ON THE INTERACTION BETWEEN ATOMIC NUCLEI AND ELECTRONS

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H. B. G. CASIMIR

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We have tried to give a survey of those phenomena in which the interaction between the nucleus and the electrons can be described by means of ordinary quantummechanics, and which nevertheless depend on other nuclear properties than charge and mass.

The main part of our paper is formed by a discussion of the theory of hyperfine structure, i.e. the theory of the interaction of the nucleus in its stationary state with the atomic electrons. It was not our object to give a complete derivation or enumeration of all formulae which are of importance in the investigation of hyperfine structure. But we have tried to analyse carefully and systematically the foundations of the theory. Details were only given in cases where we believed that we could add something new to the existing treatment.

Our calculations are based on the assumption that the action of the nucleus on the electrons can be described as the action of a normal quantummechanical system, and one of the most important questions is, whether this is permissible. We arrive at the result that this assumption is not necessarily correct in the case of the so called isotope shift; also in the case of the magnetic interaction small deviations from the theory might occur. From this point of view the theory of the interaction of the electrons with the electric quadrupole moment is the most reliable part of our calculations.

In the sections 20—24 we have given a short survey of the theory of internal conversion. In this case the theory is based on an assumption which is analogous to that occurring in the theory of hyperfine structure.

The last section contains some speculations on the structure of the nucleus.

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§ 1. *General theory of the interaction between a nucleus in a stationary state and a number of electrons.*

We assume that the nucleus in its normal state has an angular momentum $i\hbar$ ($\hbar =$ PLANCK'S constant/2π). The normal state is then $(2i + 1)$-fold degenerate; the non-degenerate states, which together form the normal state, can be described by wave-functions $\varkappa_k$ $(-i \leqslant k \leqslant i)$. The angular momentum (in units $\hbar$) is given by a vectoroperator $\mathbf{I}$ with components I_x, I_y, I_z; the components satisfy the well-known commutability relations. For a suitable choice of the $\varkappa_k$ the matrix elements are given by:

$$
\begin{aligned}
(k \,|\, I_z \,|\, k) &= k \\
(k \,|\, I_x + iI_y \,|\, k - 1) &= \sqrt{(i + k)\,(i - k + 1)} \qquad (1,\ 1) \\
(k \,|\, I_x - iI_y \,|\, k + 1) &= \sqrt{(i - k)\,(i + k + 1)},
\end{aligned}
$$

all other matrix elements vanish. We have:

$$I_x^2 + I_y^2 + I_z^2 = i(i + 1).$$

This relation is independent of the choice of the $\varkappa_k$.

The states of the electrons in a field of a point-charge are described by wavefunctions $\psi\ (n,\ j,\ m)$. Here j is the total angular momentum; m the magnetic quantum number, which takes all (integral or half-integral) values between $+ j$ and $- j$, and n stands for all other quantum numbers. The energy is a function of n and j; the $(2j + 1)$ states belonging to one and the same combination n, j are degenerate with each other. The operators of angular momentum, are diagonalmatrices with respect to n and j; the matrix elements for a given value of j are given by formulae exactly analogous to (1, 1).

The states of the system nucleus + electrons are in this approximation $(2i + 1)(2j + 1)$-fold degenerate. These states will now suffer a perturbation, the perturbation operator S being given by the difference between the true interaction and the interaction of the electrons and a point-charge. Let W be the total interaction, then

$$S = W - \sum_i \frac{-Ze^2}{r_i} \qquad (1, 2)$$

the summation is carried out over all electrons, r_i is the distance of the i^{th} electron from the centre of the nucleus, Ze the nuclear charge.

Let us assume, that the separations caused by the perturbation operator S are small compared with the distances of the unperturbed energy levels (i.e. that the hyperfine structure is small compared with the fine structure). In this case only those matrix elements of S have to be taken into account, which are diagonal elements with respect to j and n. The level with energy $E(n, j)$ is separated into a number of levels; the distances of those levels from the unperturbed level are given by the characteristic values of the matrix with elements

$$(k', m' \mid S \mid k'', m'') = \int \psi^* (n', j', m') \, \varkappa^*_{k'} \, S \, \psi(n', j', m'') \, \varkappa_{k''}.$$

Now S is invariant under simultaneous rotation of nucleus and electrons. Hence the matrix S commutes with the components of the total angular momentum. These components are given by

$$F_x = I_x + J_x$$
$$F_y = I_y + J_y$$
$$F_z = I_z + J_z.$$

If we transform the matrix $F^2 = F_x^2 + F_y^2 + F_z^2$ into diagonal form by replacing the products $\psi(n, j, m) \, \varkappa_k$ by proper linear combinations of these products, then also the perturbation operator will be transformed into diagonal form and to every characteristic value of F^2 there corrresponds a characteristic value of S. The characteristic values of F^2 are equal to $f(f+1)$ where f takes all integral (or half-integral) values between $(i+j)$ and $|i-j|$. A state with total angular momentum f is $(2f+1)$-fold degenerate.

More simply our results may be stated as follows: The existence of a nuclear angular momentum and of an interaction which is not exactly equal to the interaction of electrons and a point-charge will cause a splitting of energy levels. The number of levels into which a level with electronic angular momentum j is separated can be determined with the aid of the vectormodel.

§ 2. *Magnetic interaction.*

The main part of the perturbation operator S is due to magnetic interaction. According to the general formalism of quantummechanical perturbation theory one can determine this interaction by calculating by means of classical electrodynamics the interaction energy of the current distribution of the electrons with the current distribution in the nucleus and taking this expression with negative sign. The appearance of this factor (-1) is connected with the well-known fact that the sum of the Hamiltonian for the motion of a particle in an exterior field and the field energy of this exterior field is not equal to the total energy of the system exterior field + particle, but we will not dwell upon this point at present. Let $\mathbf{A}(\mathbf{r})$ be the vectorpotential of the field arising from the nuclear current distribution and $\mathbf{s}(\mathbf{r})$ the current density of the electrons, then the magnetic interaction energy is given by:

$$S_m = -\frac{1}{c}\int(\mathbf{A}\,.\,\mathbf{s})\,d\tau. \tag{2, 1}$$

Outside the nucleus the field of the nucleus can be expanded in a series: field of a dipole, field of a quadrupole and so on; only the first term of this series leads to an interaction energy of measurable order of magnitude. The vector-potential of a magnetic dipole can be written in the form:

$$\mathbf{A} = \frac{[\boldsymbol{\mu} \times \mathbf{r}]}{|r|^3}; \tag{2, 2}$$

here $\boldsymbol{\mu}$ is the dipole moment, $\mathbf{r}$ the radiusvector from the centre of the nucleus to the point considered.

It follows that

$$S_m = -\frac{1}{c}\int \frac{([\boldsymbol{\mu} \times \mathbf{r}] \, . \, \mathbf{s})}{|r|^3} d\tau = -\frac{1}{c}\int (\boldsymbol{\mu} \, . \, \frac{[\mathbf{r} \times \mathbf{s}]}{|r|^3} d\tau).$$

Now

$$\frac{1}{c}\int \frac{[\mathbf{r} \times \mathbf{s}]}{|r|^3} d\tau = \mathbf{H}_0, \tag{2, 3}$$

where $\mathbf{H}_0$ is the field caused by $\mathbf{s}(\mathbf{r})$ at the point $r = 0$. Thus we find:

$$S_m = -(\boldsymbol{\mu} \, . \, \mathbf{H}_0). \tag{2, 4}$$

One must bear in mind, however, that this expression will only hold when the part of the current distribution $\mathbf{s}$ which is lying inside the nucleus does not appreciably contribute to S_m. If this part of the current distribution gives rise to a field $\delta\mathbf{H}^0$ at $r = 0$, then S^m will differ from (2, 4) by an amount of the order of magnitude $-(\boldsymbol{\mu} \, . \, \delta\mathbf{H})$. Only for *s*-electrons $\delta\mathbf{H}_0$ is not quite negligible; one finds:

$$\delta\mathbf{H}_0/\mathbf{H}_0 \sim \left(\frac{RZ}{a}\right)^{2\sqrt{1-Z^2\alpha^2}-1} \tag{2, 5}$$

(R nuclear radius, $\alpha = e^2/\hbar c = 1/137$; $a = \hbar^2/me^2 =$ radius of the first hydrogen orbit). For the heaviest nuclei this will amount to about 5%. If the magnetic moment of a nucleus is calculated from empirically determined interaction energies by means of Eq. (2, 4), then errors of this order of magnitude may occur. The accuracy of such calculations is at present usually considerably less, so that it is not necessary to take these errors into account.

According to a general theorem on matrix vectors one can always write:

$$\boldsymbol{\mu} = \frac{e\hbar}{2mc}\,\frac{m}{M_p}\,\gamma\mathbf{I}; \tag{2, 6}$$

here m is the mass of the electrons, M_p the mass of the proton and γ a numerical factor (LANDÉ factor). The $j \mid j$ part of $\mathbf{H}_0$ can be written as:

$$\mathbf{H}_0 = C\mathbf{J}$$

where C does not depend on the magnetic quantumnumber. C can be determined by calculating the $m = j \mid m = j$ matrix element of H_z (we omit the suffix o).

$$C = \frac{1}{j}\,(n, j; j \mid H_z \mid n, j; j)$$

or, briefly,

$$C = \frac{1}{j}\,\overline{(H_z)}_{m=j}.$$

Thence

$$S_m = -\frac{e\hbar}{2mc}\left(\frac{m}{M_p}\right)\gamma\overline{(H_z)}_{m=j}\;\frac{1}{j}\,(\mathbf{I}\,.\,\mathbf{J}).$$

Now

$$F^2 = (I + J)^2 = I^2 + J^2 + 2(\mathbf{I}\,.\,\mathbf{J})$$

and hence

$$(\mathbf{I}\,.\,\mathbf{J}) = \tfrac{1}{2}(F^2 - I^2 - J^2).$$

The characteristic values of S_m are thus given by

$$(S_m)_f = -\frac{e\hbar}{2mc}\left(\frac{m}{M_p}\right)\gamma\overline{(H_z)}_{m=j}\;\frac{1}{2j}\{f(f+1) - i(i+1) - j(j+1)\}. \tag{2,7}$$

If we measure H in units $(e\hbar/2mc)/a^3$ and if $\Delta_m\nu_f$ is the distance of the level with quantumnumber f from the unperturbed level measured in cm^{-1}, then

$$\Delta_m \nu_f = -\tfrac{1}{2} R\alpha^2 \left(\frac{m}{M_p}\right) \gamma \overline{(H_z)}_{m=j} \frac{1}{2j} \{f(f+1) - i(i+1) - j(j+1)\} \quad (2,8)$$

where

$$R = \tfrac{1}{2}\, \alpha^2\, mc/\hbar = 109737$$

is the RYDBERG constant, or

$$\Delta_m \nu_f = -\gamma \frac{\overline{(H_z)}_{m=j}}{j} \tfrac{1}{2} \{f(f+1) - i(i+1) - j(j+1)\} 1{,}585 \times 10^{-3}\,\mathrm{cm}^{-1}.$$

In this formula the properties of the nucleus are characterized by the numbers i and γ. The problem of magnetic hyperfine structure is now reduced to the problem of calculating $\overline{(H_z)}_{m=j}$, a quantity which only depends on the properties of the electrons and not on the structure of the nucleus.

§ 3. *Matrixelements of the magnetic interaction, which are not diagonal with respect to the quantumnumbers n and j.*

It may happen, that two or more fine structure levels are so near to each other, that their distance is not large compared to the hyperfine structure. In that case we will also have to consider matrixelements of the perturbation operator which are not diagonal with respect to j and n. As long as we describe the states of electrons + nucleus by the quantumnumbers m_j, k (and the wavefunctions $\psi(n, j, m_j)\, \varkappa_k$) these matrixelements are

$$-\,(n,\ j,\ m_j \mid H \mid n',\ j',\ m_j)\ (k \mid \mu \mid k').$$

If, however, we introduce the quantumnumbers f and m_f the $(n,\ j \mid n',\ j')$-part of the perturbation matrix is transformed into an expression of the form

$$+\,(n,\ j,\ f \mid T \mid n',\ j',\ f)\ \delta(f - f')\ \delta(m_f - m_f'). \quad (3,\ 1)$$

Thi sfollows from the fact that S_m commutes with F_x, F_y, F_z.

Now the following formulae hold (in each formula one is to take either everywhere the lower or everywhere the upper sign).

$$(n,\ j,\ m\ |H_x \pm iH_y|\ n',\ j+1, m \mp 1) =$$
$$= \pm\ (n, j\ |h|\ n', j+1)\ \sqrt{(j \mp m + 1)\ (j \mp m + 2)}$$

$$(n,\ j,\ m\ |H_z|\ n',\ j+1,\ m) =$$
$$= (n, j\ |h|\ n', j+1)\ \sqrt{(j + m + 1)\ (j - m + 1)}$$

$$(n,\ j,\ m\ |H_x \pm iH_y|\ n', j, m \mp 1) =$$
$$= (n, j\ |h|\ n', j)\ \sqrt{(j \pm m)\ (j \mp m + 1)}$$

$$(n,\ j,\ m\ |H_z|\ n',\ j,\ m) = (n,\ j\ |h|\ n',\ j)\ m$$

$$(n, j, m\ |H_x \pm iH_y|\ n', j-1, m \mp 1) = \tag{3, 2}$$
$$= \mp\ (n, j, |h|\ n', j-1)\ \sqrt{(j \pm m)\ (j \pm m - 1)}$$

$$(n, j, m\ |H_z|\ n', j-1, m) = (n, j\ |h|\ n', j-1)\ \sqrt{(j-m)\ (j+m)}$$

all other matrixelements are zero.

The quantities $(n,\ j\ |h|\ n',\ j')$ can be determined by calculating one matrixelement of one component of **H** for every possible combination $(n,\ j\ |\ n',\ j')$, for instance:

$$(n,\ j\ |h|\ n', j+1) = \frac{1}{\sqrt{2j+1}}\ (n,\ j,\ j\ |H_z|\ n', j+1,\ j)$$

$$(n,\ j\ |h|\ n',\ j) = \frac{1}{j}\ (n,\ j,\ j\ |H_z|\ n',\ j,\ j) \tag{3, 3}$$

$$(n, j\ |h|\ n', j-1) = \frac{1}{\sqrt{2j-1}}\ (n, j, j-1\ |H_z|\ n', j-1, j-1).$$

Also T can now be expressed in terms of these quantities. One obtains (11):

$$(n, j, f\ |T|\ n', j+1, f) = -\gamma\ \frac{e\hbar}{2mc}\left(\frac{m}{M_p}\right)(n, j\ |h|\ n',\ j+1)\ .$$
$$\cdot \tfrac{1}{2}\sqrt{(f+j-i+1)\ (f-j+i)\ (f+j+i+2)\ (j+i+1-f)}$$

$$(n, j, f \mid T \mid n', j, f) = -\gamma \frac{e\hbar}{2mc}\left(\frac{m}{M_p}\right)(n, j \mid h \mid n', j).$$
$$\cdot\tfrac{1}{2}\{f(f+1) - i(i+1) - j(j+1)\}$$

$$(n, j, f \mid T \mid n', j-1, f) = -\gamma \frac{e\hbar}{2mc}\left(\frac{m}{M_p}\right)(n, j \mid h \mid n', j-1).$$
$$\cdot\tfrac{1}{2}\sqrt{(f+j+i+1)\,(j+i-f)\,(f+j-i)\,(f-j+i+1)} \quad (3, 4)$$

In actual applications the matrixelements will of course be expressed in cm^{-1} and $(e\hbar/2mc)/a^3$ will be chosen as the unit of magnetic fieldstrength.

§ 4. *Electrostatic interaction between nucleus and electrons.* In this section we will examine the $(n, j \mid n, j)$ matrixelements of the electrostatic interaction or, more accurately, of the difference between the true electrostatic interaction and the interaction between the electrons and a point-charge. The $(n, j, m, k \mid n, j, m', k')$ matrixelement of this difference is given by

$$(n, j, m, k \mid S_{el} \mid n, j, m', k') =$$
$$= -e^2 \int_{(6)} (n, j, m \mid \rho_e(\mathbf{r}_e) \mid n, j, m')\,(k \mid \rho_k(\mathbf{r}_k) \mid k')\,\frac{1}{|\mathbf{r}_k - \mathbf{r}_e|}\,d\tau_k\,d\tau_e$$
$$+ e^2 Z \delta(k-k') \int_{(3)} (n, j, m \mid \rho_e(\mathbf{r}_e) \mid n, j, m')\,\frac{1}{r_e}\,d\tau_e. \quad (4, 1)$$

Here $-e\,\rho_e(\mathbf{r}_e)$ is the charge density of the electrons, (ρ_e is the probability density) and $e\rho_k(\mathbf{r}_k)$ the charge density of the nucleus. Let R be the radius of the nucleus or more accurately, let $\rho_k(\mathbf{r}_k)$ be negligible for $r_k > R$. We will first consider that part of the total region of integration for which $r_e > R$. We can then expand $1/|\mathbf{r}_k - \mathbf{r}_e|$ in a series:

$$\frac{1}{|\mathbf{r}_k - \mathbf{r}_e|} = \frac{1}{r_e} + \frac{r_k}{r_e^2} P_1(\cos\Theta) + \frac{r_k^2}{r_e^3} P_2(\cos\Theta) + \ldots.$$

where Θ is the angle between the directions of $\mathbf{r}_k$ and $\mathbf{r}_e$.

