned}\right\} \qquad \text{(A II, 4)}$$

or

$$\left.\begin{aligned} A + B &= \frac{r_1^2}{2} K_1(q_0 r_1) \left(I_0 K_1 + K_0 I_1\right) \\ I_1 &= \frac{r_1}{2 q_0} K_1(q_0 r_1). \end{aligned}\right\} \qquad \text{(A II, 5)}$$

b. Evaluation of the straight-line matrix element

(i) *General procedure*

When the non-relativistic Coulomb eigenfunctions are put into eq. (3.3), the φ-part of the integration is easily carried out:

$$\left.\begin{aligned}&\int_{-\pi}^{\pi} d\varphi\, e^{-im\varphi} K_0\left(q_0\left(r^2\sin^2\theta + p^2 - 2\,pr\sin\theta\cos\varphi\right)^{1/2}\right)\\ &\qquad = 2\pi\begin{cases}K_m(q_0\, r\sin\theta)\, I_m(q_0\, p), & r\sin\theta > p\\ K_m(q_0\, p)\, I_m(q_0\, r\sin\theta), & r\sin\theta < p\end{cases}\\ &\qquad = 2\pi\int_0^\infty dt\,\frac{t}{t^2+q_0^2}\, J_m(pt)\, J_m(rt\sin\theta)\end{aligned}\right\}\quad (\mathrm{A\ II,\ 6})$$

(see H.T.F. 7.14, 2, eqs. (77) and (57)).

Then

$$\left.\begin{aligned}\mathrm{M}_p(l,m) &= 2\pi N_i N_f^{l,k}(-1)^m\left[\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m!)}\right]^{1/2}\frac{1}{2\sqrt{\pi}}\\ &\times\int_0^\infty dt\,\frac{t}{t^2+q_0^2}\, J_m(pt)\int r^2\, dr\sin\theta\, d\theta\, e^{-\alpha r}\, e^{iq_0 r\cos\theta}\\ &\qquad\times P_l^m(\cos\theta)\, R_l\left(\frac{r}{\lambda}\right) J_m(rt\sin\theta)\end{aligned}\right\}\quad (\mathrm{A\ II,\ 7})$$

with

$$\lambda = i/k = i\eta a,\quad a = -\frac{a_0}{Z_2}.$$

The θ-part of the integral is given by

$$I_\theta = \int_0^\pi d\theta\sin\theta\, e^{iq_0 r\cos\theta}\, P_l^m(\cos\theta)\, J_m(rt\sin\theta). \qquad (\mathrm{A\ II,\ 8})$$

Introducing the Gegenbauer polynomials, we obtain

$$\left.\begin{aligned}I_\theta &= \frac{(-1)^m(2m)!}{2^m\, m!}\int_0^\pi d\theta(\sin\theta)^{m+1}\, e^{iq_0 r\cos\theta}\, C_{l-m}^{m+\frac{1}{2}}(\cos\theta)\, J_m(rt\sin\theta)\\ &= \frac{(-1)^m(2m)!}{2^m\, m!}\, i^{l-m}\sqrt{2\pi}\,(rs)^{-\frac{1}{2}}\left(\frac{t}{s}\right)^m C_{l-m}^{m+\frac{1}{2}}\left(\frac{q_0}{s}\right) J_{l+\frac{1}{2}}(sr)\end{aligned}\right\}\quad (\mathrm{A\ II,\ 9})$$

(cf. ref. 17, p. 379, eq. (1)).

Here

$$s^2 = t^2 + q_0^2.$$

From this we have

$$\left.\begin{aligned} \mathrm{M}_p(l,m) = \sqrt{\pi}\, N_i N_f^{l,k}\, \frac{(2\,m)!}{2^m\, m!}\left[\frac{2\,l+1}{2}\,\frac{(l-m)\,!}{(l+m)\,!}\right]^{1/2} i^{l-m} \\ \times \int_0^\infty dt\, t^{m+1} J_m(pt)\, s^{-m-\frac{5}{2}}\, C_{l-m}^{m+\frac{1}{2}}\left(\frac{q_0}{s}\right) \\ \times \int_0^\infty r^2\, dr\, r^{-\frac{1}{2}} e^{-\alpha r} J_{l+\frac{1}{2}}(sr)\, R_l(r/\lambda). \end{aligned}\right\} \quad (\mathrm{A\,II},\ 10)$$

Expressing the ordinary Bessel function $J_{l+\frac{1}{2}}(s\,r)$ in terms of a Whittaker function, we obtain the following radial integral:

$$I_r = \frac{2^{-2\,l-\frac{5}{2}}\, i^{-l-1}\,\lambda}{\Gamma\left(l+\frac{3}{2}\right)}\, s^{-\frac{1}{2}} \int_0^\infty dr\, e^{-\alpha r} M_{0,l+\frac{1}{2}}(2\,i\,sr)\, M_{-i\eta,\,l+\frac{1}{2}}(-2\,ikr). \quad (\mathrm{A\,II},\ 11)$$

This integral can be evaluated by means of a formula given by ERDÉLYI$^{(25)}$:

$$\left.\begin{aligned} \int_0^\infty dr\, e^{-\alpha r} M_{0,\,l+\frac{1}{2}}(2\,isr)\, M_{-i\eta,\,l+\frac{1}{2}}(-2\,ikr) \\ = (2\,is)^{l+1}(-2\,ik)^{l+1}(\alpha+i(s-k))^{-(2\,l+3)}\,\Gamma(2\,l+3) \\ \times F_2\left\{2\,l+3,\, l+1,\, l+1+i\eta,\, 2\,l+2,\, 2\,l+2;\, \frac{2\,is}{\alpha+i(s-k)},\, \frac{-2\,ik}{\alpha+i(s-k)}\right\}. \end{aligned}\right\} \quad (\mathrm{A\,II},\ 12)$$

Eq. (3.5) is now easily derived.

(ii) *Simplification of some hypergeometric functions*

1. Using relations given by APPELL and KAMPÉ DE FÉRIET$^{(26)}$, we find

$$\left.\begin{aligned} \alpha_1 F_2(\alpha_1+1,\beta,\beta',\alpha_1,\alpha_1;x,y) = (\alpha_1-\beta-\beta')\,F_2(\alpha_1,\beta,\beta',\alpha_1,\alpha_1;x,y) \\ +\beta F_2(\alpha_1,\beta+1,\beta',\alpha_1,\alpha_1;x,y)+\beta'\,F_2(\alpha_1,\beta,\beta'+1,\alpha_1,\alpha_1;x,y) \\ = (1-x)^{-\beta}(1-y)^{-\beta'}\Big\{[(\alpha_1-\beta-\beta')-(\beta'-\beta)(1-x)^{-1}] \\ \times {}_2F_1\left(\beta,\beta',\alpha_1;\ \frac{xy}{(1-x)(1-y)}\right) \\ +\beta'\,[(1-x)^{-1}+(1-y)^{-1}]\,{}_2F_1\left(\beta,\beta'+1,\alpha_1;\frac{xy}{(1-x)\,(1-y)}\right)\Big\}. \end{aligned}\right\} \quad (\mathrm{A\,II},\ 13)$$

Putting

$$\left.\begin{aligned} \alpha_1 &= 2\,l+2 \\ \beta &= l+1 \\ \beta' &= l+1+i\eta \\ x &= \frac{2\,is}{\alpha+i(s-k)} \\ y &= \frac{-2\,ik}{\alpha+i(s-k)}\,, \end{aligned}\right\} \quad \text{(A II, 14)}$$

we deduce

$$\left.\begin{aligned} F_2 = \frac{1}{l+1}\left(\frac{\alpha-i(s+k)}{\alpha+i(s-k)}\right)^{-(l+1)} \left(\frac{\alpha+i(s+k)}{\alpha+i(s-k)}\right)^{-(l+1+i\eta)} \\ \times \frac{1}{\alpha-i(s+k)}\left\{(-i\eta)\,(\alpha-ik)\,{}_2F_1\left(l+1,\,l+1+i\eta,\,2\,l+2;\,\frac{4\,sk}{\alpha^2+(s+k)^2}\right)\right. \\ \left. +\,(l+1+i\eta)\,\alpha\,\frac{\alpha+i(s-k)}{\alpha+i(s+k)}\,{}_2F_1\left(l+1,\,l+2+i\eta,\,2\,l+2;\,\frac{4\,sk}{\alpha^2+(s+k)^2}\right)\right\}. \end{aligned}\right\} \quad \text{(A II, 15)}$$

2. According to H.T.F. 2.8, eq. (9) we have

$${}_2F_1(1,1+i\eta,2;-z) = \sum_{n=1}^{\infty}\binom{-i\eta}{n} z^n \frac{1}{z(-i\eta)} = ((1+z)^{-i\eta}-1)\frac{1}{(-z\,i\eta)}. \quad \text{(A II, 16)}$$

Using the analogous formula for ${}_2F_1(1,2+i\eta,2;-z)$, we easily deduce eq. (3.8).

c. Some integrals leading to modified Bessel functions of the third kind and of complex order

In eq. (3.21) we treat the terms in the integral separately. In

$$I_1 = \int_{-\infty}^{\infty} dw\, e^{i\xi\varepsilon\sinh w+i\xi w} \quad \text{(A II, 17)}$$

we make the transformation

$$w \longrightarrow -w',$$

which leads to

$$I_1 = 2\,e^{-\frac{\pi}{2}\xi}\,K_{i\xi}(\varepsilon\,\xi) \quad \text{(A II, 18)}$$

(cf. ref. 17, p. 182, eq. (10)).

In

$$I_2 = \int_{-\infty}^{\infty} dw\, e^{i\,\xi\,(\varepsilon \sinh w + w) - bd\,\varepsilon \cosh w} \qquad \text{(A II, 19)}$$

we put

$$e^w = y.$$

Then

$$I_2 = \int_0^{\infty} \frac{dy}{y^{1-i\,\xi}}\, e^{\frac{\varepsilon}{2}\,((-y\,(-i\,\xi + bd) - \frac{1}{y}\,(i\,\xi + bd))}.$$

Making the substitution

$$y\,\frac{\varepsilon}{2}\,(bd - i\xi) = t,$$

we obtain

$$I_2 = \left(\frac{2}{\varepsilon}\,\frac{1}{bd - i\xi}\right)^{i\,\xi} \int_0^{\infty - i\,\infty} \frac{dt}{t^{1-i\,\xi}}\, e^{\left(-t - \frac{\varepsilon^2}{4\,t}\,(b^2\,d^2 + \xi^2)\right)}.$$

Hence,

$$I_2 = \left(\frac{bd + i\xi}{bd - i\xi}\right)^{\frac{i\,\xi}{2}} K_{-i\,\xi}\left(\varepsilon\sqrt{b^2 d^2 + \xi^2}\right) \qquad \text{(A II, 20)}$$

(cf. ref. 17, p. 183, eq. (15)).

The integrals

$$I_3 = \int_{-\infty}^{\infty} dw\, e^{i\,\xi\,(\varepsilon \sinh w + w) + w - bd\,\varepsilon \cosh w} \qquad \text{(A II, 21)}$$

and

$$I_4 = \int_{-\infty}^{\infty} dw\, e^{i\,\xi\,(\varepsilon \sinh w + w) - w - bd\,\varepsilon \cosh w} \qquad \text{(A II, 22)}$$

may be treated in exactly the same way as I_2.

Thus,

$$I_3 = 2\left(\frac{bd + i\xi}{bd - i\xi}\right)^{\frac{1 + i\,\xi}{2}} K_{-1-i\,\xi}\left(\varepsilon\sqrt{b^2\,d^2 + \xi^2}\right) \qquad \text{(A II, 23)}$$

$$I_4 = 2\left(\frac{bd + i\xi}{bd - i\xi}\right)^{\frac{-1 + i\,\xi}{2}} K_{1-i\,\xi}\left(\varepsilon\sqrt{b^2\,d^2 + \xi^2}\right). \qquad \text{(A II, 24)}$$

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THE ENERGY-MOMENTUM COMPLEX IN THE GENERAL THEORY OF RELATIVITY

BY

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København 1959
i kommission hos Ejnar Munksgaard

CONTENTS

Synopsis

It is shown that the expression for the complex of energy-momentum derived in an earlier paper from physical arguments also follows directly from the mathematical invariance properties of the theory. The usual method of infinitesimal coordinate transformations is generalized to the case of a variational principle where the integrant of the integral to be varied depends on the derivatives of the field variables of arbitrarily high order. The method is then applied separately to the gravitational field and the matter field. The transformation properties of the complex under arbitrary space-time transformations are derived, and a closer specification of the notion of "local systems of inertia" is given.

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1. Introduction and Summary

In a generally covariant theory like Einstein's theory of gravitation, where the field equations are derivable from a variational principle, it is possible to define a large number of quantities which are "conserved" (1). Therefore, extra criteria are needed in order to select out of this multitude of conserved quantities those which have a physical meaning. In particular, it becomes a problem to find the correct expressions for the pseudo-tensor of energy and momentum. For a Langrangean system where the field equations are derivable from a Langrangean density $\mathfrak{L}$, which is a function of the field variables and their first order derivatives only and which transforms like a scalar density under arbitrary space-time transformations, the well-known "method of infinitesimal transformations" leads to a natural choice of the energy-momentum complex.*

In the case of gravitational fields, the field equations may now be written in the Langrangean form with a Langrangean density $\mathfrak{L} = \mathfrak{L}\,(g^{ik},\ g_l^{ik})$ which is a scalar density only under arbitrary *linear* transformations. Therefore, in applying the method of infinitesimal transformations, one is restricted to linear transformations, and the "canonical" energy-momentum complex $\Theta_i^{\ k}$ obtained in this way does not possess all the transformation properties required for a physical interpretation of its components. The canonical complex $\Theta_i^{\ k}$ following from the invariance of $\mathfrak{L}$ under arbitrary infinitesimal linear transformations is of the form

$$\Theta_i^{\ k} = \sqrt{-g}\,(T_i^k + \vartheta_i^{\ k}) = s_i^{\ kl}{}_{,l}. \tag{1}$$

Here, T_i^k is the matter tensor which appears on the right-hand side of the gravitational field equations

$$G_{ik} \equiv R_{ik} - \frac{1}{2}\, g_{ik}\, R = -\varkappa\, T_{ik}. \tag{2}$$

---

* We adopt the terminology of Lorentz who used the denotation *complex* for a covariant quantity with tensor indices which, however, behaves like a tensor or tensor density under *linear* space-time transformations only.

$g = \det\{g_{ik}\}$ is the determinant of the metric tensor g_{ik} and

$$\sqrt{-g}\,\vartheta_i{}^k = \frac{1}{2\varkappa}\left\{\frac{\partial\,\mathfrak{L}}{\partial\, g_k^{lm}}\, g_i^{lm} - \delta_i^k\, \mathfrak{L}\right\}. \tag{3}$$

Further,

$$s_i{}^{kl} = \frac{1}{\varkappa}\frac{\partial\,\mathfrak{L}}{\partial\, g_l^{im}}\, g^{km} \tag{4}$$

is the quantity introduced by EINSTEIN and by TOLMAN (2), and $\Theta_i{}^k$ satisfies the divergence relation

$$\Theta_i{}^k{}_{,\,k} \equiv \frac{\partial\,\Theta_i{}^k}{\partial\, x^k} = 0\,. \tag{5}$$

A simple calculation shows (3) that $s_i{}^{kl}$ is of the form

$$s_i{}^{kl} = h_i{}^{kl} + a_i{}^{klm}{}_{,\,m} \tag{6}$$

where

$$\left.\begin{aligned} h_i{}^{kl} &= -h_i{}^{lk} = \frac{g_{in}}{2\varkappa\sqrt{-g}}\left[(-g)\,(g^{kn}\,g^{lm} - g^{ln}\,g^{km})\right]_{,m} \\ a_i{}^{klm} &= -a_i{}^{kml} = \frac{\sqrt{-g}}{2\varkappa}\,(\delta_i^l\,g^{km} - \delta_i^m\,g^{kl}). \end{aligned}\right\} \tag{7}$$

On account of the antisymmetry of the last quantity in l and m, $a_i{}^{klm}{}_{,\,l,\,m}$ is zero and, by (1) and (6), $\Theta_i{}^k$ may be expressed in terms of the "superpotentials" $h_i{}^{kl}$ as

$$\Theta_i{}^k = h_i{}^{kl}{}_{,\,l}\,. \tag{8}$$

Now, since $h_i{}^{kl}$ is antisymmetric in k and l, the relation (5) is a simple consequence of (8).

Although the integrals

$$P_i = \frac{1}{c}\int \Theta_i{}^4\, dx^1\, dx^2\, dx^3 \tag{9}$$

give correct values for the total energy and momentum of a closed system, at least if one applies quasi-Galilean coordinates, $\Theta_i{}^k$ is not the correct expression for the complex of energy and momentum, since it fails in a physically meaningful manner to account for the distribution of the energy and the energy current in space. In a recent paper in the Annals of Physics⁽⁴⁾, a different expression for the energy-momentum complex was proposed. It is defined by

$$\mathcal{T}_i{}^k = \sqrt{-g}\,(T_i{}^k + t_i{}^k) \tag{10}$$

$$\sqrt{-g}\, t_i{}^k = \sqrt{-g}\left(-\frac{1}{\varkappa} G_i^k + 2\,\vartheta_i{}^k\right) - \delta_i^k\, h_r{}^{rl}{}_{,l} + h_r{}^{rk}{}_{,i}. \tag{11}$$

If T_i^k is eliminated by means of the field equations (2), $\mathcal{T}_i{}^k$ may be expressed in terms of a superpotential $\chi_i{}^{kl}$ as

$$\mathcal{T}_i{}^k = \chi_i{}^{kl}{}_{,l} \tag{12}$$

with

$$\chi_i{}^{kl} = -\chi_i{}^{lk} = 2\,h_i{}^{kl} - \delta_i{}^k\, h_r{}^{rl} + \delta_i{}^l\, h_r{}^{rk} = \frac{\sqrt{-g}}{\varkappa}\,(g_{in,\,m} - g_{im,\,n})\, g^{km}\, g^{ln}, \tag{13}$$

and thus

$$\mathcal{T}_i{}^k{}_{,\,k} = 0. \tag{13'}$$

For a closed system, the complex $\mathcal{T}_i{}^k$ gives the same values for the total momentum and energy

$$P_i = \frac{1}{c}\int \mathcal{T}_i{}^4\, dx^1\, dx^2\, dx^3 \tag{14}$$

as the canonical quantity $\Theta_i{}^k$ in (9), at least in cases where the latter expressions give meaningful results at all. But the expressions (14) are more general and give correct values for the energy also when the integration is extended over finite regions of space. This is connected with the fact that $\mathcal{T}_4{}^k$ in contrast to $\Theta_4{}^k$, transforms like a vector density under arbitrary purely spatial transformations

$$\bar{x}^\iota = f^\iota(x^\varkappa), \quad \bar{x}^4 = x^4, \tag{15}$$

a property which is a necessary condition for the possibility of interpreting $\mathcal{T}_4{}^4$ and $\mathcal{T}_4{}^\varkappa$ as densities of energy and energy current, respectively. Moreover, in later papers⁽⁵⁾, it was shown that the pseudo-tensor density $\mathcal{T}_i{}^k$ defined by (10)–(13) is uniquely determined by this requirement. From a physical point of view, it would therefore seem that $\mathcal{T}_i{}^k$ is the correct expression for the complex of energy and momentum, but the fact remains that the method of infinitesimal transformations applied to the Lagrangean $\mathfrak{L}$ leads to the expression $\Theta_i^{\ k}$ which speaks in favour of the canonical quantity $\Theta_i^{\ k}$.

In the present paper we shall see, however, that the method of infinitesimal space-time transformations leads exactly to the complex $\mathcal{T}_i^{\ k}$ if one starts from another form of the variational principle. It is well known that the gravitational field equations may be obtained from a non-Lagrangean variational principle where the integrant of the integral to be varied is the curvature scalar density

$$\mathfrak{R} = \sqrt{-g}\, R \tag{16}$$

which is a function of the g^{ik} and their first *and* second order space-time derivatives. In fact, this variational principle is usually the starting point in the derivation of the Lagrangean principle. In contrast to the Lagrangean $\mathfrak{L}$, $\mathfrak{R}$ is a scalar density under *arbitrary* space-time transformations. The method of infinitesimal transformations applied to $\mathfrak{R}$ instead of $\mathfrak{L}$ therefore leads to a complex with more extended invariance properties and, as we shall see in section **3**, it just leads to the quantity $\mathcal{T}_i^{\ k}$.

In section **2**, the "method of infinitesimal transformations" is described in the general case of field equations derivable from a non-Lagrangean variational principle where the integrant V in the variation integral depends also on derivatives of the field variables of higher than the first order. In section **3**, the method is applied to the gravitational field, where V is equal to $\mathfrak{R}/\varkappa$. As mentioned above, this leads directly to the relations (10) – (13). As an illustration, we also apply the method to the matter Lagrangean density in which case of course the well-known results of ROSENFELD and of BELINFANTE(6) regarding the symmetrical form of the matter energy tensor are obtained. This is shown in section **4**. In the remaining sections, the transformation properties of $\mathcal{T}_i^{\ k}$ under arbitrary space-time transformations are investigated in some detail. The results obtained suggest a specification of the notion of a local system of inertia.

2. The Method of Infinitesimal Transformations for a Non-Lagrangean System of Fields

Consider a generally non-closed system of fields with the field variables $Y^A(x)$ and their space-time derivatives

$$Y^A_i \equiv \frac{\partial\, Y^A}{\partial\, x^i}, \qquad Y^A_{i,\,k} \equiv \frac{\partial^2\, Y^A}{\partial\, x^i\, \partial\, x^k}, \; \ldots,$$

the field equations of which are derivable from a variational principle. Let us first assume that the integrand V in the variation integral is an algebraic function of the Y^A and their first and second order derivatives only. The field equations will then be of the form

$$\frac{\delta\, V}{\delta\, Y^A} = -J^A, \tag{17}$$

where the J^A are the "sources" of the field depending in general also on variables other than the Y^A and their derivatives. Further, the

$$\frac{\delta\, V}{\delta\, Y^A} = \frac{\partial\, V}{\partial\, Y^A} - \left(\frac{\partial\, V}{\partial\, Y^A_i}\right)_{,\,i} + \left(\frac{\partial\, V}{\partial\, Y^A_{i,\,k}}\right)_{,\,i,\,k} \tag{18}$$

are the "variational derivatives" of V with respect to Y^A. The partial derivatives occurring in (18) are of a somewhat symbolic character, since the Y^A, Y^A_i, $Y^A_{i,\,k}$ are not in general truly independent variables. They are defined in the following way. Consider arbitrary variations $\delta\, Y^A$ of the Y^A, which imply definite variations

$$\delta\, Y^A_i = (\delta\, Y^A)_{,\,i}, \qquad \delta\, Y^A_{i,\,k} = (\delta\, Y^A)_{,\,i,\,k} \tag{19}$$

of the Y^A_i and $Y^A_{i,\,k}$ as well as of the algebraic expression $V(Y^A, Y^A_i, Y^A_{i,\,k})$. The partial derivatives in (18) are now *defined* as the coefficients of $\delta\, Y^A$, $\delta\, Y^A_i$, and $\delta\, Y^A_{i,\,k}$, respectively, in the variation $\delta\, V$ of V, i. e.

$$\delta\, V = \frac{\partial\, V}{\partial\, Y^A}\,\delta\, Y^A + \frac{\partial\, V}{\partial\, Y^A_i}\,\delta\, Y^A_i + \frac{\partial\, V}{\partial\, Y^A_{i,\,k}}\,\delta\, Y^A_{i,\,k} \tag{20}$$

(summation over A, i and k!)

Since $\delta\, Y^A_{i,\,k} = \delta\, Y^A_{k,\,i}$, we can arrange the terms in (20) such as to make the coefficients of $\delta\, Y^A_{i,\,k}$ and $\delta\, Y^A_{k,\,i}$ equal. With this convention we have

$$\frac{\partial\, V}{\partial\, Y^A_{i,\,k}} = \frac{\partial\, V}{\partial\, Y^A_{k,\,i}}. \tag{21}$$

If the variables Y^A are not independent, as in some of the later applications, say if $Y^A = Y^{A'}$, we use a similar symmetrization rule so as to make

$$\frac{\partial V}{\partial Y^A} = \frac{\partial Y}{\partial Y^{A'}}. \tag{22}$$

Now, consider an arbitrary infinitesimal space-time transformation

$$\overline{x}^i = x^i + \xi^i(x). \tag{23}$$

In all cases considered in the following, the local variation

$$\delta Y^A = \overline{Y}^A(x) - Y^A(x) \tag{24}$$

of $Y^A(x)$ is of the form

$$\delta Y^A = u^{Ak}_{\ \ i} \xi^i_{,\,k} - Y^A_i \xi^i, \tag{25}$$

where the $u^{Ak}_{\ \ i}$ are linear functions of the field variables. Hence, by (19),

$$\delta Y^A_l = u^{Ak}_{\ \ i} \xi^i_{k,\,l} + (u^{Ak}_{\ \ i,\,l} - Y^A_i \delta^k_l) \xi^i_{,\,k} - Y^A_{i,\,l} \xi^i. \tag{26}$$

In order to assure general covariance of the field equations (17) we shall now assume that V is a scalar density. Therefore, we must have

$$\delta V + (V \xi^k)_{,\,k} = 0 \tag{27}$$

at every point in 4-space and for arbitrary functions $\xi^i(x)$. If we integrate (27) over a finite region Ω in 4-space, we get by partial integrations for all functions $\xi^i(x)$ which vanish, together with their first and second order derivatives, at the boundary surface of Ω

$$\int \delta V\, dx = \int \frac{\delta V}{\delta Y^A} \delta Y^A\, dx = 0, \tag{28}$$

where $\frac{\delta V}{\delta Y^A}$ is the variational derivative defined by (18).

Hence, by (25), after a further partial integration,

$$-\int \left[\frac{\delta V}{\delta Y^A} Y^A_i + \left(\frac{\delta V}{\delta Y^A} u^{Ak}_i \right)_{,\,k} \right] \xi^i\, dx = 0. \tag{29}$$

Since the functions $\xi^i(x)$ can be chosen arbitrarily inside Ω, we must have the identity

$$\frac{\delta V}{\delta Y^A} Y_i^A + \left(\frac{\delta V}{\delta Y^A} u_i^{Ak}\right)_{,k} = 0. \tag{30}$$

The expression (20) for the variation of V may also be written

$$\delta V = \frac{\delta V}{\delta Y^A} \delta Y^A + \left[\left[\frac{\partial V}{\partial Y_k^A} - \left(\frac{\partial V}{\partial Y_{k,l}^A}\right)_{,l}\right] \delta Y^A + \frac{\partial V}{\partial Y_{k,l}^A} \delta Y_l^A\right]_{,k}. \tag{31}$$

If we introduce the expressions (25) and (26) for δY^A and δY_l^A into (31), we get an expression containing the ξ^i and their derivatives of the first and second order. After some rearrangements, and using the identity (30), the equation (27) may then be written in the form

$$-S_{i\ ,k}^{k}\,\xi^i - \left[S_i^{k} - V_{i\ ,l}^{kl}\right] \xi^i_{,k} + \left[V_i^{kl} + V_{i\ ,m}^{klm}\right] \xi^i_{,k,l} + V_i^{klm}\,\xi^i_{,k,l,m} = 0, \tag{32}$$

where we have used the abbreviations

$$S_i^{k} = -\frac{\delta V}{\delta Y^A} u^{Ak}_{i} + \left[\frac{\partial V}{\partial Y_k^A} - \left(\frac{\partial V}{\partial Y_{k,l}^A}\right)_{,l}\right] Y_i^A + \frac{\partial V}{\partial Y_{k,l}^A} Y_{i,l}^A - V \delta_i^k, \tag{33}$$

$$V_i^{kl} = \left[\frac{\partial V}{\partial Y_l^A} - \left(\frac{\partial V}{\partial Y_{l,m}^A}\right)_{,m}\right] u^{Ak}_{i} + \frac{\partial V}{\partial Y_{l,m}^A} \left(u^{Ak}_{i,m} - Y_i^A \delta_m^k\right), \tag{34}$$

$$V_i^{klm} = V_i^{kml} = u^{Ak}_{i} \frac{\partial V}{\partial Y_{l,m}^A}. \tag{35}$$

Since (32) has to hold for arbitrary choice of the functions $\xi^i(x)$, we get the following identities:

$$S_{i\ ,k}^{k} = 0, \tag{36}$$

$$S_i^{k} = V_{i\ ,l}^{kl}, \tag{37}$$

$$V_i^{kl} + V_i^{lk} + \left(V_i^{klm} + V_i^{lkm}\right)_{,m} = 0, \tag{38}$$

$$V_i^{klm} + V_i^{lmk} + V_i^{mkl} = 0, \quad V_i^{klm} = V_i^{kml}. \tag{39}$$

(36) shows that the quantity (33) satisfies a divergence relation and the method leads, apart from an arbitrary constant factor, uniquely to the expression (33). If we were only interested in deriving (33) and (36), we could have obtained this result much more easily by considering a "rigid infinitesimal parallel displacement" of the system of coordinates where the ξ^i are constants ε^i. In that case, we have by (25) and (26)

$$\delta Y^A = -Y^A_i \varepsilon^i, \quad \delta Y^A_l = -Y^A_{i,l}\varepsilon^i. \tag{40}$$

Introduction of these expressions into (31) and (27) gives directly, by means of the identity (30),

$$-\varepsilon^i S_{i,k}^{\,k} = 0, \tag{41}$$

which then leads to (36) on account of the arbitrariness in the choice of the constants ε^i.