Further

$$r_k\, P_1\,(\cos\Theta) = \frac{r_k}{r_e}\,(\mathbf{r}_k\,.\,\mathbf{r}_e)$$

$$P_2(\cos\Theta) = \sum_{s=-2}^{s=2} P_2^{s}(\vartheta_e,\, \varphi_e)\, P_2^{-s}(\vartheta_k,\, \varphi_k)$$

where ϑ_e, φ_e and ϑ_k, φ_k are the polar coordinates of $\mathbf{r}_e$ and $\mathbf{r}_k$ respectively; the spherical harmonics P_2^s will be chosen as follows:

$$P_2^{\pm 2} = \frac{3}{2\sqrt{6}}\,(x \pm iy)^2/r^2$$

$$P_2^{\pm 1} = \frac{3}{\sqrt{6}}\,z(x \pm iy)/r^2$$

$$P_2^{0} = (\tfrac{3}{2}\,z^2 - \tfrac{1}{2}r^2)/r^2 = (z^2 - \tfrac{1}{2}x^2 - \tfrac{1}{2}y^2)/r^2.$$

The integral from $r_e = R$ to $r_e = \infty$ reduces to (we omit temporarily the indices of ρ_e):

$$-\,e^2 \int_{r_e>R} \rho_e(\mathbf{r}_e)\,\frac{1}{r_e}\,d\tau_e \int (k\,|\,\rho_k\,|\,k')\,d\tau_k\, + \qquad (a)$$

$$+\,Ze^2 \int_{r_e>R} \rho_e(\mathbf{r}_e)\,\frac{1}{r_e}\,d\tau_e\,.\,\delta(k - k')\, - \qquad (b)$$

$$-\,e^2 \left(\int_{r_e>R} \rho_e(\mathbf{r}_e)\,\frac{1}{r_e^3}\,\mathbf{r}_e\,d\tau_e\,.\int (k\,|\,\rho_k\,|\,k')\,\mathbf{r}_k\,d\tau_k\right) - \qquad (c)$$

$$-\,e^2 \sum_{s=-2}^{s=2} \int_{r_e>R} \rho_e(\mathbf{r}_e)\,\frac{1}{r_e^3}P_2^{+s}(\vartheta_e,\,\varphi_e)\,d\tau\,.\int (k\,|\rho_k|\,k')\,r_k^2 P_2^{-s}(\vartheta_k,\,\varphi_k)\,d\tau_k. \qquad (d)$$

The first two terms cancel, for

$$\int (k\,|\,\rho_k\,|\,k')\,d\tau_k = Z\delta(k - k').$$

The third term is zero, for ρ_k is invariant under an inversion with respect to the origin (a change of sign of all rectangular coordinates) whereas $\mathbf{r}_k$ changes its sign. So only (*d*) remains. In this term it is permissible to integrate from $r_e = 0$, if the integration over the angles ϑ and φ is carried out before the integration over r_e. For if the electronic wavefunctions are written as a sum of products of single electron wavefunctions, it is easily seen that those terms in ρ_e which do not vanish for $r_e = 0$, have spherical symmetry; but if these terms are multiplied by $P_2^s(\vartheta_e, \varphi_e)$ and integrated over ϑ_e, φ_e the result is zero. These spherically symmetric terms are the only terms which give an appreciable contribution to the integral from $r_e = 0$ to $r_e = R$. They give rise to a displacement of the energylevels which does not depend on j and which will be discussed more accurately in the next section.

We will now deduce a simple expression for the characteristic values of (d). According to a general theorem, which can be proved by grouptheoretical methods, one has:

$$\int (m \mid \rho_e \mid m') \frac{1}{r_e^3} P_2^s \, d\tau_e = (n, j \mid C_e \mid n, j)\,(m \mid \Pi_2^s(J) \mid m') \quad (4,\ 2)$$

where Π_2^s (J) is the symmetrical harmonic polynomial which is constructed from the components J_x, J_y, J_z in the same way as r^2 P_2^s is constructed from x, y, z, or explicitly:

$$\Pi_2^{\pm 2} = \frac{3}{2\sqrt{6}} (J_x \pm iJ_y)^2$$

$$\Pi_2^{\pm 1} = \frac{3}{2\sqrt{6}} \{J_z (J_x \pm iJ_y) + (J_x \pm iJ_y) J_z\}$$

$$\Pi_2{}^0 = (\tfrac{3}{2} J_z^2 - \tfrac{1}{2} J_x^2 - \tfrac{1}{2} J_y^2 - \tfrac{1}{2} J_z^2).$$

We will only write down the matrixelements of $\Pi_2{}^0$.

$$(m \mid \Pi_2{}^0 \mid m') = \{\tfrac{3}{2} m^2 - \tfrac{1}{2} j(j+1)\}\ \delta(m - m'). \quad (4,\ 3)$$

The quantity C_e can be determined by calculating the left-hand side of Eq. (4, 2) for $m = m' = j$ and $s = 0$:

$$(n, j \mid C_e \mid n, j)\ (\tfrac{3}{2} j^2 - \tfrac{1}{2} j(j+1)) =$$

$$= \int (n, j, m = j \mid \rho_e \mid n, j, m = j) \frac{1}{r_e^3} P_2{}^0 \, d\tau_e$$

whence

$$(n, j \mid C_e \mid n, j) =$$
$$= \frac{1}{j(2j-1)} \int (n, j; j \mid \rho_e \mid n, j; j) \frac{1}{r_e^3} (3 \cos^2 \vartheta - 1)\, d\tau_e. \quad (4,\ 4)$$

In the same way

$$\int (k \mid \rho_k \mid k')\, r_k^2\, P_2^s\, d\tau_k = C_k\, (k \mid \Pi_2^s(I) \mid k') \qquad (4,\ 5)$$

with

$$C_k = \frac{1}{i(2i-1)} \int (i \mid \rho_k \mid i)\, (3z^2 - r^2)\, d\tau_k. \qquad (4,\ 6)$$

The interaction matrix reduces to

$$- e^2\, C_e C_k \sum_{s=-2}^{s=+2} \Pi_2^s(J)\; \Pi_2^{-s}(I). \qquad (4,\ 7)$$

When F^2 is transformed to diagonal form the sum in Eq. (4, 7) is also transformed to diagonal form. The characteristic values of this expression have been calculated by KRAMERS (*26*), by means of a method which is also applicable to higher harmonics. His result is, that the characteristic values are given by:

$$\tfrac{3}{8}\, K(K+1) - \tfrac{1}{2} i\, (i+1)\, j(j+1) \qquad (4,\ 8)$$

where

$$K = f\, (f+1) - i\, (i+1) - j\, (j+1).$$

This result can also be derived in the following more elementary way. We must calculate:

$$A = (J_z^2 - \tfrac{1}{2} J_x^2 - \tfrac{1}{2} J_y{}^2)\; (I_z^2 - \tfrac{1}{2} I_x^2 - \tfrac{1}{2} I_y^2) +$$
$$+ \left(\frac{3}{2\sqrt{6}}\right)^2 \{J_z(J_x + iJ_y) + (J_x + i\,J_y)J_z\}\, \{I_z(I_x - iI_y) + (I_x - iI_y)I_z\}$$
$$+ \left(\frac{3}{2\sqrt{6}}\right)^2 \{J_z(J_x - iJ_y) + (J_x - i\,J_y)J_z\}\, \{I_z(I_x + iI_y) + (I_x + iI_y)I_z\}$$
$$+ \left(\frac{3}{2\sqrt{6}}\right)^2 (J_x + iJ_y)^2 (I_x - iI_y)^2 +$$
$$+ \left(\frac{3}{2\sqrt{6}}\right)^2 (J_x - iJ_y)^2\, (I_x + iI_y)^2.$$

If now J_x, J_y, J_z and also I_x, I_y, I_z were commutable, then this expression would be equal to

$$B = \tfrac{3}{2}(J_xI_x + J_yI_y + J_zI_z)^2 - \tfrac{1}{2}(J_x^2 + J_y^2 + J_z^2)\ (I_x^2 + I_y^2 + I_z^2).$$

The difference between A and B is, that in A there appears a term

$$a = \tfrac{3}{4}(J_xJ_z + J_zJ_x)\ (I_xI_z + I_zI_x)$$

in stead of a term

$$b = \tfrac{3}{2}(J_xJ_zI_xI_z + J_zJ_xI_zI_x)$$

which occurs in B (and analogously for the combinations xy and yz). The difference can easily be calculated by means of the commutability relations; one finds:

$$a - b = \tfrac{3}{4}\ J_yI_y$$

and hence

$$A = B + \tfrac{3}{4}(J_xI_x + J_yI_y + J_zI_z) = \tfrac{3}{8}\,.\,2(J\,.\,I)\{2(I\,.\,J)+1)\} - \tfrac{1}{2}J^2I^2$$

which leads immediately to KRAMERS' result.

It is of some importance to notice, that the centre of gravity of the term n, j is not displaced by an interaction of this type, or in other words, that

$$\sum_f\ (2f + 1)\ (\Delta_f\ \nu)_{el} = 0. \qquad (4, 9)$$

To prove this we remark, that the lefthand side of Eq. (4, 9) is the diagonal sum of the $(2i + 1)\ (2j + 1)$-dimensional perturbation matrix and therefore equal to (we write Sp for the diagonal sum):

$$-\,Sp\ (e^2C_eC_k \sum_{s=-2}^{s=2} \Pi_2^s(J)\ \Pi_2^{-s}(I) =$$

$$= -\,e^2\ C_eC_k \sum_{s=-2}^{s=2} Sp\ \ [\Pi_2^s(J)]\ .\ Sp\ \ [\Pi_2^{-s}(I)].$$

But

$$Sp[\Pi_2^s(J)] = Sp\ \ [\Pi_2^{-s}(I)] = 0.$$

For $s = 0$ this can easily be verified; by a simple grouptheoretical argument one can infer, that the result holds for all s.

Further we remark, that for $i = 0$ and $i = \frac{1}{2}$, $\Pi_2^s(I)$ is identically zero; this follows also from general theorems. In the same way $\Pi_2^s(J) \equiv 0$ for $j = 0$ and $j = \frac{1}{2}$.

If we measure the energies in cm^{-1}, the radius r_e in units a and the length r_k in 10^{-12} cm, the separation caused by the electrostatic interaction is given by:

$$(\Delta_f\nu)_{el} = -\overline{\left\{\frac{3\cos\vartheta_e - 1)}{r_e^3}\right\}}_{j,j} Q \frac{1}{(2i-1)(2j-1)ij}\left[\tfrac{3}{8}K(K+1) - \right.$$
$$\left. - \tfrac{1}{2}ij(i+1)(j+1)\right] . 7{,}9 \times 10^{-3}\,\mathrm{cm}^{-1}. \quad (4,\ 10)$$

The expression in { } is the mean value for the state $m_j = j$ (or in other words the $(n,\ j,\ j \mid n,\ j,\ j)$ matrixelement).

Q is given by:

$$Q = \overline{\{3z_k^2 - r_k^2\}}_{i,i}$$

measured in 10^{-24} cm^2.

The total expression can be interpreted as the interaction between the electrons and an electric quadrupole.

Perhaps it would be more rational to use the quantity e^2/mc^2 (the classical radius of the electron) as a unit of length for the nucleus. Then the factor $7{,}9 \times 10^{-3}$ must be replaced by $2R\alpha^4 = 0{,}62 \times 10^{-3}$.

§ 5. *Interaction with the spherical terms in the charge distribution.*

We will now discuss the influence of the interior part of the perturbation integral on the energylevels; it is given by:

$$I_e = -e^2 \int\limits_{r_e<R} \int \rho_e(r_e)\, \rho_k(r_k) \frac{1}{|r_e - r_k|}\, d\tau_k\, d\tau_e +$$
$$+ Ze^2 \int\limits_{r_e<R} \rho_e(r_e) \frac{1}{r_e}\, d\tau_e. \quad (5,\ 1)$$

We have already called attention to the fact that those terms in ρ_e which do not vanish for $r_e = 0$ have spherical symmetry. It follows that for small values of r_e the matrix ρ_e will be of the form:

$$(n, j, m \mid \rho_e \mid n, j, m') = \delta(m - m')\ (n, j \mid \rho_e^0 \mid n, j)$$

and thence I_e is of the form

$$(m, k \mid I_e \mid m', k') = \delta(m - m')\ \delta(k - k')\ I_e^0.$$

In calculating I_e^0, however, we meet with an interesting difficulty. For states with spherical charge distribution (s and $p_{\frac{1}{2}}$ states) the solutions of Dirac's wave equation for the motion of an electron in the field of a point-charge become infinite at $r = 0$. We can write

$$(n, j \mid \rho_e^0 \mid n, j) = (n, j \mid \rho_e^1 \mid n, j)\ r^{-\beta} \qquad (5, 2)$$

with

$$\beta = 2 - 2\sqrt{1 - Z^2\alpha^2}$$

and where ρ_e^1 does not depend on r. Using this expression we can calculate I_e^0. The result is:

$$I_e^0 = + e^2\, \rho_e^1 \frac{4\pi}{(3 - \beta)(2 - \beta)} \int (k \mid \rho_k \mid k)\, r^{2-\beta}\, d\tau_k. \qquad (5, 3)$$

The infinity of ρ_e at the origin, however, is a consequence of the assumption of a point nucleus; the exact wavefunctions corresponding to a continuous distribution of nuclear charge will remain finite at $r_e = 0$. If these exact wavefunctions were used, the value of I_e would also be modified. From a formal point of view this modification would correspond to a higher approximation of the perturbation theory but in our case it seems rather doubtful whether the second order terms will really be small. In order to estimate the order of magnitude of these second order terms we will also calculate I_e on the assumption (assumption B) that the charge density is correctly represented by Eq. (5, 2) outside the nucleus, but is constant inside the nucleus. The charge density inside the nucleus is then equal to

$$\rho_e^1 R^{-\beta}$$

which leads to

$$I_e^0 = + e^2 \rho_e^1 \frac{4\pi}{2\,.\,3} R^{-\beta} \int (k \mid \rho_k \mid k)\, r^2\, d\tau_k. \qquad (5,\ 4)$$

Let us suppose that the nuclear charge is homogeneously distributed over a sphere with radius R (according to the theory of HEISENBERG and MAJORANA this would approximately be the case). Then we find in first approximation

$$(I_e)_A = + Z e^2\, \rho_e^1\, R^{2-\beta} \frac{3\,.\,4\pi}{(5-\beta)\,(3-\beta)\,(2-\beta)}$$

and on assumption B

$$(I_e)_B = + Z e^2\, \rho_e^1\, R^{2-\beta} \frac{3\,.\,4\pi}{5\,.\,3\,.\,2}.$$

For heavy nuclei the difference between these expressions is by no means negligible. For

$$\beta = 0{,}4 \ (Z = 82) \ (I_e^0)_B = 0{,}64 \ (I_e^0)_A.$$

Of course it is always possible to use an expression of the form

$$I_e^0 = + Z e^2\, \rho_e^1 \frac{2\pi}{5} R_e^{2-\beta}$$

but for heavy nuclei a rigorous determination of the „effective" radius R_e in terms of the distribution of nuclear charge would only be possible by means of much more elaborate calculations than we have given here.

The perturbation calculated in this section does not depend on the value of f; as long as only one isotope is considered it leads to a displacement and not to a separation of energylevels. The effective nuclear radii of the various isotopes of one element will however be slightly different and thus the centres of gravity of the hyperfine structures belonging to different isotopes will be displaced relative to one another.

§ 6. *Discussion of the assumptions underlying our formulae.* Before proceeding to actual applications of our formulae we will try to analyse the assumptions underlying our calculations. With respect to the electrons in the atom, no other assumptions have been made than that the laws of quantummechanics are valid and that the separations of the finestructure levels are so large that we can confine ourselves to the first approximation of perturbation theory. Moreover, by § 3 and § 8, this last assumption is not essential.

Further we have assumed, that certain general results of quantummechanics can be applied to the nucleus, and that the action of the nucleus on the electrons can be described as the action of a current- and a charge-distribution. It is important to emphasize, that this is not equivalent to assuming that the nucleus can be described by the same wave-equations as the atomic electrons. Even if it should prove impossible to define a current- and charge density inside the nucleus, one would still expect that it should be possible to describe the external action of the nucleus in terms of an electric charge, a magnetic dipole, an electric quadrupole, ... connected with the angular momentum according to the general rules of grouptheory. The case is different, however, for that part of the interaction that takes place inside the nucleus.

The results of § 5 are not very certain because of the (mathematical) difficulties involved in their derivation. But also the foundations of these calculations give rise to some doubts. It seems quite possible, that the displacements caused by the interaction of the nucleus and the spherical part of the electronic charge density cannot be expressed in terms of the nuclear charge distribution, but that they depend on other properties of the nucleus. In the same way the possibility cannot be excluded, that besides the magnetic interaction between the nucleus and an *s*-electron (which itself is not completely determined by the magnetic moment of the nucleus) there exists another type of interaction which is proportional to $(\mathbf{I}\,.\,\mathbf{J})$. It is difficult to say a priori whether the relative magnitude of this effect will be of the same order as the quantity $\delta H_0/H_0$ introduced in § 2.

§ 7. *Hyperfine structure and magnetic interaction.*

Let us assume, that, starting from measurements on hyperfine structure of spectral lines, one has succeeded in deducing the position of the energylevels, in determining which levels belong to one and the same isotope, and in assigning f-values to these levels. Also the values of i for the various isotopes will then be known.

We know then the energies

$$E(n,\ j,\ f)_M$$

(where M denotes the massnumber) or better, the relative differences of the energies belonging to a state $n,\ j$.

We will first confine ourselves to the levels belonging to one isotope. It has been found, that in general they follow rather accurately the intervalrule, i.e. the energies are given by a formula (we write ν for the energy expressed in cm^{-1}):

$$\nu(n, j, f) = \nu(n, j)^0 + \frac{A}{2}\,[f(f+1) - i\,(i+1) - j\,(j+1)] \quad (7,\ 1)$$

where $\nu(n,\ j)^0$ is the centre of gravity, and hence

$$\nu(n,\ j;\ i+j) - \nu(n,\ j;\ i+j-1) = A(i+j),$$

$$\nu(n,\ j;\ i+j-1) - \nu(n,\ j;\ i+j-2) = A(i+j-1),$$

and so on.

The question must now be examined whether the separations can be ascribed to a nuclear moment and the magnitude of this moment determined. In order to do this one has to know the quantity $(\overline{H_z})_{j,j}$, the mean value of the z-component of the magnetic field at the nucleus produced by the electrons in the state $m = j$. The calculation of this quantity is comparatively easy for an atom with one electron outside a closed shell. We will return later on to the formulae applying to that case and to the foundations of their derivation. The problem is far more difficult for an atom with more than one valence-electron. To a first approximation the wavefunction for a state of these electrons can be written as a sum of products of wavefunctions for the separate electrons, only such wavefunctions being used which correspond to one definite configuration (i.e. one set of values, n_i, l_i).

Detailed calculations of $(\overline{H_z})_{j,j}$ for such cases have been carried out by BREIT and WILLS (*6*), while at an earlier date GOUDSMIT (*21*) had already worked out a method, based on the application of sumrules, which made it possible to calculate the separations caused by the electrons separately from the splittings of the different terms belonging to one configuration.

It has been found, however, that the approximation to the wavefunctions by „functions of a given configuration'' is not always permissible. In general every configuration will be more or less perturbed; the configurations will thus get mixed up. If a given configuration is perturbed by another configuration with large hyperfine structure, the influence of the perturbation on the hyperfine structure will be considerable, even when the perturbation is small. FERMI and SEGRÉ (*16*) have called attention to this circumstance.

The result of the most recent examinations is, that there is no reason to doubt the essential correctness of the assumption, that the separations are due to the interaction of the electrons with a magnetic dipole. In those cases, in which reliable calculations are possible, there is a satisfactory agreement between the values of the magnetic moment calculated from the separations of different terms.