From (39) we get

$$\left(V_i{}^{mkl} + \frac{1}{2} V_i{}^{klm}\right)_{,l,m} = \frac{1}{2}\left(V_i{}^{mkl} + V_i{}^{lkm} + V_i{}^{klm}\right)_{,l,m} = 0. \tag{42}$$

Thus, if we define a new quantity $U_i{}^{kl}$ by

$$U_i{}^{kl} = V_i{}^{kl} - \frac{2}{3}\left(V_i{}^{mkl} + \frac{1}{2} V_i{}^{klm}\right)_{,m} \tag{43}$$

we get by (37) and (42)

$$S_i{}^k = U_i{}^{kl}{}_{,l}. \tag{44}$$

This expression has the advantage that $U_i{}^{kl}$ is antisymmetric in k, l so that (36) is an immediate consequence of (44).

In fact we have, by (43), (38) and (39),

$$U_i{}^{kl} + U_i{}^{lk} = V_i{}^{kl} + V_i{}^{lk} - \frac{2}{3}\left[V_i{}^{mkl} + V_i{}^{mlk} + \frac{1}{2}\left(V_i{}^{klm} + V_i{}^{lkm}\right)\right]_{,m}$$

$$= \left[V_i{}^{mkl} - \frac{4}{3} V_i{}^{mkl} - \frac{1}{3}\left(V_i{}^{klm} + V_i{}^{lmk}\right)\right]_{,m} = 0,$$

i. e.

$$U_i{}^{kl} = -U_i{}^{lk}. \tag{45}$$

We can therefore also write U_i^{kl} in the manifestly antisymmetric form

$$\left.\begin{aligned} U_i^{kl} &= \frac{1}{2}(U_i^{kl} - U_i^{lk}) = \frac{1}{2}(V_i^{kl} - V_i^{lk}) - \frac{1}{6}(V_i^{klm} - V_i^{lkm})_{,\,m} \\ U_i^{kl} &= \frac{1}{2}\left\{\left(\left[\frac{\partial V}{\partial Y^A_l} - \left(\frac{\partial V}{\partial Y^A_{l,\,m}}\right)_{,\,m}\right] u^{Ak}{}_i + \frac{\partial V}{\partial Y^A_{l,\,m}}\, u^{Ak}{}_{i,\,m} - \frac{1}{3}\left[u^{Ak}{}_i \frac{\partial V}{\partial Y^A_{l,\,m}}\right]_{,\,m}\right) - \left(\overset{\leftarrow}{\underset{\rightarrow}{k,\, l}}\right)\right\} \end{aligned}\right\} \quad (46)$$

where the last term is obtained from the first by interchanging the indices k and l.

Thus, the method of infinitesimal transformations leads (apart from an arbitrary constant factor) uniquely to a quantity $S_i^{\,k}$ which satisfies the divergence relation (36) and which, by (44), is derivable from a "super-potential" defined by (43), (34), (35) or (46).

The preceding considerations are easily generalized to the case where V is a function of the Y^A and their derivatives of arbitrarily high order. The variational derivative of V with respect to Y^A is here defined as

$$\frac{\delta V}{\delta Y^A} = \sum_{n=0} (-1)^n \left(\frac{\partial V}{\partial Y^A_{i_1,\, i_2,\, \ldots\, i_n}}\right)_{,\, i_1,\, i_2,\, \ldots\, i_n}. \quad (47)$$

(Summation over n and for each n independent summation over the indices $i_1, i_2, \ldots i_n$!)

(47) obviously reduces to (18), if V does not depend on derivatives of Y^A of higher than the second order. Similarly, we introduce the variational derivatives of V with respect to Y^A_i, $Y^A_{i,\,k}, \ldots$ by

$$\left.\begin{aligned} \frac{\delta V}{\delta Y^A_i} &= \frac{\partial V}{\partial Y^A_i} - \left(\frac{\partial V}{\partial Y^A_{i,\, i_1}}\right)_{,\, i_1} + \cdots = \sum_{n=0} (-1)^n \left(\frac{\partial V}{\partial Y^A_{i,\, i_1,\, \ldots\, i_n}}\right)_{,\, i_1,\, \ldots\, i_n} \\ \frac{\delta V}{\delta Y^A_{i,\, k}} &= \frac{\partial V}{\partial Y^A_{i,\, k}} - \left(\frac{\partial V}{\partial Y^A_{i,\, k,\, i_1}}\right)_{,\, i_1} + \cdots = \sum_{n=0} (-1)^n \left(\frac{\partial V}{\partial Y^A_{i,\, k,\, i_1,\, \ldots\, i_n}}\right)_{,\, i_1,\, \ldots\, i_n} \end{aligned}\right\} \quad (48)$$

etc. In this general case, the method of infinitesimal transformations leads to the following energy-momentum complex $S_i^{\,k}$ satisfying the divergence relation (36):

$$\left.\begin{aligned} S_i{}^k &= -\frac{\delta V}{\delta Y^A} u^{Ak}{}_i + \frac{\delta V}{\delta Y^A_k} Y^A_i + \frac{\delta V}{\delta Y^A_{k,l_1}} Y^A_{i.\,l_1} + \cdots - \delta^k_i V \\ &= -\frac{\delta V}{\delta Y^A} u^{Ak}{}_i + \sum_{n=0} \left(\frac{\delta V}{\delta Y^A_{k,\,l_1,\,\dots\,l_n}}\right) Y^A_{i,\,l_1,\,\dots\,l_n} - \delta^k_i V. \end{aligned}\right\} \tag{49}$$

In the first place, it is clear that the identity (30) still is true, since the considerations in connection with the equations (27–(30) are valid also here. Then, if we consider a rigid displacement with $\xi^i = \varepsilon^i =$ constant, where

$$\delta Y^A_{l_1,\,\dots\,l_n} = -Y^A_{i,\,l,\,\dots\,l_n} \varepsilon^i, \tag{50}$$

one easily finds that the equations (41), and consequently (36), hold also in this case with $S_i{}^k$ given by (49).

3. Gravitational Fields

It is well known that the gravitational field may be treated as a Lagrangean system with the Lagrangean density

$$\mathfrak{L} = \sqrt{-g}\, g^{ik} (\Gamma^l_{ik} \Gamma^m_{lm} - \Gamma^m_{il} \Gamma^l_{km}), \tag{51}$$

the Γ^i_{kl} being the Christoffel symbols. In fact we have for all variations of the field variables g^{ik} which vanish at the surface of a region Ω in 4-space

$$\delta \int\limits_{\Omega} \mathfrak{L}\, dx = \int\limits_{\Omega} \frac{\delta \mathfrak{L}}{\delta g^{ik}} \delta g^{ik}\, dx = \int\limits_{\Omega} \mathfrak{G}_{ik}\, \delta g^{ik}\, dx, \tag{52}$$

where

$$\mathfrak{G}_{ik} = \sqrt{-g}\, G_{ik} = \sqrt{-g}\, (R_{ik} - \frac{1}{2} g_{ik} R). \tag{53}$$

Therefore, the field equations are of the form

$$\frac{1}{\varkappa} \frac{\delta \mathfrak{L}}{\delta g^{ik}} = \frac{1}{\varkappa} \mathfrak{G}_{ik} = -\sqrt{-g}\, T_{ik}. \tag{54}$$

Comparing (54) with (17) we see that we are dealing with a special case of the systems treated in section 2. The field variables Y^A are here the quantities g^{ik}, and $V = \mathfrak{L}/\varkappa$ is a function of the Y^A and their first derivatives only. Hence,

$$\frac{\delta V}{\delta Y^A} = \frac{1}{\varkappa} \frac{\delta \mathfrak{L}}{\delta g^{ik}} = \frac{1}{\varkappa} \left[\frac{\partial \mathfrak{L}}{\partial g^{ik}} - \left(\frac{\partial \mathfrak{L}}{\partial g^{ik}_l} \right)_{,l} \right] \tag{55}$$

Since $g^{ik} = g^{ki}$, we have here a case where some of the Y^A are equal. Thus, with the convention mentioned on page 7 equations (22) hold, i. e.,

$$\frac{\partial \mathfrak{L}}{\partial g^{ik}} = \frac{\partial \mathfrak{L}}{\partial g^{ki}}, \quad \frac{\delta \mathfrak{L}}{\delta g^{ik}} = \frac{\delta \mathfrak{L}}{\delta g^{ik}}. \tag{56}$$

However, $V = \mathfrak{L}/\varkappa$ is a scalar density only under *linear* space-time transformations. Therefore, only the identities (36) and (37) can be derived in this case, since $\xi^i_{,k,l} = \xi^i_{,k,l,m} = 0$ for linear transformation, which means that the last two terms in (32) are missing. A simple calculation shows that $S_i^{\ k}$ and $V_i^{\ kl}$ in this case are

$$S_i^{\ k} = 2\,\Theta_i^{\ k}, \quad V_i^{\ kl} = 2\,s_i^{\ kl} \tag{57}$$

with $\Theta_i^{\ k}$ and $s_i^{\ kl}$ given by (1), (3), and (4). Furthermore, (30) becomes identical with the contracted Bianchi identities

$$G^k_{i;\,k} \equiv \frac{1}{\sqrt{-g}} \frac{\partial \sqrt{-g}\, G^k_i}{\partial x^k} + \frac{1}{2} g^{rs}_i G^{rs} = 0. \tag{58}$$

However, this equation cannot here be derived by the method used in section 2, since this would require invariance of $\int\limits_\Omega V dx = \frac{1}{\varkappa} \int\limits_\Omega \mathfrak{L}\, dx$ under *arbitrary* space-time transformations.

We get a more satisfactory description by treating the gravitational field as a non-Lagrangean system of the type considered in section **2** with

$$V = \mathfrak{R}/\varkappa = \sqrt{-g}\, R/\varkappa \tag{59}$$

which is a function of the g^{ik} and their first *and* second order derivatives g^{ik}_l and $g^{ik}_{l,m}$. Also in this case we have an equation of the type (52), i. e.,

$$\delta\int_{\Omega}\mathfrak{R}\,dx=\int_{\Omega}\frac{\delta\mathfrak{R}}{\delta g^{ik}}\,\delta g^{ik}\,dx=\int_{\Omega}\mathfrak{G}_{ik}\,\delta g^{ik}\,dx \tag{60}$$

i. e.,

$$\frac{\delta\mathfrak{R}}{\delta g^{ik}}=\mathfrak{G}_{ik}. \tag{61}$$

The reason for this is that $\mathfrak{R}$ differs from $\mathfrak{L}$ by a divergence term only. In fact, we have

$$\left.\begin{aligned}\mathfrak{R}&=\mathfrak{L}+\mathfrak{h},\\ \mathfrak{h}&=\varkappa h_{r}{}^{rl}{}_{,l}.\end{aligned}\right\} \tag{62}$$

This follows at once from (1) and (8) if we remark that

$$\left.\begin{aligned}\Theta_{r}{}^{r}=\sqrt{-g}\,(T_{r}^{r}+\vartheta_{r}{}^{r})&=\frac{\sqrt{-g}}{\varkappa}\,G_{r}^{r}+\frac{1}{2\varkappa}\left[\frac{\partial\mathfrak{L}}{\partial g_{r}^{lm}}\,g_{r}^{lm}-4\,\mathfrak{L}\right]\\ &=\frac{1}{\varkappa}(\mathfrak{R}-\mathfrak{L}).\end{aligned}\right\} \tag{63}$$

In the last equation, we have used the fact that $\mathfrak{L}$ is a homogeneous function of the g_{r}^{lm} of degree 2. With $h_{i}{}^{kl}$ given by (7) a simple calculation shows that

$$h_{r}{}^{rl}=\frac{1}{\varkappa}\left(\sqrt{-g}\,g_{m}^{lm}+2\,g^{lm}(\sqrt{-g})_{,\,m}\right)=\frac{1}{\varkappa\sqrt{-g}}\left(-g\,g^{lm}\right)_{,\,m} \tag{64}$$

(see, for instance, the Appendix of reference [4]).

For arbitrary variations δg^{ik} which vanish at the surface of Ω, we now have

$$\delta\int_{\Omega}\mathfrak{h}\,dx=\int_{\Omega}\frac{\delta\mathfrak{h}}{\delta g^{ik}}\,\delta g^{ik}\,dx=\varkappa\int_{\Omega}(\delta\,h_{r}{}^{rl})_{,\,l}\,dx=0, \tag{65}$$

i. e.,

$$\frac{\delta\mathfrak{h}}{\delta g^{ik}}=0. \tag{66}$$

With

$$V=\frac{1}{\varkappa}\mathfrak{R} \tag{67}$$

the field equations take the form (17), i. e.,

$$\frac{1}{\varkappa}\mathfrak{G}_{ik} = \frac{1}{\varkappa}\frac{\delta\,\mathfrak{L}}{\delta\, g^{ik}} = \frac{1}{\varkappa}\frac{\delta\,\mathfrak{R}}{\delta\, g^{ik}} = -\sqrt{-g}\,T_{ik}\,. \tag{68}$$

Since $\mathfrak{R}$ is a scalar density under arbitrary space-time transformations, all the relations (32)–(46) of section **2** are valid here. For an infinitesimal transformation (23), we now have

$$\delta\, g^{rs} = g^{sk}\,\xi^{r}_{\ ,k} + g^{rk}\,\xi^{s}_{\ ,k} - g^{rs}_{i}\,\xi^{i} \tag{69}$$

which, by comparison with (25), gives

$$u^{Ak}_{\ \ \ i} = u^{rsk}_{\ \ \ \ i} = \delta^{r}_{i}\,g^{sk} + g^{rk}\,\delta^{s}_{i}\,. \tag{70}$$

Then we get in the first place from (30), (68), and (70)

$$\frac{2}{\varkappa}\left[\frac{\partial\,\mathfrak{G}^{k}_{i}}{\partial\, x^{k}} + \frac{1}{2}\,g^{rs}_{i}\,\mathfrak{G}_{rs}\right] = 0\,, \tag{71}$$

i. e., the Bianchi identity (58). Next, by (33), (59), (61), (62), and (70)

$$\left.\begin{aligned} S_{i}^{\ k} = -\frac{2}{\varkappa}\mathfrak{G}^{k}_{i} + \frac{1}{\varkappa}\left[\frac{\partial\,\mathfrak{L}}{\partial\, g^{lm}_{k}}\,g^{lm}_{i} - \delta^{k}_{i}\,\mathfrak{L}\right] + \frac{1}{\varkappa}\left[\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k}} - \left(\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k,\,l}}\right)_{,\,l}\right] g^{rs}_{i} \\ + \frac{1}{\varkappa}\left(\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k,\,l}}\right) g^{rs}_{i,\,l} - \frac{1}{\varkappa}\,\delta^{k}_{i}\,\mathfrak{h} \end{aligned}\right\} \tag{72}$$

or, using (3) and the field equations (2),

$$S_{i}^{\ k} = \sqrt{-g}\left(T^{k}_{i} + 2\,\vartheta_{i}^{\ k} - \frac{1}{\varkappa}\,G^{k}_{i}\right) + A^{k}_{i} - K^{kl}_{i,\,l} \tag{73}$$

with

$$\varkappa\,A^{k}_{i} = \left[\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k}} - \left(\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k,\,l}}\right)_{,\,l}\right] g^{rs}_{i} - \left(\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k,\,l}}\right)_{,\,i} g^{rs}_{l} + \left[\left(\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{l,\,m}}\,g^{rs}_{l}\right)_{,\,m} - \mathfrak{h}\right]\delta^{k}_{i} \tag{74}$$

$$K^{kl}_{i} = \frac{1}{\varkappa}\left(\delta^{k}_{i}\,\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{l,\,m}} - \delta^{l}_{i}\,\frac{\partial\,\mathfrak{h}}{\partial\, g^{rs}_{k,\,m}}\right) g^{rs}_{m} = -K^{lk}_{i}\,. \tag{75}$$

As shown in Appendix A, A^{k}_{i} is identically zero with $\mathfrak{h}$ given by (62) and (64), and K^{kl}_{i} becomes

$$K^{kl}_{i} = \delta^{k}_{i}\,h_{r}^{\ rl} - \delta^{l}_{i}\,h_{r}^{\ rk}. \tag{76}$$

Hence,

$$S_i^{\,k} = \sqrt{-g}\,(T_i^k + t_i^{\,k}), \tag{77}$$

where

$$\sqrt{-g}\, t_i^{\,k} = -\frac{1}{\varkappa}\mathfrak{S}_i^k + 2\sqrt{-g}\,\vartheta_i^{\,k} - (\delta_i^k\, h_r^{\,rl} - \delta_i^l\, h_r^{\,rk})_{,\,l}, \tag{78}$$

i. e., the quantity defined by (11). Thus, the "conserved" quantity $S_i^{\,k}$ is in this case just the pseudo-tensor density of energy and momentum defined by (10).

For the superpotential $U_i^{\,kl}$ we get by (46), (62), and (70)

$$\varkappa\, U_i^{\,kl} = \left(\frac{\partial\,\mathfrak{L}}{\partial\, g_l^{im}}\, g^{km} + \left[\frac{\partial\,\mathfrak{h}}{\partial\, g_l^{is}} - \left(\frac{\partial\,\mathfrak{h}}{\partial\, g_{l,\,m}^{is}}\right)_{,\,m}\right] g^{ks} + \frac{\partial\,\mathfrak{h}}{\partial\, g_{l,\,m}^{is}}\, g_m^{ks} - \frac{1}{3}\left[\frac{\partial\,\mathfrak{h}}{\partial\, g_{l,\,m}^{is}}\, g^{ks}\right]_{,\,m}\right) - \left(\overset{\leftarrow}{\underset{\rightarrow}{k,\, l}}\right), \tag{79}$$

$$U_i^{\,kl} = s_i^{\,kl} - s_i^{\,lk} + B_i^{kl} - B_i^{lk}, \tag{80}$$

where $s_i^{\,kl}$ is the quantity given by (4) – (7) and

$$\varkappa\, B_i^{kl} = \left[\frac{\partial\,\mathfrak{h}}{\partial\, g_l^{is}} - \left(\frac{\partial\,\mathfrak{h}}{\partial\, g_{l,\,m}^{is}}\right)_{,\,m}\right] g^{ks} + \frac{\partial\,\mathfrak{h}}{\partial\, g_{l,\,m}^{is}}\, g_m^{ks} - \frac{1}{3}\left(\frac{\partial\,\mathfrak{h}}{\partial\, g_{l,\,m}^{is}}\, g^{ks}\right)_{,\,m}. \tag{81}$$

The calculation of B_i^{kl} and of $U_i^{\,kl}$ is completed in Appendix A and the result is that $U_i^{\,kl}$ in the present case is equal to the superpotential $\chi_i^{\,kl}$ given by (13), which makes the equation (44) identical with the equation (12) for $\mathcal{T}_i^{\,k}$. Thus, the method of infinitesimal transformations leads, apart from an arbitrary constant factor, directly to the expressions (10) – (13) for the pseudo-tensor density of energy and momentum. The arbitrary factor is fixed by the condition that the integrals P_i in (14) for "closed" systems must have the right values and it turns out that, with $V = \mathfrak{R}/\kappa$, this factor has to be equal to one.

4. The Matter Field

We shall now assume that the "matter" which produces the gravitational field has the character of a tensor field described by a number of field variables $Q^a(x)$. (For simplicity, we exclude spinors). Further, we assume that this field is of the Lagrangean type, i. e., the matter field equations are of the form

$$\frac{\delta \mathfrak{M}}{\delta Q^a} = 0, \tag{82}$$

where $\mathfrak{M}$ is a scalar density depending on the $Q^a(x)$, $g^{ik}(x)$ and their first order derivatives, and the symmetrical matter tensor is obtained by derivation of $\mathfrak{M}$ with respect to g^{ik}, i. e.,

$$\frac{\delta \mathfrak{M}}{\delta g^{ik}} = \sqrt{-g}\, T_{ik}. \tag{83}$$

In all practical cases, $\mathfrak{M}$ does even not depend on g^{ik}_l:

$$\mathfrak{M} = \mathfrak{M}(g^{ik},\ Q^a,\ Q^a_{,i}). \tag{84}$$

This implies that both the gravitational field equations (2) and the matter field equations (82) are derivable from the variational principle

$$\delta \int \left(\frac{1}{\varkappa} \mathfrak{R} + \mathfrak{M} \right) dx = 0 \tag{85}$$

for independent variations of the g^{ik} and the Q^a.

We may now apply the general considerations of section **2** to the non-closed system with

$$\left. \begin{aligned} V &= \mathfrak{M} \\ Y^A &= \left\{ g^{ik},\ Q^a \right\}. \end{aligned} \right\} \tag{86}$$

As we shall see now, this leads to a special case of the well-known connection between the symmetrical and the "canonical" matter tensor discovered by ROSENFELD and by BELINFANTE [6]. With $V = \mathfrak{M}(g^{ik}, Q^a, Q^a_{,i})$ we get from (33), (70), and (83)

$$S_i^{\ k} = -2\sqrt{-g}\, T^k_i - \frac{\delta \mathfrak{M}}{\delta Q^a} u^{ak}_{\ \ i} + \frac{\partial \mathfrak{M}}{\partial Q^a_k} Q^a_{,i} - \mathfrak{M}\, \delta^k_i. \tag{87}$$

On the other hand, we have, by (44) and (46), in the present case

$$\left. \begin{aligned} U_i^{\ kl} &= \frac{1}{2} \left[\frac{\partial \mathfrak{M}}{\partial Q^a_{,l}} u^{ak}_{\ \ i} - \frac{\partial \mathfrak{M}}{\partial Q^a_{,k}} u^{al}_{\ \ i} \right], \\ S_i^{\ k} &= U_i^{\ kl}{}_{,l}. \end{aligned} \right\} \tag{88}$$

Thus, we get from (87) and (88)

$$\sqrt{-g}\,T_i^k = \sqrt{-g}\,(\breve{T}_i^k + \widehat{T}_i^k) \tag{89}$$

with

$$\sqrt{-g}\,\breve{T}_i^k = \frac{\partial\,\mathfrak{M}/2}{\partial\,Q^a_{,\,k}}\,Q^a_{,\,i} - (\mathfrak{M}/2)\,\delta_i^k \tag{90}$$

$$\sqrt{-g}\,\widehat{T}_i^k = -\frac{\delta\,\mathfrak{M}/2}{\delta\,Q^a}\,u^{ak}{}_i - \frac{1}{2}\left[\frac{\partial\,\mathfrak{M}/2}{\partial\,Q^a_{,\,l}}\,u^{ak}{}_i - \frac{\partial\,\mathfrak{M}/2}{\partial\,Q^a_{,\,k}}\,u^{al}{}_i\right]_{,\,l} \tag{91}$$

$\breve{T}_i{}^k$ is the generally unsymmetric canonical matter tensor derivable from the "matter Lagrangean"

$$\mathfrak{L}^{(m)} = -\,\mathfrak{M}/2 \tag{92}$$

and $\widehat{T}_i{}^k$ is the term which has to be added to $\breve{T}_i{}^k$ in order to give the symmetrical matter tensor T_i^k. The first term in (91) is zero on account of the field equations (82) and, for a matter-system confined to a final part of 3-space, the last term will give no contribution to the total matter energy and momentum. In fact, we have

$$\left.\begin{aligned} P_i^{(m)} &= \frac{1}{c}\int\sqrt{-g}\,T_i^4\,dx^1\,dx^2\,dx^3 = \frac{1}{c}\int\sqrt{-g}\,\breve{T}_i{}^4\,dx^1\,dx^2\,dx^3 \\ &\quad - \frac{1}{2\,c}\int U_i{}^{4\lambda}{}_{,\,\lambda}\,dx^1\,dx^2\,dx^3 = \frac{1}{c}\int\sqrt{-g}\,\breve{T}_i{}^4\,dx^1\,dx^2\,dx^3. \end{aligned}\right\} \tag{93}$$

In general, $P_i^{(m)}$ is not constant in time. Only the sum of the matter part and the gravitational part, i. e.,

$$P_i = \frac{1}{c}\int T_i^4\,dx^1\,dx^2\,dx^3 = \frac{1}{c}\int\sqrt{-g}\,\left[T_i^4 + t_i{}^4\right]\,dx^1\,dx^2\,dx^3 \tag{94}$$

is conserved for a closed system.

As an example, we consider the case where the matter field is a purely electromagnetic field. Here, we have

$$\left.\begin{aligned} \mathfrak{M} &= \frac{1}{2}\sqrt{-g}\,g^{rl}\,g^{sm}\,F_{rs}\,F_{lm} \\ F_{ik} &= A_{k,\,i} - A_{i,\,k} = -\,F_{ki}\,. \end{aligned}\right\} \tag{95}$$

As the field variables Q^a we may take the components A_i of the four-potential. Then, we get

$$\frac{\partial \mathfrak{M}}{\partial A_i} = 0, \qquad \frac{\partial \mathfrak{M}}{\partial A_{i,\,k}} = -2\sqrt{-g}\, F^{ik} \tag{96}$$

and the field equations (82) are the Maxwell equations

$$\frac{\delta \mathfrak{M}}{\delta A_i} = -\frac{\partial}{\partial x^k}\left(2\sqrt{-g}\, F^{ik}\right) = 0\,. \tag{97}$$

Further, since for any variation of the g^{ik}

$$\delta\left(\sqrt{-g}\, g^{rl}\, g^{sm}\right) = \frac{\sqrt{-g}}{2}\left[-g_{ik}\, g^{rl}\, g^{sm} + g^{sm}\left(\delta_i^r\, \delta_k^l + \delta_k^r\, \delta_i^l\right) + g^{rl}\left(\delta_i^s\, \delta_k^m + \delta_k^s\, \delta_i^m\right)\right] \delta g^{ik},$$

we have, by (83)

$$\left.\begin{aligned} \sqrt{-g}\, T_{ik} &= \frac{\partial \mathfrak{M}}{\partial g^{ik}} = \frac{1}{2} F_{rs}\, F_{lm} \frac{\partial\left(\sqrt{-g}\, g^{rl}\, g^{sm}\right)}{\partial g^{ik}} \\ &= \sqrt{-g}\left[F_{il}\, F_k^{\ l} - \frac{1}{4} g_{ik}\, F_{lm}\, F^{lm}\right] \end{aligned}\right\} \tag{98}$$

which is the usual expression for the electromagnetic energy-momentum tensor.

On the other hand, the canonical tensor is, by (90), (95), and (96),

$$\sqrt{-g}\, \breve{T}_i^{\ k} = \frac{\partial \mathfrak{M}/2}{\partial A_{l,\,k}} A_{l,\,i} - (\mathfrak{M}/2)\, \delta_i^k = -\sqrt{-g}\, F^{lk} A_{l,\,i} - \frac{\sqrt{-g}}{4} F_{lm}\, F^{lm}\, \delta_i^k\,. \tag{99}$$

It differs from (98) by the term $\sqrt{-g}\, \widehat{T}_i^{\ k}$ given by (91). Since A_i is a four-vector, we have for an infinitesimal transformation

$$\delta A_r = -A_i \xi^i_{\ ,\,r} - A_{r,\,i}\, \xi^i = u_{r\ i}^{\ k}\, \xi^i_{\ ,\,k} - A_{r,\,i}\, \xi^i, \tag{100}$$

i. e.,

$$u^{ak}_{\ \ i} \equiv u_{r\ i}^{\ k} = -\delta_r^k\, A_i\,.$$

Thus, by (91) and (96),

$$\sqrt{-g}\,\widehat{T}_i{}^k = -\left(\frac{\partial\,\mathfrak{M}/2}{\partial\,A_{r,\,l}}\right)_{,\,l}\delta^k_r\,A_i + \frac{1}{2}\left[\frac{\partial\,\mathfrak{M}/2}{\partial\,A_{r,\,l}}\,\delta^k_r\,A_i - \frac{\partial\,\mathfrak{M}/2}{\partial\,A_{r,\,k}}\,\delta^l_r\,A_i\right]_{,\,l}$$

$$= \left(\sqrt{-g}\,F^{kl}\right)_{,\,l}A_i - \frac{1}{2}\left[\sqrt{-g}\,F^{kl}\,A_i - \sqrt{-g}\,F^{lk}\,A_i\right]_{,\,l}$$

or

$$\sqrt{-g}\,\widehat{T}_i{}^k = -\sqrt{-g}\,F^{kl}\,A_{i,\,l}. \tag{101}$$

By adding the expressions (99) and (101) we get again the expression (98) for the symmetrical matter tensor, in accordance with the general equation (89).