One must not forget, however, that the accuracy with which the calculations can be carried out is not very high; with the one exception of Li II the errors may easily amount to 10%. So the possibility remains, that corrections of this order of magnitude must be applied to Eq. (2, 8) even in cases where the intervalrule strictly holds.

§ 8. *Deviations from the intervalrule.*

More accurate measurements show, that the hyperfine structure levels do not always follow the intervalrule. These deviations have two different causes. In the first place, they can be a consequence of electric interaction with the nucleus; in the second place they can be due to a second order effect in the magnetic interaction. Such a second order effect is to be expected whenever the distance of two fine structure levels is not large compared with the hyperfine structure separations.

For simplicity we will first consider the case where only two fine structure levels (n, j) and (n', j') lie close together; let D be their separation. By the magnetic interaction with the nucleus both levels are separated into a number of components; and one f-value can occur twice: once for a level belonging to the first finestructure level and once for a level belonging to the second one. The two levels with the same f-value will now perturb each other and in order to find the true energylevels one has to determine the roots of a two rowed secular equation. This equation will be given by (the energy is measured in cm^{-1}):

$$\begin{vmatrix} \begin{array}{l} \varepsilon - \nu^0(n',j') - \frac{1}{2}A(n',j'). \\ .\{f(f+1) - i(i+1) - j'(j'+1)\} \end{array} & (n'\, j',\, f\, |T|\, n,\, j,\, f) \\ (n,\, j,\, f\, |\, T\, |\, n',\, j',\, f) & \begin{array}{l} \varepsilon - \nu^0(n,j) - \frac{1}{2}A(n,j). \\ .\{f(f+1) - i(i+1) - j(j+1)\} \end{array} \end{vmatrix} = 0 \quad (8,\ 1)$$

The matrixelements of T are given in § 3. We repeat the formulae introducing the units mentioned at the end of § 3.

$$(n,j,f\,|\,T\,|\,n',j+1,f) = -\gamma\,\frac{(n,j,j\,|\,H_z\,|\,n',j+1,j)}{\sqrt{2j+1}}\,\cdot$$

$$\cdot\tfrac{1}{2}\sqrt{(f+j+i+2)\,(f+j-i+1)\,(j+i+1-f)\,(f-j+i)} \times 1{,}585\times 10^{-3}\ \mathrm{cm}^{-1}$$

$$(n,j,f\,|\,T\,|\,n',j,f) = -\gamma\,\frac{(n,j,j\,|\,H_z\,|\,n',j,j)}{j}\,\cdot$$

$$\cdot\tfrac{1}{2}[f(f+1)-i(i+1)-j(j+1)] \times 1{,}585\times 10^{-3}\,\mathrm{cm}^{-1} \qquad (8,\,2)$$

$$(n,j,f\,|\,T\,|\,n',j-1,f) = -\gamma\,\frac{(n,j,j-1\,|\,H_z\,|\,n',j-1,j-1)}{\sqrt{2j-1}}\,\cdot$$

$$\cdot\tfrac{1}{2}\sqrt{(f+j-i)\,(f-j+i+1)\,(f+j+i+1)\,(j+i-f)} \times 1{,}585\times 10^{-3}\,\mathrm{cm}^{-1}.$$

Further we have

$$\begin{aligned} A(n',j') &= -\gamma\,\frac{(n',j',j\,|\,H_z\,|\,n',j',j)}{j'} \times 1{,}585\times 10^{-3}\,\mathrm{cm}^{-1} \\ A(n,j) &= -\gamma\,\frac{(n,j,j\,|\,H_z\,|\,n,j,j)}{j} \times 1{,}585\times 10^{-3}\ \mathrm{cm}^{-1}. \end{aligned} \qquad (8,\,3)$$

In the same way we can write down the secular determinant in the case that more than two n, j levels are lying close together.

In most cases the influence of the higher order corrections will be small compared with the total hyperfine structure. An approximate solution of the secular equation is then sufficient. The result is as follows:
put

$$\begin{aligned} \nu_1(n,j,f) &= \nu(n,j)^0 + \tfrac{1}{2}A\,(n,j)\,[f(f+1)-i(i+1)-j(j+1)] \\ \nu_1(n',j',f) &= \nu(n',j')^0 + \tfrac{1}{2}A\,(n',j')[f(f+1)-i(i+1)-j'(j'+1)] \end{aligned} \qquad (8,4)$$

and let $\nu(n', j', f)$ and $\nu(n, j, f)$ be the respective energy values, then

$$\begin{aligned} \nu(n',\,j',\,f) &= \nu_1(n',\,j',\,f) + \delta\nu \\ \nu(n,\,j,\,f) &= \nu_1(n,\,j,\,f) - \delta\nu \end{aligned} \qquad (8,\,5)$$

with

$$\delta\nu = \frac{|(n,j;f\,|\,T\,|\,n',j';f)|^2}{\nu_1(n',j';f) - \nu_1(n,j;f)}. \qquad (8,\ 6)$$

One may replace ν_1 in the denominator by ν; in most cases one can even write

$$\delta\nu = \frac{|(n,j,f\,|\,T\,|\,n',j',f)|^2}{\nu_0(n',j') - \nu_0(n,j)} = \frac{|(n,j,f\,|\,T\,|\,n',j',f)|^2}{D}. \qquad (8,\ 7)$$

The perturbation results in a symmetric repulsion of the two terms.

The rigorous formulae are as follows. If we write the secular equation in the form

$$\begin{vmatrix} \varepsilon - \nu_1 & T \\ T & \varepsilon - \nu_1' \end{vmatrix} = 0$$

then the roots are given by

$$\varepsilon = \frac{\nu_1 + \nu_1'}{2} \pm \frac{\nu_1 - \nu_1'}{2}\left[\sqrt{1 + \frac{4T^2}{(\nu_1 - \nu_1')^2}}\right]. \qquad (8,\ 8)$$

Also here the result is a symmetrical repulsion of the two levels; further we see that in Eq. (8, 6) only quantities of the order T^4/D^3 have been neglected. When more than two levels perturbe each other, the influence of these perturbations can in first approximation be described as a mutual repulsion in each pair of two levels.

We can state the following rules, which enable us to picture the influence of the higher order perturbations without further calculation.

a) Levels with equal f repel one another.

b) The order of magnitude of the repulsion is given by (hyperfine structure splitting)^2/(separation of non perturbed levels), for T is of the same order as A.

c) Only levels with $j' - j = 0$ or ± 1 perturb one another.

d) The ratios of the repulsions of pairs of levels with the same n, j and n', j' but different f can be deduced from the Eqs. (8, 2).

These rules do not depend on special assumptions concerning the wavefunctions of the states n, j and n', j'.

Only if we want to calculate the quantity $(n, j, j\,|H_z|\,n', j', j\rangle$ must approximate expressions for the wavefunctions be introduced.

As an example we discuss the perturbations in the hyperfine structure of the 6^3D_1 and 6^1D_1 terms of Hg. For the isotopes Hg_{199} and Hg_{201} the i-values are 1/2 and 3/2 respectively. The ratio of the magnetic moments is 0.9/1, that of the γ-factors

$$\gamma_{199}/\gamma_{201} = 2{,}7/1$$

SCHÜLER and JONES (*34*) have observed the levels shown

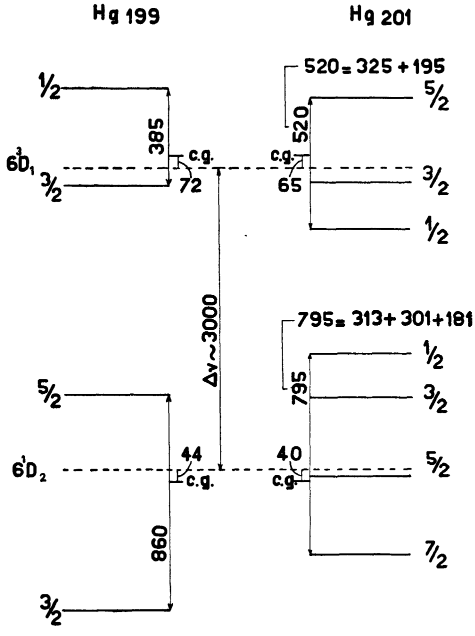

Fig. 1.

in our figure (the distances are given in 10^{-3} cm^{-1}). For the term 6^1D_2 of Hg_{201} the intervalrule does not hold. Now the levels with equal f will repel each other. The order of magnitude of the repulsion is roughly (400/3000) × 400 $\sim$ 50 and this is of the same order of magnitude as the deviations from the intervalrule. For Hg_{199} there is only one pair of terms with equal f, for Hg_{201} there are three (with $f = \frac{1}{2}$, $f = \frac{3}{2}$, $f = \frac{5}{2}$). For the ratio of the repulsions of these terms one finds:

$$\delta_{1/2} : \delta_{3/2} : \delta_{5/2} = 1 : 2{,}8 : 3.$$

The repulsion can be calculated in detail, if with SCHÜLER and JONES we admit the assumption that the centres of gravity of the unperturbed terms of the odd isotopes coincide with the terms of the even isotopes. For the repulsion of the levels with $f = \frac{3}{2}$ of Hg_{199} one finds $\delta_{3/2} = 108$, whence

$$\frac{1}{3500}\left\{\Upsilon_{199}(6^3D_1;\ 1\,|H_z|\,6^3D_2;\ 1)\,\frac{1}{\sqrt{3}}\,.\right.$$

$$\left.\quad .\ \tfrac{1}{2}\,.\ 1{,}585 \times 10^{-3})\right\}^2 \times 3 \times 5 \times 1 \times 1 = 108$$

and

$$\left\{\Upsilon_{201}(6^3D_1;\ 1\,|H_z|\,6^3D_2;\ 1)\,\frac{1}{\sqrt{3}}\,.\right.$$

$$\left.\quad .\ \tfrac{1}{2}\,.\ 1{,}585 \times 10^{-3}\right\}^2 = \frac{3500 \times 108}{15 \times (2{,}7)^2} = 3460;$$

it follows that

$$\delta_{1/2} = \frac{1}{2200} \times 3460 \times 1 \times 1 \times 5 \times 3 = 24$$

$$\delta_{3/2} = \frac{1}{2500} \times 3460 \times 2 \times 2 \times 6 \times 2 = 66$$

$$\delta_{5/2} = \frac{1}{3100} \times 3460 \times 2 \times 2 \times 7 \times 1 = 70.$$

If with these values we calculate the position of the unperturbed terms, the deviations from the intervalrule are indeed appreciably reduced. The agreement with the intervalrule is however not perfect and the discrepancies are larger than the limits of error admitted by SCHÜLER ($\pm 5 \times 10^{-3}$ cm^{-1}). The agreement cannot be improved by assuming a displacement of the centre of gravity. One might at first be inclined to believe that the remaining deviations are caused by electrostatic interaction but the way in which they depend on f seems to exclude that possibility. SCHÜLER and JONES have shown that the intervalrule is satisfied, if

$$\delta_{1/2} = 42; \quad \delta_{3/2} = 64; \quad \delta_{5/2} = 78.$$

It seems to us that the question has not yet been completely cleared up. The most simple way of explaining the difficulty is to assume with GOUDSMIT and BACHER (*22*), that the remaining discrepancies are partly due to errors of measurement, partly to perturbations by other terms.

As a second example we examine the perturbations in the hyperfine structure of the 6^3D_1 and 7^3D_1 term of Indium. For Indium $i = 9/2$. The only term, by which n^3D_1 can be perturbed, is the term n^3D_2. The distance D is 34 cm^{-1} for 6^3D_1, 18 cm^{-1} for 7^3D_1. The separations for $6D_1$ and $7D_1$ are almost equal; roughly we have:

$$\nu(11/2) - \nu(9/2) \sim 950 \times 10^{-3} \text{ cm}^{-1}$$
$$\nu(9/2) - \nu(7/2) \sim 800 \times 10^{-3} \text{ cm}^{-1}.$$

In calculating the repulsion of levels with equal f, we will only take into account the interaction of the nucleus and the s-electron. This is permissible, for the fact that the separations of $6D$ and $7D$ are nearly equal shows, that the interaction of the nucleus with the d-electron is small. (It must not be forgotten, that the perturbations we want to calculate, form only a small part of the total hyperfine structure). Further we assume RUSSELL-SAUNDERS coupling. The distance between the ^1D term and the ^3D terms is much larger than the mutual distances between the ^3D terms themselves; moreover for the ^3D terms LANDÉ's intervalrule is accurately fulfilled. The wavefunctions of the ^3D terms can now be written as linear combinations of products of functions d_m of the coordinates of the d-electron $(-2 \leqslant m \leqslant 2)$ with functions $s_n(-1 \leqslant n \leqslant 1)$ of the coordinates of the s-electron and the spin of the s- and the d-electron. The linear combinations corresponding to a $^3D_2$, $m = 1$ state and a $^3D_1$, $m = 1$ state can be written down directly by means of general formulae. In practical calculation, however, it is usually easier to construct the functions in the following way. We start from the function d_2s_1 corresponding to the state $^3D_3$, $m = 3$; if the operator $J_x + iJ_y = (d_x + id_y) + + (s_x + is_y)$ (where d_x, d_y, d_z are the components of the orbital angular momentum, s_x, s_y, s_z the components of the resultant spin) is applied to this function there results a function proportional to the function $^3D_3$, $m = 2$. The function $^3D_2$, $m = 2$ is orthogonal to this function.

Applying the operator $J_x + iJ_y$ to the functions $^3D_3$, $m = 2$ and $^3D_2$, $m = 2$, we obtain the functions $^3D_3$, $m = 1$ and $^3D_2$, $m = 1$; the function $^3D_1$, $m = 1$ is orthogonal to these functions.

In this way we obtain the following scheme:

	$^3D_3$	$^3D_2$	$^3D_1$
$m=3$	$d_2 s_1$		
$m=2$	$\frac{1}{\sqrt{6}}(2\, d_1s_1 + \sqrt{2}\, d_2s_0)$	$\frac{1}{\sqrt{6}}(\sqrt{2}\, d_1s_1 - 2\, d_2s_0)$	(8.9)
$m=1$	$\frac{1}{\sqrt{15}}(\sqrt{6}\, d_0s_1 + 2\sqrt{2}\, d_1s_0 + + d_2s_{-1})$	$\frac{1}{\sqrt{6}}(\sqrt{3}\, d_0s_1 - d_1s_0 - - \sqrt{2}\, d_2s_{-1})$	$\frac{1}{\sqrt{10}}(d_0s_1 - \sqrt{3}\, d_1s_0 + + \sqrt{6}\, d_2s_{-1})$

In simple cases the construction of such a scheme takes less time than the application of general formulae.

We will now calculate the matrixelements of H_z.

Putting

$$(s_1 \,|\, H_z \,|\, s_1) = H_s$$

we have

$$(s_1 \,|H_z|\, s) = H_s$$

$$(s_0 \,|H_z|\, s_0) = 0$$

$$(s_{-1} \,|H_z|\, s_{-1}) = -H_s$$

and

$$({}^3D_1;\, 1 \,|H_z|\, {}^3D_1;\, 1) = -\tfrac{1}{2}H_s$$

$$({}^3D_1;\, 1 \,|H_z|\, {}^3D_2;\, 1) = +\frac{3}{2\sqrt{5}}H_s$$

$$({}^3D_2;\, 2 \,|H_z|\, {}^3D_2;\, 2) = +\tfrac{1}{3}H_s.$$

For the unperturbed separations of the ${}^3D_1$ terms we find

$$\Delta\nu_f = +\gamma\,\tfrac{1}{2}H_s\,\tfrac{1}{2}[f(f+1) - i(i+1) - j(j+1)] \times$$
$$\times\ 1{,}585 \times 10^{-3}\ \mathrm{cm}^{-1}.$$

It is easily seen, that H_s must be a negative quantity, the term with the largest f-value being the lowest one. The measured separation of 1760 units leads to

$$H_s\gamma \times 1{,}585 = -350.$$

With this value we can now roughly calculate the position of the hyperfine structure levels of ${}^3D_2$. The result is shown

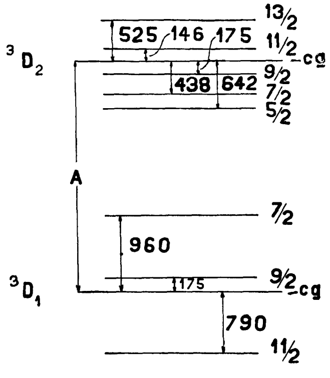

Fig. 2.

in our figure. The object of this calculation is only to obtain a sufficient approximation for the distance between levels with equal f. Let D be the distance between the centres of gravity, then we have:

for the distance $7/2 \to 7/2$: $D - 1400$;
for the distance $9/2 \to 9/2$: $D - 350$;
for the distance $11/2 \to 11/2$: $D + 940$.

Using these values we find (applying Eq. (8, 6))

$$\delta_{11/2} = 1{,}61/(D + 940)$$
$$\delta_{9/2} = 1{,}76/(D - 350)$$
$$\delta_{7/2} = 1{,}06/(D - 1400).$$

For 6^3D we have $D = 34000$ and hence

$$\delta_{11/2} = 46{,}2; \qquad \delta_{9/2} = 52{,}3; \qquad \delta_{7/2} = 32{,}5.$$

The perturbation leads to a decrease of 6,1 units in the distance $\nu(11/2) - \nu(9/2)$ and to an increase of 19,8 units in the distance $\nu(9/2) - \nu(7/2)$.

According to PASCHEN (*30*) the separations are:

$$\nu(11/2) - \nu(9/2) = 950{,}5$$
$$\nu(9/2) - \nu(7/2) = 798{,}3.$$

The unperturbed separations become:

$$\nu(11/2) - \nu(9/2) = 956{,}6$$
$$\nu(9/2) - \nu(7/2) = 778{,}5 = (9/11) \times 956{,}6 - 4.$$

The deviation from the intervalrule, which amounted to 20 units for the experimental separations, is thus reduced to 4 units.

This result is satisfactory. But for the $7D$ terms the result is less satisfactory. Here $D = 18$ and hence

$$\delta_{11/2} = 85{,}0; \qquad \delta_{9/2} = 99{,}7; \qquad \delta_{7/2} = 63{,}8$$

The measured separations are

$$\nu(11/2) - \nu(9/2) = 952{,}6$$
$$\nu(9/2) - \nu(7/2) = 811{,}5 = \tfrac{9}{11} \times 952{,}6 + 32$$

The unperturbed distances become

$$\nu(11/2) - \nu(9/2) = 967{,}3$$

$$\nu(9/2) - \nu(7/2) = 775{,}6 = \tfrac{9}{11} \times 967{,}3 - 16.$$

In this case the calculated perturbation is too large. We have not succeeded in explaining the discrepancy. The fact that the deviations for 7^3D are larger than for 6^3D seems to exclude an explanation in terms of electrostatic interaction. It may be, however, that the assumption of Russell-Saunders-coupling is not quite justified or that the terms are influenced by other perturbations than those considered in our calculation.

Perturbations of the type examined in this section, have been found for the first time by Schüler (*33*) in the Li II spectrum and have been discussed theoretically by Pauli and Güttinger (*23*). The discussion of the perturbations in the Hg spectrum given above is almost identical with that of Casimir (*9*). Later on the same problem has been studied by Goudsmit and Bacher (*22*), using a different method. They have also calculated the value of the constant, which is here derived from the experimentally determined position of the levels of Hg_{199}; their assumptions about the state of coupling, however, are not quite justified. Their results are in agreement with those given here.

Though the application of Goudsmit's method to a special case is undoubtedly much simpler than the derivation of the general formulae used in this paper, we nevertheless believe that our method of treating the perturbations has considerable advantages in showing in how far the results obtained depend or do not depend on special assumptions concerning the wavefunctions.

§ 9. *Detailed discussion of the influence of an electric quadrupole moment.*

Deviations from the intervalrule may also arise from the electrostatic interaction between the nucleus and the outer electrons. In § 4 we derived the following formula:

$$(\Delta\nu_f)_{el} = -\overline{\left\{\frac{3\cos^2\vartheta - 1}{r^3}\right\}}_{j,j} \cdot$$

$$\cdot Q \cdot \frac{[\frac{3}{8}K(K+1) - \frac{1}{2}ij(i+1)(j+1)]}{ij(2i-1)(2j-1)} \times 7{,}9 \times 10^{-3}\,\text{cm}^{-1} \quad (9,1)$$

with

$$K = f(f+1) - i(i+1) - j(j+1)$$

and

$$Q = \overline{(3z_k^2 - r_k^2)}_{i,i}.$$

The expression in { } is an average over the charge density of the electrons (we have omitted the suffix e), the radius of the first hydrogen orbit being chosen as unit of length; Q is an average over the charge density in the nucleus; here the unit of length is 10^{-12}.

The mean value of $(3\cos^2\vartheta - 1)$ is a measure for the deviation from spherical symmetry of the charge density of the electrons, it is zero for a spherical distribution, positive for a prolate distribution and negative for an oblate distribution. The expression in curly brackets is thus positive or negative according as the charge distribution of the electrons is prolate or oblate in the direction of angular momentum. Following SCHÜLER and SCHMIDT (*35*) this may be illustrated by a schematical representation (Fig. 3).

In the same way Q is positive or negative according as the nucleus is prolate or oblate in the direction of its angular momentum. The quantity Q will be called the electric quadrupole moment of the nucleus.

It is now easily seen, that in the state in which j and i are parallel to each other the interaction energy is negative when both distributions are prolate or both are oblate. The factor

$$\frac{\frac{3}{8}K(K+1) - \frac{1}{2}ij(i+1)(j+1)}{(2i-1)(2j-1)ij}$$

is the quantummechanical analogue of the classical expression

$$\tfrac{1}{4}(\tfrac{3}{2}\cos^2(i, j) - \tfrac{1}{2})$$

and reduces to this expression in the limit of high quantumnumbers.

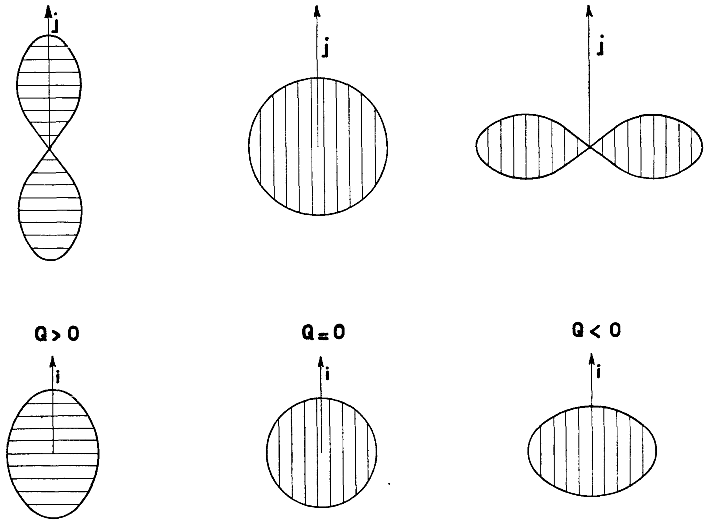

Fig. 3.

If now for a definite term separations have been found which do not obey the intervalrule, while there are no neighbouring terms which can give rise to deviations of the right order of magnitude, then one will try a formula of the type

$$\nu_f - \nu_0 = \frac{A}{2} K + B\,[\tfrac{3}{8}K(K+1) - \tfrac{1}{2}\, i\, j(i+1)(j+1)]. \quad (9, 2)$$

If for this term the number of hyperfine structure levels is larger than three, then the examination of the levels corresponding to only one finestructure term will already give a check of our assumption. If there are only three possible f-values, however, one can always represent the separations by a formula of the form (9, 2). In general a reliable determination of the quadrupole moment will only be possible in cases where deviations from the intervalrule have been determined for several terms, so that the Q values derived from the separations of these terms can be compared with each other.

In order to derive Q from B in Eq. (9, 2) one must know the quantity

$$C_e = \overline{\left\{\frac{3\cos^2\vartheta - 1}{r^3}\right\}}_{j,j}.$$

We will give approximate expressions for this quantity, confining ourselves to those cases in which only one electron contributes to C_e.

Let us consider one electron without spin and with orbital angular monentum l. The wavefunctions will be of the form

$$\psi_{n,l,m,}(r, \vartheta, \varphi) = f_{n,l}(r)\ Y_l^m(\vartheta, \varphi)$$

whence

$$\overline{\left\{\frac{3\cos^2\vartheta - 1}{r^3}\right\}}_{m,m} = \overline{\left(\frac{1}{r^3}\right)}_{n,l}\ \overline{(3\cos^2\vartheta - 1)}_{m,m}$$

where the mean value $(1/r^3)$ does not depend on m. A simple integration yields

$$\overline{(3\cos^2\vartheta - 1)}_{l,l} = -\frac{2l}{2l+3} \qquad (9, 3)$$

and hence

$$\overline{(3\cos^2\vartheta - 1)}_{m,m} = -\frac{3m^2 - l\,(l+1)}{(2l-1)\,l} \cdot \frac{2l}{2l+3}. \qquad (9, 4)$$

The negative sign in (9, 4) corresponds to the fact that in an orbital model the plane of the orbit is perpendicular to the angular momentum vector.

If now an l-orbit is coupled to a spinvector S (the corresponding wavefunctions are denoted by S_m) then the wavefunction for the state j, $m_j = j$ will be given by an expression

$$\Psi_j = \sum_{m_l} A\ (l, S)_{j,\, m_l}\, f_{n,\, l}(r)\ Y_l^{m_l}\, S_{j-m_l} \tag{9, 5}$$

It follows that

$$\overline{\left\{\frac{3\cos^2\vartheta - 1}{r^3}\right\}}_{j,\, j} = \left(\overline{\frac{1}{r^3}}\right)_{n,\, l}\ \overline{(3\cos^2\vartheta - 1)}_{j,\, j}$$

and

$$\overline{(3\cos^2\vartheta - 1)}_{j,\, j} =$$

$$= -\sum_{m_l} \mid A(l,\ S)_{j,\, m_l} \mid^2 \cdot \frac{3m_l^2 - l(l+1)}{l(2l-1)} \cdot \frac{2l}{2l+3}. \tag{9, 6}$$

Using general formulae for $A_{j,\, m_l}$ we can now calculate the required avarage for any set of values of l, S and j.

We will here give only the values of $\mid A_{j,\, m_l}\mid^2$ for two cases of special importance.

a) An orbital angular momentum l is coupled to a spin momentum 1; this case will occur in two-electron spectra. For the wavefunctions we find by means of the procedure explained in § 8:

m_j	${}^3L_{l+1}$	${}^3L_l$	${}^3L_{l-1}$
$l+1$	$s_1\, l_l$		
l	$\frac{1}{\sqrt{2l+2}}(\sqrt{2}\, s_0\, l_l + \sqrt{2l}\, s_1\, l_{l-1})$	$\frac{1}{\sqrt{2l+2}}(\sqrt{2l}\, s_0\, l_l - \sqrt{2}\, s_1\, l_{l-1})$	
$l-1$	$\frac{1}{4\sqrt{(l+1)(2l+1)}}(2s_{-1}\, l_l + 4\sqrt{l}\, s_0\, l_{l-1} +$ $+ 2\sqrt{l(2l-1)}\, s_1\, l_{l-2})$	$\frac{1}{2\sqrt{l(l+1)}}(2\sqrt{l}\, s_{-1}\, l_l + 2(l-1)\, s_0\, l_{l-1} -$ $- 2\sqrt{2l-1}\, s_1\, l_{l-2})$	$\frac{1}{\sqrt{l(2l+1)}}(\sqrt{2l}\, s_0\, l_l - \sqrt{2}\, s_1\, l_{l-1}$ $- \sqrt{2l-1}\, l_{l-1}\, s_0 + l_{l-2}\, s_1)$

It follows:

${}^3L_{l+1}\quad \mid A_{l+1,\, l}\mid^2 = 1$

${}^3L_l\quad \mid A_{l,\, l}\mid^2 = \frac{l}{l+1},\quad \mid A_{l,\, l-1}\mid^2 = \frac{1}{l+1}$

${}^3L_{l-1}\quad \mid A_{l-1,\, l}\mid^2 = \frac{2l-1}{2l+1},\quad \mid A_{l-1,\, l-1}\mid^2 = \frac{2l-1}{l(2l+1)},\quad \mid A_{l-1,\, l-2}\mid^2 = \frac{1}{l(2l+1)}.$

b) In the same way we find for a *p*-electron coupled with a spin S of arbitrary value the following scheme:

	$m_l = 1$	$m_l = 0$	$m_l = -1$
$j = S + 1$	1		
$j = S$	$\frac{1}{S+1}$	$\frac{S}{S+1}$	
$j = S - 1$	$\frac{1}{S(2S+1)}$	$\frac{2S-1}{S(2S+1)}$	$\frac{2S-1}{2S+1}$

In the case of two-electron configurations deviations from R-S-coupling can easily be taken into account. The wavefunctions for the state ${}^3L_{l+1}$ and ${}^3L_{l-1}$ will not be changed; the wavefunctions for the ${}^3L_l$ and ${}^1L_l$ state will be of the form:

$$\begin{aligned} {}^3\Psi'_l &= \alpha\,{}^3L_l + \beta\,{}^1L_l = \cos\vartheta\,{}^3L_l + \sin\vartheta\,{}^1L_l \\ {}^1\Psi'_l &= -\beta\,{}^3L_l + \alpha\,{}^1L_l = -\sin\vartheta\,{}^3L_l + \cos\vartheta\,{}^1L_l. \end{aligned} \qquad (9,\ 7)$$

For ${}^3L_l$ it follows that

$$\overline{(3\cos^2\vartheta - 1)}_{l,l} = -\frac{2l}{2l+3}\left\{\frac{l^2+l-3}{l(l+1)} + \beta^2\frac{3}{l(l+1)}\right\} \qquad (9,\ 8)$$

and for ${}^1L_l$

$$\overline{(3\cos^2\vartheta - 1)}_{l,l} = -\frac{2l}{2l+3}\left\{1 - \frac{3\beta^2}{l(l+1)}\right\}. \qquad (9,\ 9)$$

β can be determined from the position of the finestructure terms in the following way (compare § 11). Let d be the distance of the „singlet" and the „triplet" term and Δ the distance between the observed position of the triplet term and the position it should have according to the LANDÉ-rule, then

$$\sin^2\vartheta = \frac{\Delta}{d}. \qquad (9,\ 10)$$

The most important application of our formula is to the case of P and D terms. The results for these terms are:

	$\overline{(3\cos^2\vartheta - 1)}_{j,j}$		$\overline{(3\cos^2\vartheta - 1)}_{j,j}$
$^3D_3$	$-\frac{4}{7}$	$^3P_2$	$-\frac{2}{5}$
$^3D_2$	$-\frac{2}{7}(1 + \beta^2)$	$^3P_1$	$+\frac{1}{5}(1 - 3\beta^2)$
$^3D_1$	$-\frac{1}{5}$	$^3P_0$	0
$^1D_2$	$-\frac{4}{7}(1 - \frac{1}{2}\beta^2)$	$^1P_1$	$-\frac{2}{5}(1 - \frac{3}{2}\sin^2\vartheta)$

We will also recall the well-known formula for the mean value of $1/r^3$ (expressed in units $1/a^3$):

$$\overline{\left(\frac{1}{r^3}\right)} = \frac{Z_i Z_0^2}{n^{*3} l(l + \frac{1}{2})(l + 1)}\,. \tag{9, 11}$$

Here Z_i, the nuclear charge number for the „interior part'' of the orbit, is equal to the total nuclear charge number diminished by a screening correction; Z_0 is the exterior charge number (for neutral atoms $Z_0 = 1$) and n^* is the effective quantumnumber.

On the other hand the doublet separation (in cm^{-1}) is given by the formula

$$\delta = (2l + 1)\, Z_i \overline{\left(\frac{1}{r^3}\right)} \times 2{,}911\ \mathrm{cm}^{-1} \tag{9, 12}$$

whence

$$\overline{\left(\frac{1}{r^3}\right)} = \frac{\delta/2{,}911}{(2l + 1)\, Z_i}\,.$$

We will return later on to the derivation of these formulae.

§ 10. *The hyperfine structure of Europium and Cassiopeium.* Deviations from the intervalrule of the type described in the preceding section have been found for the first time by SCHÜLER and SCHMIDT (*35*) in the hyperfine structure of Europium. There are two isotopes, Eu_{151} and Eu_{153}; for both isotopes $i = 5/2$. The value of the magnetic moment of Eu_{151} is roughly twice the value of the magnetic moment of Eu_{153}. The deviations from the intervalrule for the heavy isotope, however, are about twice as large as those for the light isotope. From this fact it follows with certainty, that the deviations from the intervalrule cannot be caused by second order perturbation, since in that case the perturbations for the light isotope should be four times as large as the perturbations for the heavy one. It was shown by the author, that the deviations are in quantitative agreement with the assumption, that they are due to electric interaction with the nucleus. For the quadrupole moments the following values were found:

$$\mathrm{Eu}_{151} \qquad (3z^2 - r^2)_{i,\,i} = +\,1{,}5 \times 10^{-24}$$

$$\mathrm{Eu}_{153} \qquad (3z^2 - r^2)_{i,\,i} = +\,3{,}2 \times 10^{-24}.$$

As to the reliability of these results, we believe that they establish beyond doubt the existence of an electric quadrupole moment. Three terms were investigated (viz. ${}^{10}P_{9/2}$, ${}^{10}P_{7/2}$, ${}^{8}P_{7/2}$; the discussion can be carried out by means of the formulae of § 9), and the agreement between theory and experiment is such, that a fortuitous coincidence seems excluded. Also the value 3,2/1,5 = 2,1 for the ratio of the quadrupole moments follows unambiguously from the experiments. The absolute value of these moments, however, is less certain, since it is very difficult to estimate the accuracy of the value of $(1/r^3)$ calculated by means of (9, 11). The value of n^* was estimated by RUSSELL and KING (*32*); the spectrum is not sufficiently well-known for an accurate determination of the series limit to be possible. Still we do not believe, that the values of the quadrupole moment will be in error by more than 25%.

The second element concerning which data were published by SCHÜLER and SCHMIDT (*36*) is Cassiopeium (Lutetium), ($Z = 71$, $M = 175$). The spectrum of singly ionized Cp is a two-electron spectrum. The hyperfine structure was investigated for the terms $^3D_3$, $^3D_2$, $^3D_1$ and $^3P_2$, $^3P_1$. The value of i was found to be 7/2 (in determining this value SCHÜLER and SCHMIDT made use of the intensity rules). The hyperfine structure of all these terms shows deviations from the intervalrule far outside the limits of accuracy of the measurements (they are as big as 70 units!).

SCHÜLER and SCHMIDT showed, that the hyperfine structure can be represented with a high degree of accuracy (1 or 2 units) by formulae of the type

$$\nu_f - \nu_0 = a_1 \frac{K}{2ij} + a_2 \left(\frac{K}{2ij}\right)^2 . \qquad (10,\ 1)$$

This is trivial for the terms with $j = 1$ but not for the terms with $j = 3$ or $j = 2$. Instead of (10, 1) we will use the formula

$$\nu_f - \nu_0 = \tfrac{1}{2} AK + \tfrac{3}{8} BK(K+1) \qquad (10,\ 2)$$

then

$$A = \frac{1}{ij}\left(a_1 - \frac{a_2}{2ij}\right)$$

$$B = \frac{2a_2}{3i^2j^2} .$$

The experimentally determined values of a_1 and a_2 and the corresponding values of A and B are shown in the following table.

	a_1	a_2	A	B
$^3D_3$	598,9	40,3	56,86	0,244
$^3D_2$	453,5	27,1	64,41	0,369
$^3D_1$	—235,1	25,4	—68,2	1,38
$^3P_2$	676,1	66,3	96	0,903
$^3P_1$	571,1	—54,3	165	—2,96

The values of a_2 are certainly correct to within 10%. The distances of the finestructure levels being very large, perturbations of the second order are not to be expected; the fact that the separations can be represented by (10, 2), allows us to exclude this possibility altogether. Let us first consider the three ^3D terms. For β^2 one derives the value 0,066. We use the formula

$$B = \frac{1}{j(2j-1)}\,\overline{(3\cos^2\vartheta - 1)}_{j,j}\,\overline{\left(\frac{1}{r^3}\right)}\,\frac{Q}{(2i-1)i} \times 7{,}9$$

and substitute the values for $(3\cos^2\vartheta - 1)$ calculated in § 9. It follows that

$$B_3 : B_2 : B_1 = \frac{4/7}{15} : \frac{(2/7)\,1{,}066}{6} : \frac{1/5}{1} = 0{,}244 : 0{,}326 : 1{,}28$$

in rather good agreement with the experimental values for these ratios. In § 19 we will give a more accurate discussion of the B-values.

We will calculate Q from the value B_3; there are several reasons why this term is believed to give the most reliable results. In the first place the deviations from the interval-rule are very large for $^3D_3$, in the second place there are 7 possible f-values, so that a very accurate check of Eq. (10, 2) is possible and finally the relativistic corrections for this term will be small.