In conclusion, we summarize the main results of the preceding sections. The total pseudo-tensor density of energy and momentum $\mathcal{T}_i{}^k$ may be written as the sum of a "matter part" T^k_i and a "gravitational part" $t_i{}^k$:

$$\mathcal{T}_i{}^k = \sqrt{-g}\,[T^k_i + t_i{}^k] \tag{102}$$

where, by (89) – (92)

$$\sqrt{-g}\,T_i{}^k = -Q^a_{,\,i}\frac{\partial\,\mathfrak{L}^{(m)}}{\partial\,Q^a_{,\,k}} + \delta^k_i\,\mathfrak{L}^{(m)} + \frac{1}{2}\left[u^{ak}_{\;\;i}\frac{\partial\,\mathfrak{L}^{(m)}}{\partial\,Q^a_{,\,l}} - u^{al}_{\;\;i}\frac{\partial\,\mathfrak{L}^{(m)}}{\partial\,Q^a_{,\,k}}\right]_{,\,l} + u^{ak}_{\;\;i}\frac{\delta\,\mathfrak{L}^{(m)}}{\delta\,Q^a} \tag{103}$$

and, by (72) – (78),

$$\left.\begin{aligned}\sqrt{-g}\,t_i{}^k &= -\frac{1}{\varkappa}\,\mathfrak{G}^k_i + 2\sqrt{-g}\,\vartheta_i{}^k - (\delta^k_i\,h_r{}^{rl} - \delta^l_i\,h_r{}^{rk})_{,\,l}\\ &= \frac{1}{\varkappa}\left\{-\frac{\delta\,\mathfrak{R}}{\delta\,g^{il}}g^{kl} + \left[\frac{\partial\,\mathfrak{R}}{\partial\,g^{rs}_k} - \left(\frac{\partial\,\mathfrak{R}}{\partial\,g^{rs}_{k,\,l}}\right)_{,\,l}\right]g^{rs}_i + \frac{\partial\,\mathfrak{R}}{\partial\,g^{rs}_{k,\,l}}\,g^{rs}_{i,\,l} - \mathfrak{R}\,\delta^k_i\right\}.\end{aligned}\right\} \tag{104}$$

Apart from the last two terms which give no contribution to $P^{(m)}_i$, the matter part (103) has the canonical form corresponding to a matter Lagrangean $\mathfrak{L}^{(m)} = -\mathfrak{M}/2$. On the other hand, the gravitational part (104) has an entirely different structure and it can *not* be derived from a Lagrangean density according to the usual rules. This may be taken as an indication that the "quantization" of gravitational fields should be performed in a way which differs from the usual rules of ordinary quantum mechanics. It is true that $\sqrt{-g}\,t_i{}^k$ in (104) may also be written

$$\sqrt{-g}\,t_i{}^k = \sqrt{-g}\,\vartheta_i{}^k + \psi_i{}^{kl}{}_{,\,l}, \tag{105}$$

where

$$\psi_i{}^{kl} = h_i{}^{kl} - \delta_i^k\, h_r{}^{rl} + \delta_i^l\, h_r{}^{rk} \tag{106}$$

is antisymmetric in k and l. Therefore, by partial integrations, the total gravitational momentum and energy take the form

$$P_i^{(g)} = \frac{1}{c}\int \sqrt{-g}\, t_i{}^4\, dx^1\, dx^2\, dx^3 = \frac{1}{c}\int \sqrt{-g}\, \vartheta_i{}^k\, dx^1\, dx^2\, dx^3 + A_i, \tag{107}$$

where A_i depends on the gravitational variables at spatial infinity only. Formally the gravitational field may therefore be treated as a canonical system. But quite apart from the complications, already present on the "classical" level, which occur in the transition from the Lagrangean to the Hamiltonean form due to the different types of restraints (7), we are faced with the difficult problem of finding the correct order of factors in the transition to a quantal description along the usual lines of quantum mechanics. Also it should be mentioned that the division of $\mathcal{T}_i{}^k$ into a matter part and a gravitational part is to a large extent arbitrary due to the fact that the matter tensor is the source of the gravitational field. By means of these equations, a larger or smaller part of T_i^k may be eliminated in $\mathcal{T}_i{}^k$. If we eliminate T_i^k entirely, we arrive at the simple and convenient expression (12) which depends on the gravitational field variables only.

For the total momentum and energy of the system, we then get

$$P_i = \frac{1}{c}\int \mathcal{T}_i{}^4\, dx^1\, dx^2\, dx^3 = \frac{1}{c}\int \chi_i{}^{4\lambda}{}_{,\lambda}\, dx^1\, dx^2\, dx^3$$

which, by means of Gauss' theorem, may be written as a surface integral depending only on the gravitational field variables at spatial infinity.

5. Transformation Properties of $\mathcal{T}_i{}^k$ and $t_i{}^k$

The energy-momentum complex is a tensor density under *linear* transformations, only. We shall now investigate the transformation properties of $\mathcal{T}_i{}^k$ and $t_i{}^k$ under the most general space-time transformations. To this end, we consider an arbitrary vector field $a^i(x)$ and the antisymmetrical tensor density

$$\left.\begin{aligned} \mathfrak{F}^{kl} &= -\mathfrak{F}^{lk} = \frac{\sqrt{-g}}{\varkappa}(a_{n,m} - a_{m,n})\, g^{km} g^{ln}, \\ a_i(x) &= g_{ik}\, a^k(x). \end{aligned}\right\} \tag{108}$$

Further, the vector density

$$\mathfrak{F}^k = \mathfrak{F}^{kl}{}_{,l} \tag{109}$$

which, on account of the antisymmetry of $\mathfrak{F}^{kl}$ in k and l, satisfies the divergence relation

$$\mathfrak{F}^k{}_{,k} = 0 \tag{110}$$

for arbitrary vector fields $a^i(x)$.

As remarked by Komar$^{(8)}$, the vector density $\mathfrak{F}^k$ is closely related to the complex $\mathcal{T}_i{}^k$. In fact, if we let the contravariant components of the arbitrary vector field a^i be constants ε^i in a definite system of coordinates, we have by (108), (109), (12), and (13)

$$\mathfrak{F}^k = \varepsilon^i \left[\frac{\sqrt{-g}}{\varkappa}(g_{in,m} - g_{im,n})\, g^{km} g^{ln}\right]_{,l} = \varepsilon^i \chi_i{}^{kl}{}_{,l} = \varepsilon^i \mathcal{T}_i^k. \tag{111}$$

For an arbitrary vector field $a^i(x)$, we get on the other hand, since

$$\left.\begin{aligned} a_{n,m} &= a^i g_{in,m} + a^i_{,m} g_{in}, \\ \mathfrak{F}^{kl} &= a^i \chi_i{}^{kl} - a^i_{,m}\, b_i{}^{klm} \end{aligned}\right\} \tag{112}$$

where $b_i{}^{klm}$ is the tensor density of rank 4 defined by

$$b_i{}^{klm} = -b_i{}^{lkm} = \frac{\sqrt{-g}}{K}(\delta^k_i g^{lm} - \delta^l_i g^{km}). \tag{113}$$

Hence, by (109), (112), and (12),

$$\mathfrak{F}^k = a^i \mathcal{T}_i{}^k + a^i_{,l}(\chi_i^{kl} - b_i{}^{kml}{}_{,m}) - a^i_{,l,m}\, b_i^{klm}. \tag{114}$$

Now, consider an arbitrary space-time transformation $(x^i) \rightarrow (x'^i)$ with

$$\alpha^i_k(x) = \frac{\partial x'^i}{\partial x^k}, \quad \breve{\alpha}^i_k(x') = \frac{\partial x^i}{\partial x'^k}. \tag{115}$$

Since $\mathfrak{F}^k$ is a vector density, we have

$$\mathfrak{F}'^k = |\breve{\alpha}|\, \alpha^k_l\, \mathfrak{F}^l = |\breve{\alpha}|\, \alpha^k_l \{ a^r \mathcal{T}_r{}^k + a^r{}_{,m} (\chi_r{}^{lm} - b_r{}^{lnm}{}_{,n}) - a^r{}_{,m,n}\, b_r{}^{lmn}, \qquad (116)$$

where $|\breve{\alpha}| = \det\{\breve{\alpha}^i_k\}$ is the determinant of the matrix $\breve{\alpha}^i_k$. If we choose the components a'^i in the primed system to be constants ε^i, we have

$$\left.\begin{aligned} \mathfrak{F}'^k &= \varepsilon^i\, \mathcal{T}'^k_i \\ a^r &= \breve{\alpha}^r_i\, \varepsilon^i \\ a^r{}_{,m} &= \alpha^s_m\, \breve{\alpha}^r_{i,s}\, \varepsilon^i \\ a^r{}_{,m,n} &= \alpha^s_{m,n}\, \breve{\alpha}^r_{i,s}\, \varepsilon^i + \alpha^s_m\, \alpha^t_n\, \breve{\alpha}^r_{i,s,t}\, \varepsilon^i, \end{aligned}\right\} \qquad (117)$$

where

$$\breve{\alpha}^r_{i,s} = \frac{\partial^2 x^r}{\partial x'^i\, \partial x'^s}, \qquad \alpha^s_{m,n} = \frac{\partial^2 x'^s}{\partial x^m\, \partial x^n}, \qquad \breve{\alpha}^r_{i,s,t} = \frac{\partial^3 x^r}{\partial x'^i\, \partial x'^s\, \partial x'^t}, \ \ldots \qquad (118)$$

Introduction of (117) into (116) gives, since the constants ε^i are arbitrary, the following transformation law for the complex $\mathcal{T}_i{}^k$:

$$\mathcal{T}'^k_i = |\breve{\alpha}|\, \alpha^k_l\, \breve{\alpha}^m_i\, \mathcal{T}_m{}^l + |\breve{\alpha}|\, \alpha^k_l \{ \breve{\alpha}^r_{i,s}\, \alpha^s_m (\chi_r{}^{lm} - b_r{}^{lnm}{}_{,n}) - (\breve{\alpha}^r_{i,s,t}\, \alpha^s_m\, \alpha^t_n + \breve{\alpha}^r_{i,s}\, \alpha^s_{m,n})\, b_r{}^{lmn} \} \qquad (119)$$

The last term on the right-hand side of (119) represents the deviation from the transformation law of a tensor density. For linear transformations, where $\breve{\alpha}^r_{i,s} = \breve{\alpha}^r_{i,s,t} = 0$, this term is zero, in accordance with the fact that $\mathcal{T}_i{}^k$ is an affine tensor density. Moreover, for the purely spatial transformation (15), we have

$$\breve{\alpha}^r_4 = \frac{\partial x^r}{\partial x'^4} = \delta^r_4, \qquad \breve{\alpha}^r_{4,s} = 0, \qquad (120)$$

i. e.,

$$\mathcal{T}'^k_4 = |\breve{\alpha}|\, \alpha^k_l\, \mathcal{T}_4{}^l. \qquad (121)$$

This equation shows that the fourth column of the matrix $\mathcal{T}_i{}^k$ transforms like a vector density under the transformation (15), a property which was the starting point in our derivation of $\mathcal{T}_i{}^k$ in$^{(4)}$. The apparent distinction of the time direction revealed in this property is not surprising, since the densities of energy and energy current in this description are connected with the "time column" of $\mathcal{T}_i{}^k$. Actually, if a is any fixed value of the indices 1, 2, 3, 4, the a^{th} column $\mathcal{T}_a{}^k$ will also transform like a vector density under the transformations

$$x'^a = x^a, \quad x'^i = f^i(x^k) \quad \text{with} \quad i \neq a, \quad k \neq a; \tag{122}$$

for, in that case, we have

$$\left.\begin{aligned} \breve{\alpha}_a^r &= \frac{\partial x^r}{\partial x'^a} = \delta_a^r \\ \mathcal{T}'_a{}^k &= \left|\breve{\alpha}\right| \alpha_l^k \, \mathcal{T}_a{}^l . \end{aligned}\right\} \tag{123}$$

But, for $a \neq 4$, this property does not lend itself to a simple physical interpretation.

Since the matter part $\sqrt{-g}\, T_i^k$ of $\mathcal{T}_i{}^k$ transforms like a tensor density, we get for the gravitational complex $t_i{}^k$ defined by (10) and (11) the transformation law

$$t_i'^k = \alpha_l^k \, \breve{\alpha}_i^m \, t_m{}^l + \alpha_l^k \left\{ \breve{\alpha}_{i,\,s}^r \alpha_m^s \left(\chi_r{}^{lm} - b_r{}^{lnm}{}_{,\,n}\right) - \left(\breve{\alpha}_{i,\,s,\,t}^r \alpha_m^s \, \alpha_n^t + \breve{\alpha}_{i,\,s}^r \alpha_{m,\,n}^s\right) b_r{}^{lmn} \right\}. \tag{124}$$

By means of (108), (109), and (111), one finds a convenient explicit expression for $t_i{}^k$ in the following way. First, we may substitute the usual derivatives $a_{n,\,m}$ in the antisymmetrical expression (108) by covariant derivatives $a_{n;\,m}$ which are tensor components. Hence

$$\mathfrak{F}^{kl} = \frac{\sqrt{-g}}{\varkappa}\left(a^{l;\,k} - a^{k;\,l}\right)$$

and

$$\mathfrak{F}^k = \mathfrak{F}^{kl}{}_{,\,l} = \sqrt{-g}\,\left[\mathfrak{F}^{kl}/\sqrt{-g}\right]_{;\,l} = \frac{\sqrt{-g}}{\varkappa}\left(a^{l;\,k}{}_{;\,l} - a^{k;\,l}{}_{;\,l}\right). \tag{125}$$

Then, we use the commutation law for repeated covariant derivations:

$$a^{l;\,k}{}_{;\,l} = a^l{}_{;\,l}{}^{;\,k} - R_i{}^{lk}{}_l \, a^i = \left(a^l_{;\,l}\right)^{;k} - R_i^k \, a^i \tag{126}$$

where R_{iklm} is the Riemann curvature tensor, and R_{ik} is its contraction. By (125), (126), and the field equations (2) we therefore get

$$\mathfrak{F}^k = \sqrt{-g}\, T_i^k \, a^i - \frac{\sqrt{-g}\,R}{2\,\varkappa}\,\delta_i^k \, a^i + \frac{\sqrt{-g}}{\varkappa}\left[\left(a^l_{;\,l}\right)^{;\,k} - \left(a^{k;\,l}\right)_{;\,l}\right]. \tag{127}$$

Now, choose the a^i equal to constants ε^i; then, according to (111),

$$\mathfrak{T}^k = \varepsilon^i \mathcal{T}_i{}^k = \sqrt{-g}\,(T_i^k + t_i{}^k)\,\varepsilon^i \tag{128}$$

and, by a simple calculation,

$$(a^l_{;\,l})^{;\,k} - (a^{k;\,l})_{;\,l} = \left[(\Gamma^l_{il})^{,\,k} - (\Gamma^k_{il}\,g^{lm})_{,\,m} - \Gamma^k_{in}\,\Gamma^l_{ml}\,g^{mn} - \Gamma^k_{lm}\,\Gamma^m_{in}\,g^{ln}\right]\varepsilon^i. \tag{129}$$

Therefore, since the ε^i are arbitrary, the equations (127), (128) yield

$$t_i{}^k = -\frac{R}{2\,\varkappa}\,\delta^k_i + \hat{t}^k_i \tag{130}$$

with

$$\varkappa\,\hat{t}^k_i = (\Gamma^l_{il})^{,\,k} - (\Gamma^k_{il})^{,\,l} - \Gamma^k_{il}\,(g^{lm}_m + g^{lm}\,\Gamma^n_{mn}) - \Gamma^m_{in}\,\Gamma^k_{lm}\,g^{ln} \tag{131}$$

and

$$(\Gamma^i_{kl})^{,\,m} = (\Gamma^i_{kl})_{,\,n}\,g^{mn}.$$

$\hat{t}^k_i$ differs from $t_i{}^k$ by a tensor. Thus, the transformation law (124) holds also for $\hat{t}^k_i$.