The multiplet splitting is 2400 cm^{-1}. It follows that

$$\overline{\left(\frac{1}{r^3}\right)} = \frac{2400/2{,}911}{5 \times 61} = 2{,}7$$

(we use the value $Z = 61$ which perhaps will be somewhat too large). For Q we find

$$Q = +\,6{,}3$$

Let us now consider the P terms. Here $\beta^2 = 0{,}05$. For the ratio of the B-values we find

$$B_2 : B_1 = 1 : (-\,2{,}56) = 0{,}903 : (-\,2{,}30).$$

The agreement is somewhat less satisfactory; it is to be expected that in this case the relativistic corrections will be rather important.

We calculate Q from B_2. The multiplet splitting is 5189 and hence

$$\overline{\left(\frac{1}{r^3}\right)} = \frac{5189/2{,}911}{3 \times 67} = 8{,}8$$

which leads to

$$Q = 4{,}1.$$

The agreement with the value calculated from $^3D_3$ is not very good and we will see in § 19 that it is not improved by taking into account relativistic corrections. We will in that section also discuss the possible causes of the discrepancy. Here we will only point out, that it is hardly to be expected, that the large spin-orbit interactions occurring in this case should not give rise to perturbations of the configuration. In our opinion these discrepancies do by no means throw doubt on the reality of the quadrupole moment; but they make the value of the moment somewhat uncertain. We believe the value deduced from $^3D_3$ to be considerably more reliable than the value following from $^3P_2$, $^3P_1$. The multiplet splitting for the ^3D terms is smaller and the same will presumably hold for the configuration perturbations; also the fact that there is a satisfactory agreement between the three ^3D terms makes it probable, that the configuration is not appreciably perturbed.

At the time this paper was written, Eu and Cp were the only elements about which accurate data were available. Since that time SCHÜLER and SCHMIDT have given a detailed account of the deviations from the intervalrule in Hg, Cu and Bi and communicated preliminary values for the quadrupole moment of As.

The results are given in our table.

	i	μ	Q	
Cu_{63}	$^3/_2$	2,4	$-0,3 \times 10^{-24}$	(*49*)
Cu_{65}	$^3/_2$	2,6	$-0,3 \times 10^{-24}$	
As_{75}	$^3/_2$	0,5	$+0,2 \times 10^{-24}$	
Bi_{209}	$^9/_2$	3,6	$-0,4 \times 10^{-24}$	(*48*)
Hg_{201}	$^3/_2$	III	111×10^{-24}	(*46*)

§ 11. *Relativistic theory of s, l configurations.*

Following Breit and Wills (*6*) we will now give a relativistic treatment of s, l-configurations. For the s-electron there are two possible states; let the corresponding wavefunctions be denoted by $s_{\frac{1}{2}}$ and $s_{-\frac{1}{2}}$. The possible states for the l-electron can be divided into two groups: states with $j = l + \frac{1}{2}$ and states with $j = l - \frac{1}{2}$. For the corresponding wavefunctions we write $l_m^{l+\frac{1}{2}}$ and $l_m^{l-\frac{1}{2}}$ respectively. A state with total angular momentum $l + 1$ and $m = l + 1$ can be realized in one way only; the corresponding wavefunction is:

$$^3L_{l+1}^{l+1} = s_{\frac{1}{2}}\, l_{l+\frac{1}{2}}^{l+\frac{1}{2}}. \tag{11, 1}$$

In the same way there is only one state with total angular momentum $l - 1$ and $m = l - 1$; the wavefunction is:

$$^3L_{l-1}^{l-1} = \frac{1}{\sqrt{2l}} \left(s_{\frac{1}{2}}\, l_{l-{}^3/_2}^{l-\frac{1}{2}} - \sqrt{2l-1}\; s_{-\frac{1}{2}}\, l_{l-\frac{1}{2}}^{l-\frac{1}{2}}\right). \tag{11, 2}$$

A state with $j = l$ and $m = l$, however, occurs twice. We introduce the notation $(\frac{1}{2},\ l + \frac{1}{2})_l^l$ and $(\frac{1}{2},\ l - \frac{1}{2})_l^l$ for the wavefunctions. We have:

$$(\tfrac{1}{2}, l - \tfrac{1}{2})_l^l = s_{\frac{1}{2}}\, l_{l-\frac{1}{2}}^{l-\frac{1}{2}} \tag{11, 3}$$

$$(\tfrac{1}{2}, l + \tfrac{1}{2})_l^l = \frac{1}{\sqrt{2l+2}} \left(s_{\frac{1}{2}}\, l_{l-\frac{1}{2}}^{l+\frac{1}{2}} - \sqrt{2l+1}\; s_{-\frac{1}{2}}\, l_{l-\frac{1}{2}}^{l+\frac{1}{2}}\right). \tag{11, 4}$$

This last formula contains a sign convention, which will be followed throughout our further calculations. The sign of the functions $(\frac{1}{2},\ l + \frac{1}{2})_m^l$ is then fixed by the condition that the matrixelements of the total angular momentum must have the „standard form" (§ 1).

As long as the interaction of the electrons is neglected, the functions (11, 3) and (11, 4) are proper functions. In consequence of the interaction the functions $(\frac{1}{2}, l + \frac{1}{2})_l^l$ and $(\frac{1}{2}, l - \frac{1}{2})_l^l$ will be mixed and the real wavefunctions will be of the form:

$$\Psi'_l = c_1 \, (\tfrac{1}{2}, l + \tfrac{1}{2})_l^l + c_2 \, (\tfrac{1}{2}, l - \tfrac{1}{2})_l^l. \qquad (11,\ 5)$$

We determine the values c_1, c_2 using a non-relativistic approximation. We will approximate $l_m^{l+\frac{1}{2}}$ and $l_m^{l-\frac{1}{2}}$ by linear combinations of products of orbital wavefunctions l_m and spin functions $\sigma_{\pm\frac{1}{2}}$. These approximate expressions are:

$$l_{l+\frac{1}{2}}^{l+\frac{1}{2}} = l_l \, \sigma_{\frac{1}{2}}$$

$$l_{l-\frac{1}{2}}^{l+\frac{1}{2}} = \frac{1}{\sqrt{2l+1}} \left(\sqrt{2l} \, l_{l-1} \, \sigma_{\frac{1}{2}} + l_l \, \sigma_{-\frac{1}{2}} \right)$$

$$l_{l-\frac{1}{2}}^{l+\frac{1}{2}} = \frac{1}{\sqrt{2l+1}} \left(l_{l-1} \, \sigma_{\frac{1}{2}} - \sqrt{2l} \, l_l \, \sigma_{-\frac{1}{2}} \right).$$

With

$$c_1 = \sqrt{\frac{l+1}{2l+1}}, \qquad c_2 = -\sqrt{\frac{l}{2l+1}}$$

one finds

$$\Psi' = \frac{1}{\sqrt{2}} l_l \left(s_{-\frac{1}{2}} \, \sigma_{\frac{1}{2}} - s_{\frac{1}{2}} \, \sigma_{-\frac{1}{2}} \right)$$

whereas

$$c_1 = \sqrt{\frac{l}{2l+1}}, \qquad c_2 = \sqrt{\frac{l+1}{2l+1}}$$

leads to

$$\Psi' = \frac{1}{\sqrt{l+1}} l_l S_0 + \sqrt{\frac{l}{l+1}} \, l_{l-1} \, S_1$$

with

$$s_{\frac{1}{2}} \, \sigma_{\frac{1}{2}} = S_1$$

and

$$\frac{1}{\sqrt{2}} \left(s_{\frac{1}{2}} \, \sigma_{-\frac{1}{2}} + s_{-\frac{1}{2}} \, \sigma_{\frac{1}{2}} \right) = S_0.$$

These expressions correspond to the case of R-S-coupling. We put for ${}^3L_l$

$$c_1 = \sin\,(\vartheta_0 - \vartheta), \qquad c_2 = \cos\,(\vartheta_0 - \vartheta)$$

for ${}^1L_l$ (11, 6)

$$c_1 = \cos\,(\vartheta - \vartheta_0), \qquad c_2 = -\sin\,(\vartheta_0 - \vartheta)$$

and take ϑ_0 to be

$$\vartheta_0 = \text{arc tg}\sqrt{\frac{l}{l+1}} \tag{11, 7}$$

then ϑ will be zero in the case of R-S-coupling.

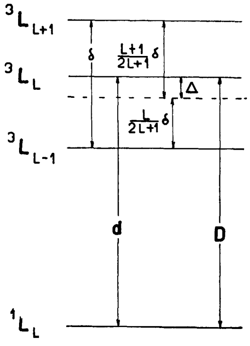

Fig. 4.

In determining ϑ we will follow WOLFE (*43*). Let us assume, that the position of finestructure levels is as shown in our figure, the broken line being the position of ${}^3L_l$ calculated by means of the LANDÉ rule, then

$$\sin^2\vartheta = \frac{\Delta}{d}. \tag{11, 8}$$

WOLFE does not only take into account the interaction of the l-orbit and the spin of the l-electron, but also the interaction of the l-orbit and the spin of the s-electron. The first mentioned interaction is much larger than the second one; it may be expressed in terms of one constant, C_2; in the same way the second interaction can be characterised by a constant C_3. According to WOLFE:

$$C_2 + C_3 = \frac{\delta}{2l + 1}$$

$$C_2 - C_3 = (\Delta D/l(l + 1))^{\frac{1}{2}}.$$

Usually only C_2 is taken into account and one arrives at the conclusion that the theory of intermediate coupling only applies when

$$\frac{\delta}{2l + 1} = \left\{\frac{\Delta D}{l(l + 1)}\right\}^{\frac{1}{2}}. \qquad (11,\ 9)$$

But the interaction of l-orbit and s-spin certainly exists and as long as no unreasonably large values for C_3 are found, the fact that (11, 9) is not strictly fulfilled is no reason to doubt the validity of (11, 8). On the other hand one must not forget, that the fact that WOLFE's equations contain as many constants as there are independent separations, makes it impossible to check the correctness of the assumptions. It would be useful to calculate the constant C_3 theoretically; the term with C_3 being a rather small correction, a rough calculation would be sufficient.

Finally we remark, that according to WOLFE's theory the doublet splitting of the l-electron is not given by δ but by $(2l + 1)C_2$.

§ 12. *Solutions of* DIRAC's *equations in a central field of force.*

Having determined the constants c_1 and c_2, we can calculate the mean value of $(3 \cos^2 \vartheta - 1)/r^3$ and of H_z.

In doing this we make use of the explicit expressions for the solutions of DIRAC's equations in a central field of force. We use the solutions in the form given by BETHE (*2*); apart from the sign, which is chosen in agreement with the convention made in § 11.

$$\left.\begin{aligned} j &= l + \tfrac{1}{2} \\ m &= l + \tfrac{1}{2} \end{aligned}\right\}$$

$$\begin{aligned} u_1 &= if\sqrt{\frac{1}{2l+3}}\, Y_{l+1}^{l} \\ u_2 &= if\sqrt{\frac{2l+2}{2l+3}}\, Y_{l+1}^{l+1} \\ u_3 &= g\, Y_l^l \\ u_4 &= 0 \end{aligned} \tag{12, 1}$$

$$\left.\begin{aligned} j &= l + \tfrac{1}{2} \\ m &= l - \tfrac{1}{2} \end{aligned}\right\}$$

$$\begin{aligned} u_1 &= -if\sqrt{\frac{2}{2l+3}}\, Y_{l+1}^{l-1} \\ u_2 &= -if\sqrt{\frac{2l+1}{2l+3}}\, Y_{l+1}^{l} \\ u_3 &= -g\sqrt{\frac{2l}{2l+1}}\, Y_l^{l-1} \\ u_4 &= +g\sqrt{\frac{1}{2l+1}}\, Y_l^l \end{aligned} \tag{12, 2}$$

$$\left.\begin{aligned} j &= l - \tfrac{1}{2} \\ m &= l - \tfrac{1}{2} \end{aligned}\right\}$$

$$\begin{aligned} u_1 &= -if\, Y_{l-1}^{l-1} \\ u_2 &= 0 \\ u_3 &= -g\sqrt{\frac{1}{2l+1}}\, Y_l^{l-1} \\ u_4 &= -g\sqrt{\frac{2l}{2l+1}}\, Y_l^l \end{aligned} \tag{12, 3}$$

f and g are functions of r only.

The functions

$$\chi_1 = rf, \qquad \chi_2 = rg$$

satisfy the equations

$$\begin{aligned} \frac{d\chi_1}{dr} + k\frac{\chi_1}{r} &= \frac{mc}{\hbar}\left(1 - \frac{E-\Phi}{E_0}\right)\chi_2 \\ \frac{d\chi_2}{dr} - k\frac{\chi_2}{r} &= \frac{mc}{\hbar}\left(1 + \frac{E-\Phi}{E_0}\right)\chi_1. \end{aligned} \tag{12, 4}$$

Here

$$\begin{aligned} k &= l+1 \quad \text{for } j = l + \tfrac{1}{2} \\ k &= -l \quad \text{for } j = l - \tfrac{1}{2} \end{aligned}$$

$E_0 = mc^2$ and Φ is the potential energy ($\Phi = -Ze^2/r$ for a Coulomb field).

Following BREIT and WILLS we characterize the quantities relating to the state $j = l + \frac{1}{2}$ by one dash, those relating to the state $j = l - \frac{1}{2}$ by two dashes; then:

$$k' = l + 1, \qquad j' = l + \tfrac{1}{2}$$

$$k'' = -l, \qquad j'' = l - \tfrac{1}{2}$$

We now take $\hbar/mc$ as unit length and put

$$\frac{E}{E_0} = P \qquad \frac{\Phi}{E_0} = -V$$

then the Eqs. (12, 4) reduce to

$$\begin{aligned} \frac{d\chi_1}{dr} + k\frac{\chi_1}{r} &= (1 - P - V)\,\chi_2 \\ \frac{d\chi_2}{dr} - k\frac{\chi_2}{r} &= (1 + P + V)\,\chi_1. \end{aligned} \qquad (12,\ 5)$$

For a Coulomb field

$$V = Z\alpha/r.$$

We will apply these equations to a valency electron moving in the field of the nucleus and of the core of the atom. The ionization energy will be of the same order of magnitude as for a hydrogen atom, and $P - 1$ will thus be of the order α^2 which is very small compared with unity. In the neighbourhood of the nucleus the potential energy is of the form:

$$-V = -(Z\alpha/r - C_a)$$

The screening constant C_a may be written as $Z\alpha/r_s$ where r_s is a certain average radius. In our units r_s will be a large number. For $r \ll r_s$ we can now neglect C_a and $P - 1$ altogether.

The Eqs. (12, 5) reduce to

$$\begin{aligned} \frac{d\chi_1}{dr} + k\frac{\chi_1}{r} &= -\frac{Z\alpha}{r}\chi_2 \\ \frac{d\chi_2}{dr} - k\frac{\chi_2}{r} &= \left(2 + \frac{Z\alpha}{r}\right)\chi_1 . \end{aligned} \tag{12, 6}$$

These equations can be solved in terms of Bessel functions; the solution is obtained most easily by elimination of χ_2. One finds

$$\begin{aligned} \chi_1 &= CZ\alpha J_{2\rho}(2\sqrt{2Z\alpha r}) \\ \chi_2 &= C\,\{J_{2\rho+1}\cdot\sqrt{2Z\alpha r} - (\rho + k)\,J_{2\rho}\}, \end{aligned} \tag{12, 7}$$

with

$$\rho = \sqrt{k^2 - Z^2\alpha^2}.$$

The first terms of an expansion in powers of r are:

$$\begin{aligned} \chi_1 &= C(Z\alpha)^{\rho+1}\frac{(2r)^\rho}{\Gamma(2\rho + 1)} \\ \chi_2 &= -C(\rho + k)\,(Z\alpha)^\rho\frac{(2r)^\rho}{\Gamma(2\rho + 1)} . \end{aligned} \tag{12, 8}$$

For large values of $\sqrt{2Z\alpha r}$ on the other hand the Bessel-functions can be expanded in an asymptotic series. The term of highest order in the series for χ_2 is:

$$\chi_2 \sim C\left(\frac{1}{\pi\sqrt{2Z\alpha r}}\right)^{\frac{1}{2}}\left\{\sqrt{2Z\alpha r}\cos(2\sqrt{2Z\alpha r} - \rho\pi - \tfrac{3}{4}\pi)\ldots\right. \tag{12, 9}$$

We will now introduce the following assumption: We assume that there exists a value r_1 in the neighbourhood of which on the one hand the solutions (12, 7) are a good approximation, and on the other hand the Bessel functions are given with a fair degree of accuracy by their asymptotic expansions.

For large values of r the relativistic corrections will be negligible and χ_2 will be a solution of the non-relativistic SCHRÖDINGER equation, χ_1 being given by

$$\chi_1 = \tfrac{1}{2}\left(\frac{d\chi_2}{dr} - k\frac{\chi_2}{r}\right).$$

In order to obtain a better idea of the dependence of the relativistic corrections on the value of r we will deduce a rigorous equation for χ_2, by eliminating χ_1 from the Eqs. (12, 5). Putting

$$\begin{aligned} \chi_1 &= \sqrt{P + V - 1}\ v_1 \\ \chi_2 &= \sqrt{P + V + 1}\ v_2 \end{aligned} \tag{12,10}$$

one finds

$$v_1^{('')} + \left\{(P + V)^2 - 1 - \frac{k(k+1)}{r^2} + \right.$$
$$\left. + \frac{\frac{1}{2}V^{('')} - (k/r)V^{(')}}{P + V - 1} - \frac{3}{4}\frac{(V^{(')})^2}{(P + V - 1)^2}\right\} v_1 = 0 \quad (12,\ 11)$$

where (′) and (″) denote the first and second derivative with respect to r and

$$v_2^{('')} + \left\{(P + V)^2 - 1 - \frac{k(k-1)}{r^2} + \right.$$
$$\left. + \frac{\frac{1}{2}V^{('')} + (k/r)V^{(')}}{P + V + 1} - \frac{3}{4}\frac{(V^{(')})^2}{(P + V + 1)^2}\right\} v_2 = 0. \quad (12,\ 12)$$

In calculating the relativistic corrections in first approximation one usually considers the term with V^2 and the term $\frac{1}{2}(k/r)\ V^{(')}$. If $V = Z\alpha/r$ Eq. (12, 12) becomes

$$v_2^{('')} + \left\{\left(P + \frac{Z\alpha}{r}\right)^2 - 1 - \frac{k(k-1)}{r^2} + \right.$$
$$\left. + \frac{rZ\alpha(1 - k)\ (1 + P) + Z\alpha^2\ (\frac{1}{4} - k)}{(P + Z\alpha/r + 1)^2\, r^4}\right\}.$$

Taking into account that $k(k - 1) = l(l + 1)$, one sees that the difference between this equation and the SCHRÖ-

DINGER equation consists in the term $(Z\alpha/r)^2$ and the term with r^4 in the denominator. Now for $Z\alpha = 0{,}5$ and $r = 5$ for instance these two terms are already very small. If there exists a value r_1 with the properties mentioned above, then for $r \geqslant r_1$ the relativistic corrections will be negligible. On the other hand it will be possible to put

$$\chi_2 = \sqrt{2}\, v_2.$$

For larger values of r we can now approximate to v_2 by a WENTZEL-KRAMERS-BRILLOUIN function. Outside of the atomic core (for very large r-values) this function may be fitted to the rigorous solution for the Coulomb field, with charge number $Z_0 = 1 + z$ (z = degree of ionization). We thus obtain a solution which is build up in the following way

$0 \leqslant r \leqslant r_1$	$r \sim r_1$	$r > r_1$	$r \gg r_1$
Bessel functions (relativistic)	Asymptotic exp. of Bessel functions	Non-relativistic W.K.B. solution	rigorous solution

The solution for $r < r_1$ does not depend on the energy.