By (10), (13'), and (71) $t_i{}^k$ satisfies the conservation law

$$\left(\sqrt{-g}\,t_i{}^k\right)_{,\,k} = -\left(\sqrt{-g}\,T^k_i\right)_{,\,k} = -\frac{\sqrt{-g}}{2}\,g_{kl,\,i}\,T^{kl} \tag{132}$$

in any system of coordinates. But, as is well known, one may always in an infinite number of ways introduce systems of coordinates which are geodesic at a given point 0 in 4-space, i. e., systems in which the first order derivatives of the metric tensor vanish at the point 0. Then, at 0, which we shall take as origin of the geodesic system, (132) reduces to

$$\left.\begin{aligned} t_i{}^k{}_{,\,k} &= 0 \\ T^k_{i,\,k} &= 0. \end{aligned}\right\} \tag{133}$$

i. e., the conservation law is of the same form as in a system of inertia in the special theory of relativity. Geodesic systems of coordinates are therefore often called *local systems of inertia*. However, the complex $t_i{}^k$ is not in general zero in a geodesic system and, as we shall see in the last section, it seems appropriate to use this denotation only for a certain restricted class of geodesic systems. In a general geodesic system, we have at the origin, according to (129), (131), (113), and (13),

$$\left.\begin{aligned} t_i{}^k &= -\delta_i^k R/2\varkappa + \hat{t}_i^k \\ \hat{t}_i^k &= (\Gamma_{il}^l)^{,k} - (\Gamma_{il}^k)^{,l} \\ \chi_i{}^{kl} &= 0, \qquad b_i{}^{klm}{}_{,l} = 0. \end{aligned}\right\} \tag{134}$$

Let us now assume that the coordinate systems (x^i) and (x'^i) in (124) are both geodesic at the point 0, which means that the first order derivatives of the $\breve{\alpha}_k^i$ must be zero at 0, i. e.,

$$\breve{\alpha}_{m,\,n}^s(0) = 0. \tag{135}$$

We shall further choose

$$\alpha_k^i(0) = \delta_k^i \tag{135'}$$

which does not imply any essential restriction. In that case, the transformation law (124) at the origin 0 of our geodesic systems takes the form

$$t_i'^k = t_i{}^k - \breve{\alpha}_{i,\,m,\,n}^{r\,(0)}\, b_r{}^{kmn}. \tag{136}$$

Here, $\breve{\alpha}_{i,\,m,\,n}^r$ may be any set of numbers symmetrical in the indices i, m, and n.

The question is now whether the coefficients $\breve{\alpha}_{i,\,m,\,n}^{r\,(0)}$ can be chosen such that the $t_i'^k$ become zero at 0. It is easily seen that this is not always possible, for the diagonal sum $t_i{}^i$ is obviously invariant under the transition from one geodesic system to another. In fact, we get from (136)

$$t_i'{}^i = t_i{}^i, \tag{137}$$

since the last term in (136) vanishes by contraction of the indices i and k on account of the symmetry of $\breve{\alpha}_{i,\,m,\,n}^r$ and the antisymmetry of $b_r{}^{imn}$ in the indices i and m.

Further, since by (134),

$$\left.\begin{aligned} \hat{t}_i^i &= (\Gamma_{il}^l)^{,i} - (\Gamma_{il}^i)^{,l} = 0 \\ t_i{}^i &= -2R/\varkappa, \end{aligned}\right\} \tag{138}$$

it is clear that a transformation (136) cannot make $t_i'^k$ zero, unless the curvature scalar is zero at the point 0. On the other hand, since $\hat{t}_i'^i = \hat{t}_i^i = 0$ and the transformation equations (136) hold also for $\hat{t}_i^k$, it seems always possible to choose a geodesic system in which all components $\hat{t}_i'^k$ vanish.

In the following sections, we shall see that this is really the case for a large group of geodesic systems, the "locally normal" systems of coordinates.

6. Normal Coordinates

Among the coordinate systems which are geodesic at a given point 0, the normal coordinates introduced already by Riemann for 2-dimensional surfaces, play a distinguished role. They are defined as follows. Let (x^i) be an arbitrary system of coordinates. Then, the geodesics may be defined by the equations

$$\frac{d^2 x^i}{d\lambda^2} + \Gamma^i_{kl} \frac{dx^k}{d\lambda} \frac{dx^l}{d\lambda} = 0, \tag{139}$$

where the parameter λ is defined only up to a linear transformation. For all geodesics, except the null-lines, λ is proportional to the invariant 4-distance s. Now, consider all the geodesics passing through the point 0. They are defined by the vector tangents at 0 with components $\beta^i = \frac{dx^i}{d\lambda}(0)$. In a certain finite domain around 0, there will be only one of these geodesics passing through a given point P. We may therefore characterize this point by the four numbers

$$\overset{\circ}{x}{}^i = \beta^i (\lambda_P - \lambda_0), \quad \beta^i = \frac{dx^i}{d\lambda}(0) \tag{140}$$

which are the normal coordinates of Riemann. They are uniquely determined since they are unchanged by a linear transformation of the parameter λ. If P approaches 0, the line joining 0 and P defines an infinitesimal vector at 0 with the contravariant components dx^i and $d\overset{\circ}{x}{}^i$ in the two systems of coordinates, respectively. Obviously, we have at 0 $d\overset{\circ}{x}{}^i = dx^i$, i. e., $\alpha^i_k(0) = \delta^i_k$ and the components of any tensor are identical in the two systems at the origin 0. Thus, for instance,

$$\overset{\circ}{g}_{ik}(0) = g_{ik}(0), \quad \overset{\circ}{R}_{iklm}(0) = R_{iklm}(0). \tag{141}$$

In this way, a uniquely defined normal system $\overset{\circ}{x}{}^i$ is connected with every x^i-system. An arbitrary transformation of the x^i-system $(x^i) \rightarrow (x'^i)$ obviously induces a *linear* transformation $(\overset{\circ}{x}{}^i) \rightarrow (\overset{\circ}{x}{}'^i)$ of the adjoint normal systems. The normal systems of coordinates are as close to the rectilinear systems of flat space as possible in a general Riemannian space. From their definition it follows that any geodesic passing through the origin 0 is described by a linear parameter representation in normal coordinates, i. e.,

$$\overset{\circ}{x}{}^i = \beta^i (\lambda - \lambda_0)$$

with constant β^i. Thus,

$$\frac{d\overset{\circ}{x}^i}{d\lambda} = \beta^i = \overset{\circ}{x}^i/(\lambda - \lambda_0), \quad \frac{d^2\overset{\circ}{x}^i}{d\lambda^2} = 0$$

and, by means of the equations (139) written in normal coordinates, we get

$$\overset{\circ}{\Gamma}{}^i_{kl}(\overset{\circ}{x})\,\overset{\circ}{x}{}^k\,\overset{\circ}{x}{}^l = 0 \tag{142}$$

at all points in 4-space. The equations (142) or the equivalent equations

$$\overset{\circ}{\Gamma}_{i,\,kl}(\overset{\circ}{x})\,\overset{\circ}{x}{}^k\,\overset{\circ}{x}{}^l = 0 \tag{143}$$

represent a sufficient and necessary condition for the system of coordinates to be a normal system.

By repeated differentiations of these equations, one finds, as shown in Appendix B, the following values for the derivatives of the metric tensor at the origin 0:

$$\left.\begin{aligned} \overset{\circ}{g}_{ik,\,l}(0) &= 0 && \text{a}\\ \overset{\circ}{g}_{ik,\,l,\,m}(0) = \overset{\circ}{g}_{lm,\,i,\,k}(0) &= -\frac{1}{3}\left[R_{ilmk}(0) + R_{imlk}(0)\right] && \text{b}\\ \overset{\circ}{g}_{ik,\,l,\,m,\,n}(0) &= \frac{1}{3}\left[R_{ilkm;\,n}(0) + R_{imkn;\,l}(0) + R_{inkl;\,m}(0)\right] && \text{c} \end{aligned}\right\} \tag{144}$$

where $R_{ilmk}(0)$ is the Riemann curvature tensor at 0. In a small surrounding of 0, we have the following approximate expression for $g_{ik}(x)$:

$$\overset{\circ}{g}_{ik}(x) = g_{ik}(0) + \frac{1}{2}\overset{\circ}{g}_{ik,\,l,\,m}(0)\,\overset{\circ}{x}{}^l\,\overset{\circ}{x}{}^m + \frac{1}{3!}\overset{\circ}{g}_{ik,\,l,\,m,\,n}(0)\,\overset{\circ}{x}{}^l\,\overset{\circ}{x}{}^m\,\overset{\circ}{x}{}^n \tag{145}$$

with coefficients given by (144). The linear terms are lacking, since a normal system, according to (144a), is a special type of a geodesic system. By means of (12), (13), and (144), we have at the point 0

$$\left.\begin{aligned} \overset{\circ}{\mathcal{T}}{}_i{}^k &= \frac{\sqrt{-g}}{\varkappa}\left(\overset{\circ}{g}_{in,\,m,\,l} - \overset{\circ}{g}_{im,\,n,\,l}\right) g^{km}\,g^{ln}\\ &= -\frac{\sqrt{-g}}{3\varkappa}\left(R_{imln} + R_{ilmn} - R_{inlm} - R_{ilnm}\right) g^{km}\,g^{ln}\\ &= -\frac{\sqrt{-g}}{\varkappa} R_{il}{}^{kl} = -\frac{\sqrt{-g}}{\varkappa} R_i^k = \sqrt{-g}\,T_i^k - \frac{1}{2}\frac{\sqrt{-g}}{\varkappa} R\,\delta_i^k. \end{aligned}\right\} \tag{146}$$

Here, we have used the symmetry properties of the Riemann tensor and the expression for the contracted curvature tensor.

A comparison of (146) with (10) and (134) gives

$$\left.\begin{aligned} \overset{\circ}{t}{}_i^k &= -\frac{R}{2\varkappa}\delta_i^k \\ \overset{\circ}{\hat{t}}{}_i^k &= 0 \end{aligned}\right\} \qquad (147)$$

at the origin of a normal system of coordinates.

Similarly, we get at 0 by (12), (13), and (144)

$$\left.\begin{aligned} \overset{\circ}{\mathcal{T}}{}_{i}{}^{k}{}_{,r} &= \frac{\sqrt{-g}}{\varkappa}(\overset{\circ}{g}_{in,m,l,r} - \overset{\circ}{g}_{im,n,l,r})\,g^{km}g^{ln} \\ &= -\frac{\sqrt{-g}}{3\varkappa}(R_{inml;r} + R_{ilmr;n} + R_{irmn;l} - R_{imnl;r} - R_{ilnr;m} - R_{irnm;l})\,g^{km}g^{ln}. \end{aligned}\right\} \qquad (148)$$

On account of the symmetry properties of the Riemann tensor and the Bianchi identities, this may be written

$$\overset{\circ}{\mathcal{T}}{}_{i}{}^{k}{}_{,r} = -\frac{2\sqrt{-g}}{3\kappa}(R_{il}{}^{kl}{}_{;r} - R_{ir}{}^{lk}{}_{;l}).$$

Further, we have

$$R_{ir}{}^{lk}{}_{;l} = R^{lk}{}_{ir;l} = -R^{lk}{}_{rl;i} - R^{lk}{}_{li;r} = R^k_{r;i} - R^k_{i;r}.$$

Thus, at the origin of a normal system, we have

$$\overset{\circ}{\mathcal{T}}{}_{i}{}^{k}{}_{,r} = -\frac{4\sqrt{-g}}{3\kappa}\left(R^k_{i;r} - \frac{1}{2}R^k_{r;i}\right). \qquad (149)$$

In accordance with (13′), the right-hand side of (149) vanishes on account of the contracted Bianchi identities if we put $r = k$ and sum over k.

7. Locally Normal Coordinates. Local Systems of Inertia in Empty Space

The normal coordinates $(\overset{\circ}{x}{}^i)$ considered in the preceding section are uniquely determined by the conditions (141), (142). Usually, however, one is interested only in systems of coordinates which are *locally* normal, i. e., where (142) is satisfied only approximately in a small region around the origin. In this connection, one can distinguish between locally normal systems of first order, second order, and third order, according as to whether only the first, the first and the second, or all three equations (144), respectively, are satisfied. The locally normal systems of first order are obviously just the geodesic systems. Starting from an arbitrary system of coordinates (x^i), the locally normal systems of n'th order may be obtained by a transformation of the form

$$\overset{\circ}{x}{}^i = P^i_{(n)}(x), \tag{150}$$

where $P^i_{(n)}(x)$ is a polynomial of degree $n+1$ in the coordinate differences $x^i - x^i_0$ with suitable coefficients. Here, (x^i_0) denotes the coordinates of the point 0 in the (x^i)-system. As shown in Appendix C, the locally normally systems of order 2, for instance, are obtained by the transformation

$$\overset{\circ}{x}{}^i = x^i + \frac{1}{2} \Gamma^i_{kl}(0)\,(x^k - x^k_0)\,(x^l - x^l_0) + \frac{1}{3!} B^i_{klm}(0)\,(x^k - x^k_0)\,(x^l - x^l_0)\,(x^m - x^m_0) \tag{151}$$

with

$$B^i_{klm} = \frac{1}{3}\left[\Gamma^i_{kl,\,m} + \Gamma^i_{lm,\,k} + \Gamma^i_{mk,\,l} + \Gamma^i_{rk}\,\Gamma^r_{lm} + \Gamma^i_{rl}\,\Gamma^r_{mk} + \Gamma^i_{rm}\,\Gamma^i_{kl}\right]. \tag{152}$$

If we omit the last term in (151) we get the usual transformation leading to the geodesic systems.