§ 13. *Calculation of the normalization integral.*

We will now deduce a formula for the normalization integral of this wavefunction. In doing this we will neglect the contribution of the range of integration $0 \leqslant r \leqslant r_1$. We consider the non-relativistic SCHRÖDINGER equation:

$$w^{('')} + \left\{2(P - 1) + 2V - \frac{l(l+1)}{r^2}\right\} w = w^{('')} + p^2 w = 0. \quad (13, 1)$$

Let P have an arbitrary value, and let w be the solution which is regular at infinity; for given P the function w is determined apart from a multiplicative constant. We differentiate this equation with respect to r and find, putting $dw/dP = w_P$:

$$w_P^{('')} + \left\{2(P - 1) + 2V - \frac{l(l+1)}{r^2}\right\} w_P = -2w. \quad (13, 2)$$

It follows that

$$\frac{d}{dr}\,(w^{(\prime)}w_P - w_P^{(\prime)}w) = w^{(\prime\prime)}w_P - w_P^{(\prime\prime)}w = +\,2w^2.$$

Integrating this equation from $r = r_1$ to $r = \infty$ we obtain

$$\int\limits_{r_1}^{\infty} w^2 dr = -\tfrac{1}{2}(w^{(\prime)}w_P - w_P^{(\prime)}w)_{r=r_1} = +\,\tfrac{1}{2}w^2 \frac{\partial}{\partial P}\left(\frac{w^{(\prime)}}{w}\right)_{r=r_1} \cdot \quad (13,3)$$

If P is now a proper value, then the value of $w^{(\prime)}/w$ is equal to the value $v_2^{(\prime)}/v_2$, where v_2 is the solution of the relativistic wave equation which is regular for $r = 0$ and does not depend on P.

It can be proved that the quantity

$$\vartheta = \operatorname{arctg}(w^{(\prime)}/w)$$

is a monotonic function of P. If the quantumnumber increases by 1, ϑ increases by π, but no general expression can be given for the dependence of ϑ on P.

Let us now consider a *W-K-B*-approximation for the function w. It will be of the form

$$w = \frac{K}{\sqrt{p}} \sin\left\{\int\limits_{r_1}^{r} p\,dr - \psi(P)\right\}. \qquad (13, 4)$$

From this we obtain

$$\int\limits_{r_1}^{\infty} w^2 dr = +\,\tfrac{1}{2}K^2 \frac{d\psi}{dP}.$$

In deducing this expression derivatives of p with respect to P were neglected in accordance with the fact that for $r < r_1$ the solutions of the wave equation do not depend on the values of P. If P increases, ψ also will increase and the proper values can be determined from the equation

$$\psi = \psi_0 + n\pi$$

so we may also write

$$\int_{r_1}^{\infty} w^2 dr = \frac{\pi}{2} K^2 \frac{dn}{dP}. \tag{13, 5}$$

There will now exist a simple functional relation between n and P and it will be permissible to calculate the value of dn/dP by means of an interpolation formula for P as a function of n. Taking into account that

$$\int_0^{\infty} \{|\chi_1|^2 + |\chi_2|^2\} \, dr \sim 2\int_0^{\infty} w^2 dr$$

and that according to Eq. (12, 9)

$$K = C\sqrt{\frac{Z\alpha}{\pi}} \tag{13, 6}$$

we find

$$N = \int_0^{\infty} \{|\chi_1|^2 + |\chi_2|^2\} \, dr = C^2 Z\alpha \Big/ \frac{dP}{dn}.$$

Measuring the energy in units $Rh = \frac{1}{2}\alpha^2 mc^2$, we obtain

$$P - 1 = \tfrac{1}{2}\alpha^2 E_R$$

$$N = C^2 \frac{2Z}{\alpha} \Big/ \frac{dE_R}{dn}.$$

For a normalized wavefunction the constant C will be given by

$$C^2 = \frac{\alpha}{2Z} \frac{dE_R}{dn}. \tag{13, 7}$$

Let us consider the nature of the dependence of n and E_R somewhat more closely. Suppose for one moment, that for $r \geqslant r_1$ the field is a Coulomb field with charge number $1 + z$. In that case the phase $\psi(P)$ of the function w would be given by $n^*\pi + b$ where b is a constant and where the relation between E_R and n^* is:

$$E_R = -\frac{(1 + z)^2}{n^{*2}}. \tag{13, 8}$$

The difference between this expression and the true phase will in first approximation be independent of the energy, when the core of the atom is small compared with the dimensions of the „orbit''. In higher approximation it will be possible to expand this difference in ascending powers of E_R. We then find:

$$\psi = n\pi + \psi_0 = n^*\pi + b + cE_R + \dots .$$

Omitting the term with E_R,

$$n = n^* + \delta_1$$

and

$$\frac{dE}{dn} = \frac{dE}{dn^*} = 2\frac{Z_0^2}{n^{*3}} \qquad (13,\ 9)$$

whence

$$C^2 = \frac{\alpha}{Z}\,\frac{Z_0^2}{n^{*3}}. \qquad (13,\ 10)$$

Taking into account the term cE_R corresponds to using the RITZ-correction.

If now dE_R/dn is determined by means of the RYDBERG-RITZ formula, the theoretical foundation of (13, 10) seems to be identical with that of the RYDBERG-RITZ formula itself. In one respect, however, this is not completely correct. In our deduction of the RYDBERG-RITZ formula it is supposed that the wavefunction for $r < r_1$ does not depend on E_R, but not that the influence of screening can be neglected. If the screening is taken into account, the value of K and therefore also the value of C will be slightly modified. Calculations of K were carried out by FERMI and his collaborators, using a potential determined by the statistical method. The corrections are not very large however and in this work they will not be taken into account.

A formula equivalent to (13, 10) is due to GOUDSMIT; a proof of this equation and the somewhat more general Eq. (13, 7) was given by FERMI and SEGRÉ (*16*). The formulation of the proof given above was the result of a discussion with Professor KRAMERS.

§ 14. *The doublet separation.*

In § 12 we have seen that in the neighbourhood of r_1 the function χ_2 is given approximately by the expression

$$\chi_2' \sim C'\left(\frac{1}{\pi\sqrt{2Z\alpha r}}\right)^{\frac{1}{2}}\{\sqrt{2Z\alpha r}\cos(2\sqrt{2Z\alpha r}-\rho'\pi-\tfrac{3}{4}\pi)-\ldots\} \qquad (14, 1)$$

for the state

$$j' = l + \tfrac{1}{2}$$

and by

$$\chi_2'' \sim C''\left(\frac{1}{\pi\sqrt{2Z\alpha r}}\right)^{\frac{1}{2}}\{\sqrt{2Z\alpha r}\cos(2\sqrt{2Z\alpha r}-\rho''\pi-\tfrac{3}{4}\pi)-\ldots\} \qquad (14, 2)$$

for the state $j'' = l + \frac{1}{2}$. Since $\rho' - \rho'' \sim 1$, these functions will be approximately identical if we choose

$$C'' \sim - C'.$$

The remaining phase difference between χ_2' and χ_2'' is $(\rho' - \rho'' - 1)\,\pi$. Hence the energy difference of those two states will be

$$(\rho' - \rho'' - 1)\,\pi\,\frac{dP}{d\psi} = (\rho' - \rho'' - 1)\,\frac{dE_R}{dn}\cdot\tfrac{1}{2}\,\alpha^2 .$$

The separation in cm^{-1} will now be given by

$$\delta = (\rho' - \rho'' - 1)\,\frac{dE_R}{dn}\,R\,. \qquad (14, 3)$$

Neglecting higher powers of $(Z\alpha)^2$ we find:

$$\rho' = \sqrt{(l+1)^2 - Z^2\alpha^2} = l + 1 - \frac{(Z\alpha)^2}{2l+2}$$

$$\rho'' = \sqrt{l^2 - Z^2\alpha^2} = l - \frac{(Z\alpha)^2}{2l}$$

$$\rho' - \rho'' - 1 = \frac{Z^2\alpha^2}{2l(l+1)}\,.$$

Writing

$$E_R = \frac{Z_0^2}{n^{*2}}$$

we obtain

$$\delta = \frac{dn^*}{dn} \frac{Z^2 Z_0^2}{n^{*3} l(l+1)} R\alpha^2. \qquad (14,\ 4)$$

If the RYDBERG formula is valid, $dn^*/dn = 1$ and Eq. (14, 4) reduces to the well-known LANDÉ formula. The formula (13, 10) was proposed by GOUDSMIT (*20*) in analogy to the formula of LANDÉ. We see now that the theoretical foundations of both formulae are the same. At the same time we have found correction factors of LANDÉ's formula, viz. a relativistic factor:

$$H = (\rho' - \rho'' - 1) \Big/ \frac{Z^2 \alpha^2}{2l(l+1)}$$

and a „RITZ correction" factor.

The fact that doublet separations for terms with small n^* in one- and two-electron spectra of heavy elements can be represented with an accuracy of 10 or 20% by means of Eq. (14, 4) when the total nuclear charge Z is diminished by 2 for a p-state and by 10 for a d-state is therefore a strong argument in favour of the validity of our formulae. The numbers „2" and „10" are somewhat arbitrary but for heavy nuclei this is of little importance. Better values of the screening corrections might be obtained by the statistical method. It would also be interesting to see how far the corrections by which Eq. (14, 4) differs from the ordinary LANDÉ formula lead to a material improvement of the agreement between theory and experiment.

It was pointed out by BREIT and WILLS that the normalization integrals for the states j' and j'' will be slightly different from each other, because of the energy difference between these states. From Eq. (13, 7) one can deduce, that the difference of the C values for the normalized wave-functions is given by

$$C'^2 - C''^2 = \frac{\alpha}{2Z} \frac{d^2 E_R}{dn^2} (\rho' - \rho'' - 1)$$

or, assuming $dn^*/dn = 1$:

$$\frac{C'^2 - C''^2}{C'^2} = - \frac{3Z^2\alpha^2}{2l(l+1)\, n^*}.$$

Though one can hardly expect that this formula will be strictly valid, one may nevertheless expect it to give an idea of the possible order of magnitude of such corrections.

It is sometimes useful to write the formula for the doublet separation in the form

$$\delta = HZ\,(l + \tfrac{1}{2}) \left(\overline{\frac{1}{r^3}}\right)_{kl} R\alpha^2;$$

the quantity $(\overline{1/r^3})_{kl}$ will be defined in the next section.

§ 15. *Calculation of the mean value of* $(3\cos^2\vartheta - 1)/r^3$.

Using the results derived in the previous sections we can now calculate the mean value of $(3\cos^2\vartheta - 1)/r^3$. We will assume that only the values $r < r_1$ will contribute appreciably to this average. The calculations do not offer any points of interest and we will confine ourselves to stating the results.

We find:

$$j = l + 1: \quad \left(\overline{\frac{3\cos^2\vartheta - 1}{r^3}}\right)_{j,j} = - \frac{2l}{2l+3} \left(\overline{\frac{1}{r^3}}\right)^{\prime,\prime}$$

$$j = l - 1: \quad \left(\overline{\frac{3\cos^2\vartheta - 1}{r^3}}\right)_{j,j} = - \frac{2(l-1)(l+1)(2l-3)}{l(2l-1)(2l+1)} \left(\overline{\frac{1}{r^3}}\right)^{\prime\prime,\prime\prime}$$

$$j = l: \quad \left(\overline{\frac{3\cos^2\vartheta - 1}{r^3}}\right)_{j,j} = - \left\{ c_1^2 \frac{(2l-1)(l+2)\,2l}{(l+1)(2l+1)(2l+3)} \left(\frac{1}{r^3}\right)^{\prime,\prime} + \right.$$

$$\left. + c_2^2 \frac{2(l-1)}{2l+1} \left(\overline{\frac{1}{r^3}}\right)^{\prime\prime,\prime\prime} - \frac{12\, c_1 c_2 \sqrt{l/(l+1)}}{(2l+1)(2l+3)} \left(\overline{\frac{1}{r^3}}\right)^{\prime,\prime\prime} \right\}$$

with

$$\overline{\left(\frac{1}{r^3}\right)}^{\prime,\,\prime} = \int\limits_0^\infty \{|\chi_1'|^2 + |\chi_2'|^2\} \frac{1}{r^3}\, dr$$

$$\overline{\left(\frac{1}{r^3}\right)}^{\prime\prime,\,\prime\prime} = \int\limits_0^\infty \{|\chi_1''|^2 + |\chi_2''|^2\} \frac{1}{r^3}\, dr$$

$$\overline{\left(\frac{1}{r^3}\right)}^{\prime,\,\prime\prime} = \int\limits_0^\infty \{\chi_1'\chi_2'' + \chi_2'\chi_1''\} \frac{1}{r^3}\, dr.$$

These quantities may be written as:

$$\overline{\left(\frac{1}{r^3}\right)}^{\prime,\,\prime} = R' \overline{\left(\frac{1}{r^3}\right)}_{kl}$$

$$\overline{\left(\frac{1}{r^3}\right)}^{\prime\prime,\,\prime\prime} = R'' \overline{\left(\frac{1}{r^3}\right)}_{kl}$$

$$\overline{\left(\frac{1}{r^3}\right)}^{\prime,\,\prime\prime} = S \overline{\left(\frac{1}{r^3}\right)}_{kl}.$$

R', R'' and S are certain relativistic correction factors; formulae and numerical values are given in § 17, and

$$\overline{\left(\frac{1}{r^3}\right)}_{kl} = C^2 \frac{Z^2\alpha^2}{l(l+\frac{1}{2})\,(l+1)} = \alpha^3 Z \frac{dE_R}{dn} / l(l+1)(2l+1).$$

Here the unit of length is still $\hbar/mc$. Introducing $a_H = \hbar/\alpha mc$ as unit of length, we have

$$\overline{\left(\frac{1}{r^3}\right)}_{kl} = \frac{Z}{l(l+1)\,(2l+1)} \frac{dE_R}{dn}.$$

Here normalization corrections were not taken into account. Putting $R' = R'' = S = 1$ and inserting for c_1 and c_2 the values for R-S-coupling our formulae reduce to the expressions derived in § 9.

Finally we repeat here the fundamental formula:

$$(\Delta_f\nu)_{el} = B\,\{\tfrac{3}{8}K(K+1) - \tfrac{1}{2}\,i(i+1)\,j(j+1)\}$$

with

$$(2j-1)\,jB = \left(\overline{\frac{3\cos^2\vartheta - 1}{r^3}}\right)_{j,\,j} \cdot \frac{Q}{(2i-1)\,i} \,.\, 7{,}9 \times 10^{-3}\ \mathrm{cm}^{-1}.$$

§ 16. *Formulae for the magnetic interaction.*

Breit and Wills have derived the following formulae. Let A be the constant in the equation

$$(\Delta_f\nu)_m = \frac{A}{2}K$$

then we have

$$j = l+1: \qquad A = \frac{a(s)}{2(l+1)} + \frac{2l+1}{2(l+1)}\,a'$$

$$j = l-1: \qquad A = -\frac{a(s)}{2l} + \frac{2l+1}{2l}\,a''$$

$$j = l: \qquad l(l+1)\,A = \tfrac{1}{2}\{(l+1)\,c_2^2 - lc_1^2\}\,a(s) +$$

$$+\tfrac{1}{2}l\,(2l+3)\,c_1^2a' + \tfrac{1}{2}(2l-1)\,(l+1)\,c_2^2\,a'' + 2c_1\,c_2\,\sqrt{l(l+1)}\,a'''.$$

Here

$$\left.\begin{matrix} a' \\ a'' \end{matrix}\right\} = \gamma\,\frac{2l(l+1)}{j(j+1)}\left(\overline{\frac{1}{r^3}}\right)_{kl} F \,.\, 1{,}585 \times 10^{-3}\ \mathrm{cm}^{-1}$$

$$a''' = -\gamma\,\frac{1}{2l+1}\left(\overline{\frac{1}{r^3}}\right)_{kl} G \,.\, 1{,}585 \times 10^{-3}\ \mathrm{cm}^{-1}$$

$$a(s) = \tfrac{8}{3}Z\,\frac{dE_R}{dn}\,F \,.\, 1{,}585 \times 10^{-3}\ \mathrm{cm}^{-1}.$$

a', a'' and $a(s)$ are the constants for one electron in the states $l+\frac{1}{2}$, $l-\frac{1}{2}$ and $l=0$, $j=\frac{1}{2}$. F and G are relativistic corrections.