Let us now first consider a domain of 4-space where there is no matter present, i. e., where

$$T^k_i = 0, \quad R^k_i = 0, \quad R_{i\ ,\,r}^{\ k} = 0. \tag{153}$$

In that case, we have, according to (10) and (130),

$$\mathcal{T}_i^{\ k} = \sqrt{-g}\, t_i^{\ k}, \quad t_i^{\ k} = \hat{t}^k_i \tag{154}$$

In empty space, it seems natural to define a local system of inertia as a system in which not only the metric tensor is locally constant to the first order, but in which also the complexes $\mathcal{T}_i^{\ k}$ and $t_i^{\ k}$ vanish at the origin. From this point of view, only normal systems of at least second order should be called local systems of inertia, for only in such systems we have, according to (146), (147), and (153),

$$\overset{\circ}{\mathcal{T}}{}_i^{\ k}(0) = \overset{\circ}{t}{}_i^{\ k}(0) = \overset{\circ}{\hat{t}}{}_i^{\ k}(0) = 0. \tag{155}$$

If the system considered is normal of even higher order, $t_i{}^k$ is also *locally constant*, for by (149) and (153)

$$\overset{\circ}{\mathcal{T}}{}_{i\,,r}^{\,k} = \overset{\circ}{t}{}_{i\,,r}^{\,k} = 0 \tag{156}$$

at the origin.

On the other hand, inside matter where T_i^k, R_i^k, and in general also R are different from zero, we have by (147) in any normal system of at least second order

$$\overset{\circ}{t}_i{}^k(0) = -\delta_i^k R(0)/2\varkappa. \tag{157}$$

Thus, the gravitational complex $t_i{}^k$ does not vanish, unless $T_i^i = R/\varkappa = 0$ as, for instance, in the case where the matter is a purely electromagnetic field. Moreover, from the considerations in section 5 it follows that it is not possible at all to find a geodesic system in which $t_i{}^k$ vanishes exactly. Only the complex $\hat{t}_i{}^k$ can in general be transformed away completely by introducing locally normal systems of second order. Inside matter, these systems thus hardly deserve the name of local systems of inertia. In a subsequent paper, it will be shown in another connection that it is more natural to reserve this denotation for a class of systems which are only approximately locally normal systems of coordinates.

Appendix A

From (62), (64),

$$\mathfrak{h} = \varkappa h_r{}^{rl}{}_{,\,l} = (\eta g^{lm}_{\;\;m} + 2 g^{lm} \eta_m)_{,\,l} \tag{A 1}$$

with

$$\eta = \sqrt{-g}, \qquad \eta_m = \frac{\partial \eta}{\partial x^m},$$

we get, for arbitrary variations of g^{ik},

$$\delta\mathfrak{h} = \eta\,\delta g^{lm}_{l,\,m} + g^{rs}_{r,\,s}\delta\eta + 3\,g^{kr}_{r}\,\delta\eta_k + 3\,\eta_l\,\delta g^{lm}_{m} + 2\,\eta_{l,\,m}\,\delta g^{lm} + 2\,g^{ik}\,\delta\eta_{i,\,k}. \tag{A 2}$$

Differentiation of the relation

$$\delta\eta = -\frac{1}{2}\eta\, g_{lm}\,\delta g^{lm} \tag{A 3}$$

yields

$$\delta\eta_k = -\frac{1}{2}[(\eta\, g_{lm})_{,\,k}\,\delta g^{lm} + \eta\, g_{lm}\,\delta g^{lm}_k] \tag{A 4}$$

$$\delta\eta_{i,\,k} = -\frac{1}{2}\left[(\eta\, g_{lm})_{,\,i,\,k}\,\delta g^{lm} + (\eta\, g_{lm})_{,\,k}\,\delta g_i^{lm} + (\eta\, g_{lm})_{,\,i}\,\delta g_k^{lm} + \eta\, g_{lm}\,\delta g_{i,\,k}^{lm}\right]. \tag{A 5}$$

After introduction of these expressions into (A 2) and some rearrangement of terms, $\delta\,\mathfrak{h}$ may be written

$$\left.\begin{aligned} \delta\,\mathfrak{h} = \eta\left[\frac{1}{2}(\delta_l^i\,\delta_m^k + \delta_l^k\,\delta_m^i) - g^{ik}\,g_{lm}\right]\delta g_{i,\,k}^{lm} \\ + \left[\frac{3}{2}(\eta_l\,\delta_m^k + \delta_l^k\,\eta_m) - \frac{3}{2}\,g_r^{kr}\,\eta\, g_{lm} - 2\,g^{rk}\,\eta\, g_{lm})_{,\,r}\right]\delta g_k^{lm} \\ + \left[2\,\eta_{l,\,m} - g^{rs}\,(\eta\, g_{lm})_{,\,r,\,s} - \frac{3}{2}\,g_s^{rs}\,(\eta\, g_{lm})_{,\,r} - \frac{1}{2}\,\eta\, g_{lm}\,g_{r,\,s}^{rs}\right]\delta g^{lm}. \end{aligned}\right\} \tag{A 6}$$

Hence, by definition,

$$\frac{\partial\,\mathfrak{h}}{\partial g^{lm}} = 2\,\eta_{l,\,m} - g^{rs}\,(\eta\, g_{lm})_{,\,r,\,s} - \frac{3}{2}\,(\eta\, g_{lm})_{,\,r}\,g_s^{rs} - \frac{1}{2}\,\eta\, g_{lm}\,g_{r,\,s}^{rs} \tag{A 7}$$

$$\frac{\partial\,\mathfrak{h}}{\partial g_k^{lm}} = \frac{3}{2}\,(\delta_l^k\,\eta_m + \eta_l\,\delta_m^k) - \frac{3}{2}\,g_r^{kr}\,\eta\, g_{lm} - 2\,g^{kr}\,(\eta\, g_{lm})_{,\,r} \tag{A 8}$$

$$\frac{\partial\,\mathfrak{h}}{\partial g_{i,\,k}^{lm}} = \eta\left[\frac{1}{2}\,(\delta_l^i\,\delta_m^k + \delta_l^k\,\delta_m^i) - g^{ik}\,g_{lm}\right]. \tag{A 9}$$

These expressions are easily seen to be in accordance with the identities (66).

From (A 9) we get, using the relation

$$\eta_i = -\frac{1}{2}\,\eta\, g_{lm}\,g_i^{lm}, \tag{A 10}$$

$$\left(\frac{\partial\,\mathfrak{h}}{\partial g_{i,\,k}^{lm}}\,g_i^{lm}\right)_{,\,k} = [\eta\, g_i^{ik} - \eta\, g^{ik}\,g_{lm}\,g_i^{lm}]_{,\,k} = [\eta\, g_i^{ik} + 2\,g^{ik}\,\eta_i]_{,\,k} = \mathfrak{h} \tag{A 11}$$

which shows that the last term in (74) is zero. Further, by (A 8) and (A 9),

$$\left.\begin{aligned} \frac{\partial\,\mathfrak{h}}{\partial g_k^{lm}} - \left(\frac{\partial\,\mathfrak{h}}{\partial g_{k,r}^{lm}}\right)_{,\,r} &= \delta_l^k\,\eta_m + \eta_l\,\delta_m^k - \frac{1}{2}\,g_r^{kr}\,\eta\, g_{lm} - g^{kr}\,(\eta\, g_{lm})_{,\,r}, \\ \left[\frac{\partial\,\mathfrak{h}}{\partial g_k^{lm}} - \left(\frac{\partial\,\mathfrak{h}}{\partial g_{k,\,r}^{lm}}\right)_{,\,r}\right] g_i^{lm} &= 2\,g_i^{kl}\,\eta_l + g_r^{kr}\,\eta_i - g^{kr}\,(\eta\, g_{lm})_{,\,r}\,g_i^{lm}, \end{aligned}\right\} \tag{A 12}$$

$$\left.\begin{aligned}\left(\frac{\partial\,\mathfrak{h}}{\partial\,g^{lm}_{k,\,r}}\right)_{,\,i} g^{lm}_r &= \left[\eta_i\,\frac{1}{2}\,(\delta^r_l\,\delta^k_m + \delta^k_l\,\delta^r_m) - g^{kr}_i\,\eta\,g_{lm} - g^{kr}\,(\eta\,g_{lm})_{,\,i}\right] g^{lm}_r \\ &= g^{kr}_r\,\eta_i + 2\,g^{kr}_i\,\eta_r - g^{kr}\,(\eta\,g_{lm})_{,\,i}\,g^{lm}_r .\end{aligned}\right\} \quad (\text{A } 13)$$

Thus, we get for the quantity A^k_i of (74),

$$A^k_i = g^{kr}\,[-\eta_r\,g_{lm}\,g^{lm}_i + \eta_i\,g_{lm}\,g^{lm}_r - \eta\,(g_{lm,\,r}\,g^{lm}_i - g_{lm,\,i}\,g^{lm}_r)] = 0\,, \quad (\text{A } 14)$$

on account of (A 10) and the relation

$$g_{lm,\,i} = -\,g_{ls}\,g^{st}_i\,g_{tm} \quad (\text{A } 15)$$

which follows from the equation

$$g_{il}\,g^{kl} = \delta^k_i \quad (\text{A } 16)$$

by differentiation.

Further, we have

$$\left.\begin{aligned}\frac{\partial\,\mathfrak{h}}{\partial\,g^{rs}_{l,\,m}}\,g^{rs}_m &= \left[\frac{\eta}{2}\,(\delta^l_r\,\delta^m_s + \delta^m_r\,\delta^l_s) - \eta\,g^{lm}\,g_{rs}\right] g^{rs}_m \\ &= \eta\,g^{lm}_m + 2\,g^{lm}\,\eta_m = \varkappa\,h^{rl}_r\end{aligned}\right\} \quad (\text{A } 17)$$

which by (75) leads to the expression (76) for K^{kl}_i.

Finally, we have to calculate the quantity B^{kl}_i defined by (81) in the text. For the first term we get by (A 12)

$$\begin{aligned}\left[\frac{\partial\,\mathfrak{h}}{\partial\,g^{in}_l} - \left(\frac{\partial\,\mathfrak{h}}{\partial\,g^{in}_{l,\,m}}\right)_{,\,m}\right] g^{kn} &= \left[\delta^l_i\,\eta_n + \eta_i\,\delta^l_n - \frac{1}{2}\,g^{lr}_r\,\eta\,g_{in} - g^{lr}\,(\eta\,g_{in})_{,\,r}\right] g^{kn} \\ &= \delta^l_i\,g^{kn}\,\eta_n + \eta_i\,g^{kl} - \frac{1}{2}\,\delta^k_i\,\eta\,g^{lr}_r - g^{lm}\,(\eta_m\,g_{in} + \eta\,g_{in,\,m})\,g^{kn}\end{aligned}$$

for the second and third terms by (A 9)

$$\frac{\partial\,\mathfrak{h}}{\partial\,g^{in}_{l,\,m}}\,g^{kn}_m = \left[\frac{1}{2}\,\eta\,(\delta^l_i\,\delta^m_n + \delta^m_i\,\delta^l_n) - \eta\,g^{lm}\,g_{in}\right] g^{kn}_m = \frac{\eta}{2}\,\delta^l_i\,g^{km}_m + \frac{\eta}{2}\,g^{kl}_i + g^{lm}\,\eta\,g_{in,\,m}\,g^{kn}_{,}$$

$$\begin{aligned}-\frac{1}{3}\left[\left(\frac{\partial\,\mathfrak{h}}{\partial\,g^{in}_{l,\,m}}\right) g^{kn}\right]_{,\,m} &= -\frac{1}{3}\left[\frac{\eta}{2}\,(\delta^l_i\,\delta^m_n + \delta^m_i\,\delta^l_n)\,g^{kn} - g^{lm}\,\eta\,g_{in}\,g^{kn}\right]_{,\,m} \\ &= -\frac{1}{6}\,\delta^l_i\,(\eta\,g^{km})_{,\,m} - \frac{1}{6}\,(\eta\,g^{kl})_{,\,i} + \frac{1}{3}\,\delta^k_i\,(\eta\,g^{lm})_{,\,m} .\end{aligned}$$

Hence,

$$\left.\begin{aligned}\varkappa B_i^{kl} = \frac{1}{2}\delta_i^l(\eta\, g_m^{km} + 2\, g^{km}\eta_m) - \frac{1}{2}\delta_i^k(\eta\, g_m^{lm} + 2\, g^{lm}\eta_m) + \frac{1}{3}\delta_i^k(\eta\, g^{lm})_{,\,m}\\ - \frac{1}{6}\delta_i^l(\eta\, g^{km})_{,\,m} + \eta_i\, g^{kl} + \frac{\eta}{2} g_i^{kl} - \frac{1}{6}(\eta\, g^{kl})_{,\,i}\end{aligned}\right\} \qquad \text{(A 18)}$$

and

$$B_i^{kl} - B_i^{lk} = \delta_i^l\, h_r^{\ rk} - \delta_i^k\, h_l^{\ rl} + \frac{1}{2\varkappa}[\delta_i^k(\eta\, g^{lm}) - \delta_i^l(\eta\, g^{km})]_{,\,m}. \qquad \text{(A 19)}$$

On the other hand, we have by (6), and (7) in the text

$$s_i^{\ kl} - s_i^{\ lk} = 2\, h_i^{\ kl} + \frac{1}{2\varkappa}[\delta_i^l(\eta\, g^{km}) - \delta_i^k(\eta\, g^{lm})]_{,\,m}$$

$$2\, h_i^{\ kl} = \frac{\sqrt{-g}}{\varkappa}\, g_{in}(g_m^{kn}\, g^{lm} - g_m^{ln}\, g^{km}) + \frac{1}{\varkappa}\left[\delta_i^k \frac{1}{\eta}(\eta^2\, g^{lm})_{,\,m} - \delta_i^l \frac{1}{\eta}(\eta^2\, g^{km})_{,\,m}\right].$$

Hence, by (64), (80),

$$\left.\begin{aligned}U_i^{\ kl} = s_i^{\ kl} - s_i^{\ lk} + B_i^{kl} - B_i^{lk} &= \frac{\sqrt{-g}}{\varkappa}\, g_{in}(g_m^{kn}\, g^{lm} - g_m^{ln}\, g^{km})\\ &= \frac{\sqrt{-g}}{\varkappa}(g_{in,\,m} - g_{im,\,n})\, g^{km}\, g^{ln} = \chi_i^{kl},\end{aligned}\right\} \qquad \text{(A 20)}$$

where $\chi_i^{\ kl}$ is given by equation (13) in the text.