§ 17. *Relativistic corrections.*

In this section we give formulae and a table for the relativistic corrections.

$$R = \frac{l(l+1)\,(2l+1)}{\rho(\rho^2-1)\,(4\rho^2-1)}\left[3k(k+1)-\rho^2+1\right]$$

$$S = \frac{2l(l+1)\sin\pi(\rho-\rho''-1)}{\pi Z^2\alpha^2}\left\{\frac{3(\rho'+k')}{8(1+\rho'')-4l-2}+\right.$$

$$\left.+\frac{3(\rho''+k'')}{8(1+\rho')+4l+2}-\frac{1}{2}\,\frac{\rho'+\rho''-1}{\rho'+\rho''+2}-\frac{6[Z^2\alpha^2+(\rho'+k')(\rho''+k'')]}{3(2l+3)\,(2l-1)-16Z^2\alpha^2}\right\}$$

$$H = \frac{2l(l+1)}{Z^2\alpha^2}\,(\rho'-\rho''-1)$$

$$G = \frac{2l(l+1)\sin\pi(\rho'-\rho''-1)}{\pi Z^2\alpha^2}$$

$$F = \frac{k(2k+1)\,(2l+1)}{\rho(4\rho^2-1)} = \frac{4j(j+\frac{1}{2})\,(j+1)}{\rho(4\rho^2-1)}$$

$$j = l+\tfrac{1}{2} \text{ for } k = l+1$$

$$j = l-\tfrac{1}{2} \text{ for } k = -l$$

$$\rho = \sqrt{k^2-Z^2\alpha^2}.$$

$l = 1,\ k' = 2,\ k'' = -1$

Z	αZ	ρ'	ρ''	H	F'	F''	G	R''	R'	S
82.2	0.6	1.9079	0.8000	1.20	1.16	2.40	1.18	—	1.35	1.74
68.5	0.5	1.9364	0.8660	1.12^6	1.11	1.73	1.12	—	1.23	1.42
54.8	0.4	1.9596	0.9165	1.08	1.07	1.39	1.08	—	1.14	1.24
41.1	0.3	1.9774	0.9539	1.04^5	1.04	1.19	1.04^5	—	1.07	1.13
27.4	0.2	1.9900	0.9798	1.02	1.01^5	1.08	1.02	—	1.03	1.05
13.7	0.1	1.9975	0.9950	1.00	1.00^5	1.02	1.00	—	1.01	1.01

$l = 2,\ k' = 3,\ k'' = -2$

82.2	0.6	2.9394	1.9079	1.05	1.06	1.16	1.05	1.48	1.13	1.13
68.5	0.5	2.9580	1.9364	1.03^5	1.04	1.11	1.03^5	1.31	1.09	1.09
54.8	0.4	2.9732	1.9596	1.02	1.03	1.07	1.02	1.18^5	1.05	1.05^5
41.1	0.3	2.9850	1.9774	1.01	1.01	1.04	1.01	1.10	1.03	1.03
27.4	0.2	2.9933	1.9900	1.00	1.00^5	1.01^5	1.00	1.05	1.01	1.01
13.7	0.1	2.9983	1.9975	1.00	1.00	1.00^5	1.00	1.01	1.00	1.00

§ 18. *Discussion of the reliability of the relativistic calculations.*

Before applying our formulae we will examine what deviations from our theory are to be expected. In the first place it is not certain that the values c_1, c_2 calculated by means of (11, 6, 7, 8) are exactly correct, these formulae being derived by means of a calculation in which only certain first order terms were taken into account. This difficulty is avoided in GOUDSMIT's method, which can also be applied to more complicated configurations. This method is based on the fact, that the sum of the values of A (and also of B) for the states ^3L_l and ^1L_l is independent of the values of c_1, c_2; it can be applied with advantage to the discussion of the magnetic separations. The case is different, however, for the electric separations. The A-value for ^1L_l is usually much smaller than the value for ^3L_l while the B values are of the same order of magnitude. On the other hand a determination of B is only possible when the hyperfine structure can be measured with a high degree of precision and the hyperfine structure must therefore be well resolved; because of the small A-value this condition will rarely be fulfilled for ^1L_l.

A second question is, whether the wavefunction can be represented with a sufficient degree of accuracy by functions of the type considered. In reality any configuration will be perturbed but it is difficult to estimate the order of magnitude of these perturbations.

Finally it remains to be discussed, whether our approximation for the relativistic wavefunctions in a central field is sufficiently accurate. In cases where the results obtained in this way can be compared with the results of accurate numerical calculations a satisfactory agreement is found (cf. BREIT (*6*)). Also the validity of LANDÉ's formula for the doublet separation is an argument in favour of the validity of this approximation.

If the magnetic moment and whenever possible the electric quadrupole moment, is calculated from the separations of a number of terms and if these values are in agreement with each other, then these values may be considered fairly reliable. If on the other hand discrepancies are found, it will be necessary to see whether these can be ascribed to one of the causes discussed in this section. It is clear, however, that it is impossible to test the theory very strictly and that deviations of the type discussed in § 2 would hardly have been detected.

§ 19. *Discussion of the hyperfine structure of* Cp.

We will now apply our theory to the hyperfine structure of Cp. We will first discuss the *D* terms. The finestructure

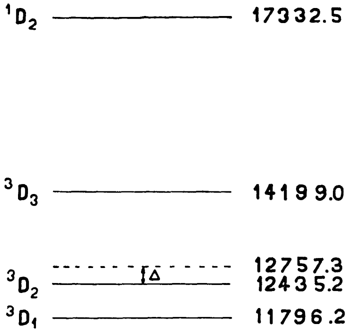

Fig. 5.

levels are shown in our figure. Application of WOLFE's formula gives:

$$\sin^2 \vartheta = \frac{322,1}{4897,3}$$

and hence

$$c_1^2 = 0,17 \qquad c_2^2 = 0,83 \qquad c_1 c_2 = 0,372$$

Further

$$C_2 + C_3 = 480,6$$

$$C_2 - C_3 = 495,6$$

We see that C_3 is small, so that the value of ϑ is well determined, even when C_3 is not taken into account.

For the relativistic correction factors we find (using the value $Z = 61$ which corresponds to applying a screening correction 10 to our formulae):

$$R' = 1{,}07 \qquad R'' = 1{,}24 \qquad S = 1{,}07$$

So we arrive at the equations

$$^3D_3 \qquad 1{,}07 \times \tfrac{4}{7} \times 7{,}9 \times \overline{\left(\frac{1}{r^3}\right)}_{kl} \times \left(\frac{Q}{21}\right) = 15 \times 0{,}244$$

$$^3D_1 \qquad 1{,}24 \times \tfrac{1}{5} \times 7{,}9 \times \overline{\left(\frac{1}{r_3}\right)}_{kl} \times \left(\frac{Q}{21}\right) = 1{,}38$$

$$^3D_2 \quad \left[\frac{4 \times 3 \times 4}{3 \times 5 \times 7} \times 1{,}07 \times 0{,}17 + \tfrac{2}{5} \times 0{,}83 \times 1{,}24 - \sqrt{\tfrac{2}{3}} \times \right.$$

$$\left. \times\, 0{,}376 \times \frac{12}{5 \times 7} \times 1{,}07\right] \times 7{,}9 \times \overline{\left(\frac{1}{r^3}\right)}_{kl} \times \left(\frac{Q}{21}\right) = 6 \times 0{,}369.$$

Using the value:

$$\overline{\left(\frac{1}{r^3}\right)}_{kl} = \frac{2403/2{,}911}{5 \times 61} = 2{,}71$$

we find

$$^3D_3 \quad Q = 5{,}8$$

$$^3D_2 \quad Q = 5{,}6$$

$$^3D_1 \quad Q = 5{,}4^5.$$

The agreement of these values is very satisfactory.

We will also discuss the magnetic part of the hyperfine structure. Introducing the notation:

$$b = \gamma \overline{\left(\frac{1}{r^3}\right)}_{kl} \cdot 1{,}585 \times 10^{-3}\,\mathrm{cm}^{-1}$$

we find

$$^3D_3 \qquad \tfrac{1}{6}\, a(s) + \tfrac{8}{7} \times 1{,}04\, b = 56{,}86$$

$$^3D_1 \quad -\tfrac{1}{4}\, a(s) + 4 \times 1{,}09\, b = -\,6{,}82$$

and hence

$$a(s) = 6 \times 53{,}5 = 321 \qquad b = 2{,}8$$

and

$$a' = 4 \qquad a'' = 9{,}8 \qquad a''' = -0{,}57$$

For the $^3D_2$ state we now have

$$6A = \tfrac{1}{2}[3 \times 0{,}83 - 2 \times 0{,}17]\ 321 + 7 \times 0{,}17 \times 4 + \\ + 4{,}5 \times 0{,}83 \times 9{,}8 - 2\sqrt{6} \times 0{,}376 \times 0{,}57$$

whence

$$A = 64{,}2$$

in excellent agreement with the experimental value

$$A = 64{,}4.$$

From the value of b it follows that

$$\gamma = 0{,}65.$$

The fact that the formulae for the magnetic interaction lead to results in agreement with experimental data is of special importance since it shows that the configuration is not appreciably perturbed. It is certainly not permissible to attach much weight to the value of γ, but still it is remarkable that it is of the same order of magnitude as the value for other nuclei with $i = 7/2$ viz. La, Cs and Sb (compare CRAWFORD and GRACE) (*12*).

We will now turn to a discussion of the P-terms.

Here we have

$$\sin^2\vartheta = \frac{490{,}8}{9720{,}1}$$

$$C_2 + C_3 = 1729{,}6 \qquad C_2 - C_3 = 1504{,}9$$

and

$$c_1^2 = 0{,}1438 \qquad c_2^2 = 0{,}8562 \qquad c_1c_2 = 0{,}351.$$

The value of C_3 does not appear unreasonably large. The relativistic correction factors are:

$$R' = 1{,}23 \qquad S = 1{,}40$$

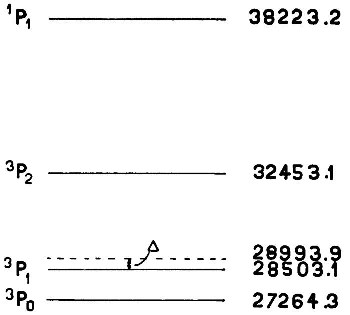

Fig. 6.

and we obtain the equations:

$$^3P_2 \qquad \left(\frac{Q}{21}\right) \times \left(\overline{\frac{1}{r^3}}\right)_{kl} \times \tfrac{2}{5} \times 1{,}23 \times 7{,}9 = 5{,}42$$

$$^3P_1 \quad \left(\frac{Q}{21}\right) \times \left(\overline{\frac{1}{r^3}}\right)_{kl} \times [0{,}1438 \times \tfrac{1}{5} \times 1{,}23 — 0{,}35 \times \tfrac{2}{5}\sqrt{2} \times 1{,}4] = —2{,}96.$$

It results that

$$^3P_2 \quad Q = 29{,}2 \Big/ \left(\overline{\frac{1}{r^3}}\right)_{kl}$$

$$^3P_1 \quad Q = 32{,}4 \Big/ \left(\overline{\frac{1}{r^3}}\right)_{kl}.$$

The agreement between these values is sufficiently good. With

$$H = 1{,}12 \text{ and } C_2/(C_2 + C_3) = 1{,}07$$

we find

$$\left(\overline{\frac{1}{r^3}}\right)_{kl} = 7{,}3$$

which leads to

$$^3P_2 \qquad Q = 4{,}0$$

$$^3P_1 \qquad Q = 4{,}4$$

The agreement of these values with those derived from the D-terms is rather bad. There are several possible explanations of this discrepancy. In the first place it is possible that the configuration is perturbed. Unfortunately the Cp-spectrum is not sufficiently well-known to make possible a further discussion of this question. It seems also possible that an application of our formulae for the doublet separation is not permissible for the very large separations occurring here, but since the effective quantumnumber is not known, this question also cannot be investigated any further. It may be of interest, however, to remark that if we calculate n^* from Eq. (14, 4) and the known doublet separation, a reasonable value is found. An investigation of the magnetic separation does not offer any new point of view. A satisfactory agreement with experimental values can be obtained with widely differing values of b. We believe that the average value for the ^3D states i.e.

$$Q = 5{,}6$$

is the most reliable value which can be given at present.

§ 20. *The problem of the internal conversion of nuclear energy.*

Let us suppose that at the moment $t = 0$ the nucleus is in an excited state M with energy $\hbar\nu_M$, while the electrons are in a state m with energy $\hbar\nu_m$. Two different processes will now be possible. The nucleus may pass to a state N with energy $\hbar\nu_N < \hbar\nu_M$ with emission of a lightquantum with frequency $\nu_M - \nu_N = \omega$; the energy $\hbar\omega$ may also be used, however, to transfer the electronic system to an excited state n with energy $\hbar\nu_n$ (such that $\nu_n - \nu_m = \omega$). In the latter case we speak of internal conversion of nuclear energy.

The problem of internal conversion consists in calculating the relative probabilities of the two processes mentioned. The formalism of quantummechanics gives a general method for calculating these probabilities. To the transition NM there belong a charge density ρ_{NM} and a current density s_{NM} of the form

$$\rho_{NM} = \rho^0_{NM}\, e^{-i\omega t} \qquad\qquad s_{NM} = s^0_{NM}\, e^{-i\omega t}$$

where ρ^0_{NM} and s^0_{NM} do not depend on the time.

The probability that during the time Δt a quantum with frequency ω will be emitted, is determined by calculating by means of classical electrodynamics the amount of energy emitted during the time Δt by a charge density $\rho_{NM} + \rho^*_{NM}$ and a current density $s_{NM} + s^*_{NM}$ and by dividing this value by $\hbar\omega$. The probability of the second process is equal to the probability that the electronic system will carry out a transition from the state m to the state n when acted upon by the electromagnetic field corresponding to ρ_{NM} and s_{NM}.

Let us compare the problem to the problem of hyperfine structure. In the case of hyperfine structure we are concerned with the change of energy levels caused by the field produced by a stationary current and charge density, in the case of internal conversion we must calculate the probability of transitions produced by a varying current and charge.

The method of calculating the probability of the transition $(M, m) \rightarrow (N, n)$ by calculating the probability of the transition $m \rightarrow n$ of the second system under influence of the field belonging to the transition $M \rightarrow N$ of the first system, is due to MØLLER (*28*), who based his considerations on the correspondence principle. BETHE and FERMI (*3*) have shown that in the case of two free electrons, which is the case originally considered by MØLLER, MØLLER's results can be deduced from quantum electrodynamics. Their considerations do not apply to the more general case which we will have to consider; moreover though MØLLER's results are proved, one does not see very clearly why MØLLER's procedure is correct. It is possible to give a general proof; the most simple formulation is obtained if following a method due to

HEISENBERG (*24*), we make use of the fact that MAXWELL'S laws for the electromagnetic field are still valid in quantummechanics. It would lead us too far, however, to give the proof here.

Such a proof has recently also been given by HULME (*45*).

In calculating the transitions $(M, m) \rightarrow (N, n)$ we must use the second approximation of the theory of radiation. If we wish also to determine the influence of the interaction of the nucleus and the electrons on the intensity of the radiation we must work out a third approximation. If only the first and second approximation are taken into account, the intensity of the electromagnetic radiation is not changed by this interaction. Originally it was assumed by HULME (*25*) and MOTT and TAYLOR (*40*) that the probability for the emission of a light quantum must be diminished by the probability that a transition $(M, m) \rightarrow (N, n)$ takes place. Later on it was found by TAYLOR and MOTT (*41*) that this assumption sometimes leads to impossible results, since it is possible to construct a model for which one would obtain a negative probability for the emission of a light quantum. They tried then to calculate the change of the number of light quanta (or in our terminology to work out the third approximation of the theory of radiation) and arrived at the result that in all practical applications this change will be negligible. Their method is as follows: they calculate the radiation emitted by the total charge density of nucleus + electrons, this charge density being calculated in second approximation by using MØLLER'S formulae for the interaction. It is not quite evident that this is correct, since MØLLER'S formulae only hold in the case of conservation of energy (i.e. when $\nu_n - \nu_m = \nu_M - \nu_N$). Recently, however MØLLER (29) has treated the radiation emitted during the collision of two particles by an analogous method and he has succeeded in showing, that his results may also be deduced from quantummechanics. His proof is very complicated, however, and an extension to more general systems would be extremely cumbersome. It is probable that here also application of HEISENBERG's method would lead to considerable simplifications.

§ 21. *Multipole radiation.*

In this § we will study the field produced by a periodically varying charge and current. We describe the field in the usual way by means of retarded potentials $\varphi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$. These will be given by:

$$\varphi(\mathbf{r}) = e^{-i\omega t}\int \frac{e^{ik|\mathbf{r}'-\mathbf{r}|}}{|\mathbf{r}'-\mathbf{r}|}\,\rho^0(\mathbf{r}')\,d\tau_{r'} \tag{21, 1}$$

$$\mathbf{A}(\mathbf{r}) = \frac{1}{c}\,e^{-i\omega t}\int \frac{e^{ik|\mathbf{r}'-\mathbf{r}|}}{|\mathbf{r}'-\mathbf{r}|}\,\mathbf{s}_0(\mathbf{r}')\,d\tau_{r'}\,. \tag{21, 2}$$

The current and charge are connected by the equation

$$\operatorname{div}\mathbf{s} + \frac{\partial\rho}{\partial t} = 0$$

and hence

$$\operatorname{div}\,\mathbf{s}^0 - i\omega\rho^0 = 0. \tag{21, 3}$$

Further we have

$$\int \rho^0\,d\tau_{r'} = 0 \tag{21, 4}$$

and

$$\operatorname{div}\mathbf{A} + \frac{1}{c}\frac{\partial\varphi}{\partial t} = 0. \tag{21, 5}$$

We assume that ρ and $\mathbf{s}$ are negligible outside a sphere with radius R and will only investigate the field for $r > R$. In (21, 1) (21, 2) we will certainly have $r > r'$ and we can expand the expression $\exp\,[ik\,|\mathbf{r}-\mathbf{r}'|]/|\mathbf{r}-\mathbf{r}'|$ in powers of r'/r.