Appendix B

A system of normal Riemann coordinates in 4-space is characterized by the equations (143) which have to be satisfied at each point. Hence, omitting the ° over the symbols, thus writing x^i, g_{ik}, . . . instead of $\overset{\circ}{x}{}^i$, $\overset{\circ}{g}_{ik}$, . . .,

$$\Gamma_{i,\,rs}(x)\, x^r\, x^s = 0. \qquad \text{(B 1)}$$

If we differentiate this equation twice with respect to x^k and x^l, and hereafter with respect to x^m, we get the following two equations:

$$(\Gamma_{i,\,rs})_{,\,k,\,l}(x)\, x^r\, x^s + 2\,[(\Gamma_{i,\,kr})_{,\,l} + (\Gamma_{i,\,lr})_{,\,k}]\, x^r + 2\,\Gamma_{i,\,kl}(x) = 0 \qquad \text{(B 2)}$$

$$\left.\begin{aligned}(\Gamma_{i,rs})_{,k,l,m}(x)\,x^r x^s + 2\left[(\Gamma_{i,mr})_{,k,l} + (\Gamma_{i,kr})_{,l,m} + (\Gamma_{i,lr})_{,k,m}\right]x^r \\ + 2\left[(\Gamma_{i,km})_{,l} + (\Gamma_{i,lm})_{,k} + (\Gamma_{i,kl})_{,m}\right] = 0\,.\end{aligned}\right\} \tag{B 3}$$

For the values of $\Gamma_{i,kl}$ and $(\Gamma_{i,kl})_{,m}$ at the origin 0, we thus get, by putting $x^i = 0$ in these equations,

$$\Gamma_{i,kl} = 0 \tag{B 4}$$

$$A_{iklm} \equiv \underset{(klm)}{\mathsf{S}}(\Gamma_{i,kl})_{,m} \equiv (\Gamma_{i,kl})_{,m} + (\Gamma_{i,lm})_{,k} + (\Gamma_{i,mk})_{,l} = 0\,. \tag{B 5}$$

Here, as in the following, the symbol $\underset{(klm)}{\mathsf{S}}$ in front of a term containing the indices k, l, and m means addition of the two terms obtained by cyclic permutation of these indices.

Similarly, one finds, by differentiation of (B 3) with respect to x^n and afterwards putting $x^i = 0$, at the point 0 the relation

$$A_{ilmnk} + B_{iklmn} = 0 \tag{B 6}$$

with

$$\left.\begin{aligned}A_{ilmnk} &= \underset{(lmn)}{\mathsf{S}}(\Gamma_{i,lm})_{,n,k} \\ B_{iklmn} &= \underset{(lmn)}{\mathsf{S}}(\Gamma_{i,kl})_{,m,n}\,.\end{aligned}\right\} \tag{B 7}$$

The equation (B 4) is equivalent to

$$g_{ik,l} = 0 \tag{B 8}$$

showing that the system is geodesic at 0.

The Christoffel symbols are defined by

$$\Gamma_{i,kl} = \frac{1}{2}(g_{ik,l} + g_{il,k} - g_{kl,i})\,. \tag{B 9}$$

Introduction of these expressions into (B 5) gives

$$A_{iklm} \equiv \underset{(klm)}{\mathsf{S}}\, g_{ik,l,m} - \frac{1}{2}\underset{(klm)}{\mathsf{S}}\, g_{kl,m,i} = 0\,,$$

which is equivalent to

$$2\,A_{iklm} + A_{kilm} \equiv 3\,g_{ik,l,m} + \frac{3}{2}(g_{il,k,m} + g_{im,k,l} - g_{lm,i,k}) = 0\,.$$

Hence, since $g_{ik,\,l,\,m}$ is symmetrical in i and k,

$$g_{ik,\,l,\,m} = -(\Gamma_{i,\,lm})_{,\,k} = -(\Gamma_{k,\,lm})_{,\,i}\,. \tag{B 10}$$

Similarly, we get for A_{ilmnk} and B_{iklmn} in (B 7), after a simple rearrangement of terms,

$$A_{ilmnk} = \mathop{\mathsf{S}}_{(lmn)} g_{il,\,m,\,n,\,k} - \frac{1}{2} \mathop{\mathsf{S}}_{(lmn)} g_{lm,\,n,\,i,\,k} \tag{B 11}$$

$$B_{iklmn} = \frac{3}{2} g_{ik,\,l,\,m,\,n} + \frac{1}{2} \mathop{\mathsf{S}}_{(lmn)} \left[g_{il,\,m,\,n,\,k} - g_{kl,\,m,\,n,\,i} \right]. \tag{B 12}$$

Since the last term on the right-hand side of (B 11), as well as the first term on the right-hand side of (B 12), is symmetrical in i and k, we get

$$B_{iklmn} - B_{kilmn} = \mathop{\mathsf{S}}_{(lmn)} \left[g_{il,\,m,\,n,\,k} - g_{kl,\,m,\,n,\,i} \right] = A_{ilmnk} - A_{klmni}\,. \tag{B 13}$$

On the other hand, we have by (B 6)

$$B_{iklmn} - B_{kilmn} = -(A_{ilmnk} - A_{klmni}),$$

which means that these differences must be zero. Hence, by (B 12) and (B 6),

$$\left.\begin{aligned} g_{ik,\,l,\,m,\,n} &= \frac{2}{3} B_{iklmn} = -\frac{2}{3} A_{ilmnk} \\ g_{ik,\,l,\,m,\,n} &= -\frac{2}{3} \mathop{\mathsf{S}}_{(lmn)} (\Gamma_{i,\,lm})_{,\,n,\,k} = -\frac{2}{3} \left[(\Gamma_{i,\,lm})_{,\,n} + (\Gamma_{i,\,mn})_{,\,l} + \Gamma_{i,\,nl})_{,\,m} \right]_{,\,k}\,. \end{aligned}\right\} \tag{B 14}$$

At the origin 0, where (B 4) and (B 8) hold, the Riemann curvature tensor R_{iklm} and its derivatives are now given by

$$\left.\begin{aligned} R_{iklm} &= (\Gamma_{i,\,kl})_{,\,m} - (\Gamma_{i,\,km})_{,\,l} \\ R_{iklm;\,n} = R_{iklm,\,n} &= (\Gamma_{i,\,kl})_{,\,m,\,n} - (\Gamma_{i,\,km})_{,\,l,\,n}\,. \end{aligned}\right\} \tag{B 15}$$

Hence, by (B 5), (B 10),

$$R_{ilmk} + R_{imlk} = 2\,(\Gamma_{i,\,lm})_{,\,k} - (\Gamma_{i,\,kl})_{,\,m} - (\Gamma_{i,\,mk})_{,\,l} = 3\,(\Gamma_{i,\,lm})_{,\,k}$$

and

$$g_{ik,\,l,\,m} = -\frac{1}{3} (R_{ilmk} + R_{imlk})\,. \tag{B 16}$$

Similarly, by (B 15), (B 6), (B 7) and (B 14)

$$\underset{(lmn)}{\mathsf{S}}\, R_{ilkm;\,n} = \underset{(lmn)}{\mathsf{S}}\, [(\Gamma_{i,\,kl})_{,\,m,\,n} - (\Gamma_{i,\,lm})_{,\,n,\,k}] = -2\, \underset{(lmn)}{\mathsf{S}}\, (\Gamma_{i,\,lm})_{,\,n,\,k}$$

and

$$g_{ik,\,l,\,m,\,n} = \frac{1}{3}\, \underset{(lmn)}{\mathsf{S}}\, R_{ilkm;\,n} = \frac{1}{3}\, [R_{ilkm;\,n} + R_{imkn;\,l} + R_{inkl;\,m}]. \qquad (\mathrm{B}\ 17)$$

The equations (B 8), (B 16), and (B 17) are just the equations (144) used in Section 6.

Appendix C

We shall in this Appendix consider the transformations leading from an arbitrary system of coordinates x^i to a normal system $\overset{\circ}{x}{}^i$ with origin at a given point 0. Put

$$\left.\begin{array}{l} \overset{\circ}{x}{}^i = f^i(x), \quad \alpha^i_k = \dfrac{\partial \overset{\circ}{x}{}^i}{\partial x^k}, \quad \alpha^i_{k,\,l} = \dfrac{\partial^2 \overset{\circ}{x}{}^i}{\partial x^k\, \delta x^l}, \;\ldots . \\[2ex] x^i = g^i(\overset{\circ}{x}), \quad \breve{\alpha}^i_k = \dfrac{\partial x^i}{\partial \overset{\circ}{x}{}^k}, \quad \breve{\alpha}^i_{k,\,l} = \dfrac{\partial^2 x^i}{\partial \overset{\circ}{x}{}^k\, \partial \overset{\circ}{x}{}^l}, \;\ldots . \end{array}\right\} \qquad (\mathrm{C}\ 1)$$

$$\alpha^i_l\, \breve{\alpha}^l_k = \breve{\alpha}^i_l\, \alpha^l_k = \delta^i_k. \qquad (\mathrm{C}\ 2)$$

By means of (C 2), the Christoffel transformation formulae

$$\overset{\circ}{\Gamma}{}^i_{kl}(\overset{\circ}{x}) = \alpha^i_r\, \breve{\alpha}^r_{k,\,l} + \alpha^i_r\, \breve{\alpha}^s_k\, \breve{\alpha}^t_l\, \Gamma^r_{st}(x)$$

may be written

$$\breve{\alpha}^i_{k,\,l} + \Gamma^i_{st}(x^m)\, \breve{\alpha}^s_k\, \breve{\alpha}^t_l = \breve{\alpha}^i_r\, \overset{\circ}{\Gamma}{}^r_{kl}(\overset{\circ}{x}). \qquad (\mathrm{C}\ 3)$$

If we multiply this equation by $\overset{\circ}{x}{}^k\, \overset{\circ}{x}{}^l$, we get by Eq. (143) in the text the following differentio-functional equations for the functions $g^i(\overset{\circ}{x})$

$$\overset{\circ}{x}{}^k\, \overset{\circ}{x}{}^l\, \frac{\partial^2 g^i}{\partial \overset{\circ}{x}{}^k\, \partial \overset{\circ}{x}{}^l} + \Gamma^i_{st}(g^m(\overset{\circ}{x}))\, \frac{\partial g^s}{\partial \overset{\circ}{x}{}^k}\, \frac{\partial g^t}{\partial \overset{\circ}{x}{}^l} = 0. \qquad (\mathrm{C}\ 4)$$

Four independent solutions of (C 4) satisfying the condition

$$g^i(0) = x^i_0, \quad \frac{\partial g^i}{\partial \overset{\circ}{x}{}^k}(0) = \delta^i_k$$

define the transformation to normal coordinates.

If we are interested in locally normal systems only, we need not consider the values of $g^i(\overset{\circ}{x})$ in large distances from 0. From the inverse relation (C 3), i. e.,

$$\alpha^i_{k,l}(x) + \overset{\circ}{\Gamma}{}^i_{st}(\overset{\circ}{x})\,\alpha^s_k(x)\,\alpha^t_l(x) = \alpha^i_r(x)\,\Gamma^r_{kl}(x) \tag{C 5}$$

we get at 0, remembering that $\alpha^i_k(0) = \delta^i_k$ and $\overset{\circ}{\Gamma}{}^i_{kl}(0) = 0$,

$$\alpha^i_{k,l}(0) = \Gamma^i_{kl}(0) \tag{C 6}$$

which, apart from a factor 2 is identical with the coefficient of the quadratic term in the transformation (151).

Now, differentiate (C 5) with respect to x^m:

$$\left.\begin{aligned}\alpha^i_{k,l,m}(x) + \overset{\circ}{\Gamma}{}^i_{st,r}(\overset{\circ}{x})\,\alpha^r_m\,\alpha^s_k\,\alpha^t_l + \overset{\circ}{\Gamma}{}^i_{st}(\overset{\circ}{x})\,(\alpha^s_{k,m}\,\alpha^t_l + \alpha^s_k\,\alpha^t_{l,m})\\ = \alpha^i_{r,m}\,\Gamma^r_{kl}(x) + \alpha^i_r\,\Gamma^r_{kl,m}(x).\end{aligned}\right\} \tag{C 7}$$

At 0, this gives

$$\alpha^i_{k,l,m}(0) + \overset{\circ}{\Gamma}{}^i_{kl,m}(0) = \alpha^i_{r,m}(0)\,\Gamma^r_{kl}(0) + \Gamma^i_{kl,m}(0). \tag{C 8}$$

Thus, since $\alpha^i_{k,l,m}$ is symmetrical in the indices k, l, m, we get, by (C 6) and the equation

$$\overset{\circ}{\Gamma}{}^i_{kl,m}(0) + \overset{\circ}{\Gamma}{}^i_{lm,k}(0) + \overset{\circ}{\Gamma}{}^i_{mk,l}(0) = 0 \tag{C 9}$$

valid in a locally normal system (see (144 b) and (B 5) in Appendix B),

$$\alpha^i_{k,l,m}(0) = \frac{1}{3} \mathop{\mathsf{S}}_{(klm)} \left[\Gamma^i_{kl,m}(0) + \Gamma^i_{rm}(0)\,\Gamma^r_{kl}(0)\right] \tag{C 10}$$

which is identical with the coefficient $B^i_{klm}(0)$ in the transformation (151). Thus, the latter transformation leads to a locally normal system of the second order. Proceeding in this way, we can by further differentiations of (C 7) and subsequently putting $x^i = 0$ derive expressions for the values of still higher derivatives of α^i_k at 0 and, thus, determine the coefficients in the higher order terms in the polynomial $P^i_{(n)}(x)$ of Eq. (150) which defines the transformations to the locally normal systems of arbitrarily high order.

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References and Notes

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