We obtain:

$$\frac{e^{ik|\mathbf{r}'-\mathbf{r}|}}{|\mathbf{r}'-\mathbf{r}|} = \frac{e^{ikr}}{r}\Big\{1 + r'\,P_1(\cos\Theta)\left[\frac{1}{r} - ik\right] + \\ + r'^2\,P_2(\cos\Theta)\left[\frac{1}{r^2} - \frac{ik}{r} - \frac{k^2}{3}\right] - \tfrac{1}{6}\,r'^2\,k^2\Big\},$$

where Θ is the angle between the direction of $\mathbf{r}'$ and $\mathbf{r}$. Further we have

$$r'\,P_1(\cos\Theta) = r'\cos\Theta = x'\frac{x}{r} + y'\frac{y}{r} + z'\frac{z}{r}$$

and

$$P_2(\cos\Theta) = \sum_{-2}^{+2} Y_2^m(\vartheta, \varphi)\,Y_2^{-m}(\vartheta', \varphi')$$

with

$$Y_2^0 = \tfrac{3}{2}\cos^2\vartheta - \tfrac{1}{2} \qquad Y_2^{\pm 1} = \frac{3}{\sqrt{6}}\cos\vartheta\sin\vartheta\,e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \frac{3}{2\sqrt{6}}\sin^2\vartheta\,e^{\pm 2i\phi}.$$

It follows that

$$\varphi = e^{-i\omega t}\frac{e^{ikr}}{r}\Big\{\left(\frac{1}{r} - ik\right)\left(\frac{\mathbf{r}}{r}\int \mathbf{r}'\,\rho^0\,d\tau_{r'}\right) + \sum_m\left(\frac{1}{r^2} - \frac{ik}{r} - \frac{k^2}{3}\right). \\ .\,Y_2^m(\vartheta, \varphi)\int r'^2\,Y_2^{-m}(\vartheta', \varphi')\,.\,\rho^0\,d\tau_{r'} - \tfrac{1}{6}k^2\int r'^2\rho^0\,d\tau_{r'} + \ldots\Big\}$$

$$\mathbf{A} = \frac{1}{c}e^{-i\omega t}\frac{e^{ikr}}{r}\Big\{\int \mathbf{s}^0(\mathbf{r}')\,d\tau_{r'} + \left(\frac{1}{r} - ik\right)\left(\frac{\mathbf{r}}{r}\int \mathbf{r}'\right)\mathbf{s}^0(\mathbf{r}')\,d\tau_{r'} + \ldots\Big\}.$$

The term

$$-\frac{k^2}{6r}\,e^{-i\omega t + ikr}\int r'^2\,\rho^0\,d\tau_{r'}$$

which occurs in φ can be removed by a change of gauge. We add to φ the expression

$$\frac{1}{c}\frac{\partial}{\partial t}\left(\frac{ik}{6r}\,e^{-i\omega t + ikr}\int r'^2\,\rho^0\,d\tau_{r'}\right)$$

and to A the quantity

$$-ik \operatorname{grad}\left\{\frac{e^{-i\omega t+ikr}}{6r}\int r'^2\,\rho^0\,d\tau_{r'}\right\} =$$

$$= ik\,\frac{e^{-i\omega t+ikr}}{6r^2}\left(\frac{1}{r}-ik\right)\mathbf{r}\int r'^2\,\rho^0\,d\tau_{r'}\,.$$

We will now reduce the integrals occurring in the expression for A. We have

$$i\omega \int \mathbf{r}'\,\rho^0\,d\tau_{r'} = \int (\operatorname{div}\mathbf{s}^0)\mathbf{r}'\,d\tau_{r'} = -\int \mathbf{s}^0(\mathbf{r}')\,d\tau_{r'}$$

and hence

$$\int \mathbf{s}^0(\mathbf{r}')\,d\tau_{r'} = -i\omega \int \mathbf{r}'\,\rho^0\,d\tau_{r'}.$$

In the same way:

$$i\omega \int x'^2\,\rho^0\,d\tau_{r'} = \int (\operatorname{div}\mathbf{s}^0)x'^2\,d\tau_{r'} = -2\int x\,s_x^0\,d\tau_{r'}$$

$$i\omega \int x'\,y'\,\rho^0\,d\tau_{r'} = \int (\operatorname{div}\mathbf{s}^0)x'\,y'\,d\tau_{r'} = -\int (x'\,s_y^0 + y'\,s_x^0)d\tau_{r'}\,.$$

For A_x we find finally

$$A_x = -ik\,\frac{e^{-i\omega t+ikr}}{r}\int x'\,\rho^0\,d\tau_{r'} -$$

$$-\frac{ik}{2}\,\frac{e^{-i\omega t+ikr}}{r}\left(\frac{1}{r}-ik\right)\left[\frac{x}{r}\int \tfrac{2}{3}\left(\tfrac{3}{2}\,x'^2 - \tfrac{1}{2}\,r'^2\right)\rho^0\,d\tau_{r'} + \right.$$

$$\left. + \frac{y}{r}\int x'\,y'\,\rho^0\,d\tau_{r'} + \frac{z}{r}\int z'\,x'\,\rho^0\,d\tau_{r'}\right] -$$

$$-\frac{1}{2c}\,\frac{e^{-i\omega t+ikr}}{r}\left[\frac{y}{r}\int (x'\,s_y^0 - y'\,s_x^0)\,d\tau_{r'} - \frac{z}{r}\int (z'\,s_x^0 - x'\,s_z^0)\,d\tau_{r'}\right].$$

The field can now be interpreted as a superposition of three different fields, viz.:

a) The field of an electric dipole

$$_D\varphi = \frac{e^{-i\omega t+ikr}}{r}\left(\frac{1}{r}-ik\right)\left(\frac{\mathbf{r}}{r}\,.\,\mathbf{P}\right) \qquad (21,6)$$

$$_D\mathbf{A} = -ik\,\frac{e^{-i\omega t+ikr}}{r}\,\mathbf{P} \qquad (21,7)$$

with

$$\mathbf{P} = \int \mathbf{r}' \rho^\circ \, d\tau_{r'}.$$

b) The field of a magnetic dipole

$$_M\varphi = 0 \qquad (21,\ 8)$$

$$_M\mathbf{A} = -\frac{e^{-i\omega t + ikr}}{r} [\mathbf{r} \times \mathbf{M}] \qquad (21, 9)$$

with

$$\mathbf{M} = \frac{1}{2c} \int [\mathbf{r}' \times \mathbf{s}^\circ] \, d\tau_{r'}.$$

c) The field of an electric quadrupole

$$_Q\varphi = \frac{e^{-i\omega t + ikr}}{r} \left(\frac{1}{r^2} - \frac{ik}{r} - \frac{k^2}{3}\right) \sum_m Y_2^m(\vartheta, \varphi) \int r'^2 Y_2^{-m}(\vartheta', \varphi') \rho^0 \, d\tau_{r'} \quad (21, 10)$$

$$_QA_x = -\frac{ik}{2} \frac{e^{-i\omega t + ikr}}{r} \left(\frac{1}{r} - ik\right) \left[\frac{x}{r} \int \tfrac{2}{3}(\tfrac{3}{2}x'^2 - r'^2) \rho^\circ d\tau_{r'} + \right.$$

$$\left. + \frac{y}{r} \int x'y' \rho^\circ \, d\tau_{r'} + \frac{z}{r} \int x'z' \rho^\circ \, d\tau_{r'} \right]. \qquad (21, 11)$$

A_y, A_z are given by analogous expressions.

The components A_x, A_y, A_z can also be witten in the form

$$A_n = -\frac{ik}{2} \frac{e^{-i\omega t + ikr}}{r} \left(\frac{1}{r} - ik)\right) \left[\sum_{p,m} \alpha_{p,n}^m \frac{x_p}{r} \int r'^2 Y_2^m \rho^\circ \, d\tau_{r'}\right] (21, 12)$$

$$(x_1 = x,\ y_1 = y,\ z_1 = z)$$

where the $\alpha_{p,\,n}^m$ are constants.

Each of these three fields separately is a solution of MAXWELL's equations in the region $r > R$ and the possibility exists that only one of these fields is different from zero. The electric field is determined by the vector **P** or in other words:.any dipole field is a superposition of three linearly independent dipole fields. In the same way any magnetic dipole field is a superposition of three linearly independent fields and any electric quadrupole field a superposition of five linearly independent quadrupole fields. These five fields can be written as follows:

$$\varphi^m = \frac{e^{-iwt+ikr}}{r}\left(\frac{1}{r^2} - \frac{ik}{r} - \frac{k^2}{3}\right) Y_2^m(\vartheta,\ \varphi)$$

$$\mathbf{A}^m = -\frac{ik}{2}\,\frac{e^{-iwt+ikr}}{r}\left(\frac{1}{r} - ik\right)\sum_p \frac{x_p}{r}\,\boldsymbol{\alpha}_p^m$$

where $-2 \leqslant m \leqslant +2$ and where $\boldsymbol{\alpha}_p^m$ is the vector with components $\alpha_{p,1}^m,\ \alpha_{p,2}^m,\ \alpha_{p,3}^m$.

In these calculations higher powers of r' than the second were neglected. If higher powers are taken into account, there appears a magnetic quadrupole field, an electric octupole field and so on; moreover these powers will lead to an additional contribution to the dipole field and the quadrupole field (cf. TAYLOR and MOTT (*41*) and especially BRINKMAN (*7*)).

In the existing literature we have found no general expressions for the n-pole field of an arbitrary distribution of charge and current. For the following considerations such expressions are not needed. As an example we quote the result for a dipole field. We find that the dipole field is determined by a vector

$$\mathbf{P}' = \int \frac{3}{k^2}\sqrt{\frac{\pi k}{2r'}}\left\{J_{3/2}(kr')\,\frac{\mathbf{r}'}{r}\,\rho^\circ + \frac{i}{c}\,J_{5/2}\left[\tfrac{3}{2}\,\frac{\mathbf{r}'}{r'^2}(\mathbf{r}'\ \mathbf{s}^\circ) - \tfrac{1}{2}\mathbf{s}^\circ\right]\right\} d\tau_r.$$

The difference $P - P'$ is of the order $k^2\ r'^3$.

The emitted energy is the sum of the energies corresponding to the separate fields. At a large distance from the origin the absolute value of the POYNTING vector will be given by

$$\frac{c}{4\pi}\,E^2 = \frac{c}{4\pi}\,({}_DE + {}_ME + {}_QE)^2$$

and it will be radially directed.

If now the flow of energy is integrated over a sphere, then the cross products will vanish. This is easily seen by using explicit expressions but may also be proved by group-theoretical methods.

We will now formulate the selection rules which hold for the three different fields. In our approximation these rules can be easily verified, but they hold also when the rigorous expressions are used.

Electric dipole radiation can only be emitted in transitions in which the angular momentum is changed by one unit:

$$i - \left| \begin{array}{l} \to i + 1 \\ \to i \\ \to i - 1 \end{array} \right.$$

moreover the transition 0 → 0 is forbidden. The symmetry with respect to inversion must be different in the final and in the initial state.

Magnetic dipole radiation. Here also we have:

$$i - \left| \begin{array}{l} \to i + 1 \\ \to i \\ \to i - 1 \end{array} \right.$$

0 → 0 is forbidden. The final and the initial state must have the same symmetry.

Electric quadrupole radiation. In this case we have:

$$i - \left| \begin{array}{l} \to i + 2 \\ \to i + 1 \\ \to i \\ \to i - 1 \\ \to i - 2 \end{array} \right.$$

The transitions

$$\begin{array}{l} 0 \to 0 \\ 0 \to 1 \\ 1 \to 0 \\ \tfrac{1}{2} \to \tfrac{1}{2} \end{array}$$

are forbidden. The initial state and the final state must have the same symmetry.

It follows that magnetic dipole radiation and electric quadrupole radiation can be emitted in the same transition.

§ 22. *The calculation of the transition probabilities.*

The problem of the internal conversion has now been reduced to a problem which only depends on the atomic electrons.

There are, however, still a number of questions to be discussed. The first question is which are the stationary states of the atom. An excited state of the nucleus will always have been preceded by a violent perturbation, usually a radioactive desintegration (and thus a change of atomic number). Is it permissible to use in our calculations the stationary states of the new atom? Quantummechanics gives an affirmative answer to this question; one has to take into account, however, that the atom may be in an excited or an ionized state. For it is clear that any state of the new atom can be represented by a wavefunction $\Sigma\, c_n\, \psi_n$ where c_n remains constant, once the perturbation has stopped (apart from a change due to spontaneous emission of radiation). To the „desorganization'' of the electrons, which would take place in classical mechanics, there corresponds in quantummechanics the existence of a finite probability that the atom is in an excited state. Now in practice usually only the absorption in the K-shell and in the L-shell is of importance and this absorption will hardly be influenced by excitation or ionization of the outer shells. Ionization of the K-shell will have a certain influence on absorption in the L-shell but it is hardly to be expected, that the probability of ionization of the K-shell in a radioactive desintegration will be comparable to unity. A calculation of this probability would certainly not be devoid of interest but for the theory of internal conversion the result would be of little importance.

The calculation of the ratio of the probabilities of the two processes (emission of radiation and internal conversion) has only to be carried out for one orientation of the electric moment and one orientation of the magnetic moment, for it is clear that the result must be independent of this orientation. It is not so evident that also in the case of electric quadrupole radiation this ratio for a field φ^m, $\mathbf{A}^m$ has a value independent of m and therefore also has this same value when the field is given by $\Sigma\, c_m \varphi^m$, $\Sigma\, c_m \mathbf{A}^m$ with arbitrary c_m. The simplest way of proving this result is to consider first the case in which a nucleus carries out a transiton $i = 2 \rightarrow i = 0$; in this case it can easily be shown that the probability of emission of a quantum and the probability of internal conversion are both independent of m; and the same will hold for their ratio.

Finally it must be shown that the total probability of internal conversion in a field which is a superposition of a dipole and a quadrupole field is equal to the sum of the probabilities belonging to these fields separately. This can be proved by a grouptheoretical argument. The dipole field and the quadrupole field will transform according to different irreducible representations of the group of threedimensional rotations.

The required result is now a special case of the following theorem. Let O_1^λ, O_2^μ be two sets of operators, transforming according to non-equivalent irreducible representations of the rotation group and let $\Psi_j^m, (-j \leqslant m \leqslant j)$, be $(2j + 1)$ wavefunctions belonging to an angular momentum j and $\Psi_{j'}^{m'}$, $(-j' \leqslant m \leqslant j')$, $2j' + 1$ wavefunctions belonging to an angular momentum j', then we have:

$$\sum_{m,m'} \left| \int \Psi_{j'}^{*m'} (O_1^\lambda + O_2^\mu)\, \Psi_j^m \right|^2 =$$

$$= \sum_{m,m'} \left| \int \Psi_{j}^{*m'}\; O_1^\lambda\, \Psi_j^m \right|^2 + \sum_{m,m'} \left| \int \Psi_{j'}^{*m'}\, O_2^\mu\, \Psi_j^m \right|^2.$$

§ 23. *The calculations of* HULME, TAYLOR *and* MOTT, FISK *and* TAYLOR.

In order to be able to carry out the calculation of the probability of internal conversion one has to introduce simplifying assumptions. In the calculations of the authors mentioned above, the problem is treated as a one-electron problem and the states of the electron are described by the wavefunctions for a Coulomb field of force. For heavy nuclei it is to be expected that this approximation will be permissible for the initial state, since the interaction of the electrons will be small compared with the interaction with the nucleus.

As to the final state, one will expect that a fairly accurate approximation will be obtained by using the wavefunctions for an electron moving in a Coulomb field screened off by the other electrons. The neglect of screening will have no appreciable influence when the energy of the final state is large ($\gg Z^2\alpha^2mc^2$) but it would be desirable to examine its influence for smaller energy values.

It must not be forgotten, however, that also when the wavefunctions for a Coulomb field are being used, the calculations are extremely cumbersome. Since the energy in the final state is usually large and on the other hand the problem is chiefly of interest for heavy nuclei, it is necessary to use relativistic wavefunctions. Indeed the non-relativistic calculations of Miss SWIRLES (*39*) lead to results which differ appreciably from those found by HULME. On the other hand the author (*10*) has tried to solve the problem by approximating to the wavefunctions by the first term of their asymptotic expansion. Though it may be proved that this procedure will lead to correct results in the limit $(\hbar\nu/mc^2) \rightarrow \infty$, HULME's calculations have shown that for energies occurring in actual applications this approximation leads to entirely erroneous results. So it is necessary to use the exact expression for the wavefunction of the final state.

The integration over the angles ϑ, φ can be carried out without difficulty. The radial wavefunction for the final state is a so called $W_{k,m}$ function and the radial integral will be of the form

$$\int W_{k,m}\, e^{(-a+ib)r}\, r^s\, dr.$$

Integrals of this type can be expressed in terms of hypergeometric functions and (after some reductions) these must be calculated numerically.

Another possibility would be to compute the wavefunction for the final state numerically and to determine the matrix elements by means of a planimeter. If one had at one's disposition a set of tables for these wavefunctions in the continuous spectrum, one would also be able to solve a number of other problems. For small values of r the wavefunctions can be determined by means of a power series, for larger values the Eq. (12, 5) must be integrated numerically and for still larger values a W-K-B-solution of the Eq. (12, 11, 12) must be fitted to these numerical values. An advantage of this numerical method is, that screening can easily be taken into account.

Though the author has computed a few wavefunctions in this way, he has lacked the time for calculating transition probabilities.

§ 24. *Results of the calculations and comparison with experiment.*

We will now give a short survey of the results obtained by the authors mentioned. Since it is extremely difficult for an outsider to judge the reliability of the experimental data, no attempt will be made at a critical discussion of these data. For some of the hard γ-rays of RaC (($\hbar\nu > mc^2$) the experimental values of the coefficient of internal conversion (i.e. the ratio (number of lightquanta)/(number of secondary electrons) are in satisfactory agreement with the values calculated for dipole radaiation, while for the other rays these coefficients are much larger and in agreement with the theoretical results for quadrupole radiation. There is only one transition for which the data are neither in agreement with the theoretical results for dipole radiation nor with those for quadrupole radiation. This is the transition with energy $1{,}416 \times 10^6$ e.V. The corresponding γ-ray has never been observed and it seems possible that the transition is a transition $0 \rightarrow 0$. In that case emission of radiation is impossible and the transition would be entirely due to the „interior'' part of the interaction which was neglected in the foregoing calculations.

For the soft γ-rays of RaB the conversion coefficients are larger than those calculated for quadrupole radiation but smaller than those calculated for magnetic dipole radiation. They can be explained by assuming that the radiation is a superposition of quadrupole and magnetic dipole radiation (TAYLOR and FISK (*17*)). We believe that one is justified in drawing the following conclusions: hard γ-rays are either dipole or quadrupole radiation, soft γ-rays consist at least partly of magnetic dipole radiation.

In our considerations the „interior'' part of the interaction i.e. the interaction of the nucleus and the electronic charge and current that is lying inside the nucleus, has been neglected. It is easily seen that this is permissible except for the transition mentioned above, if this interaction is not much larger than it would follow from the ordinary formalism of quantummechanics.

During a number of years the opinion prevailed that it was impossible to explain the experimental facts without assuming such a large interaction, but the work of HULME c.s. has proved that this conclusion was not correct. Moreover it must be pointed out that also the results concerning the hyperfine structure indicate, that abnormally large interior interactions do not exist.

One has tried to make use of the knowledge obtained concerning the type of radiation of the different transitions for the construction of a scheme of energy levels in which *i*-values are assigned to the levels, but we will not dwell upon the results obtained in this way.

§ 25. *Some considerations on nuclear structure.*

In this final section we will put forward some considerations on nuclear structure based on results which were obtained by the methods outlined in this paper.

From the investigation of hyperfine structure of spectral lines information is obtained concerning certain properties of the fundamental state of the nucleus: one can determine the angular momentum, the magnetic moment and in some cases the quadrupole moment. As to the displacements which are found in the isotope effect and which are independent of *f*, so far as they cannot be ascribed to nuclear motion (such an interpretation will only be possible for light elements) they will be due to deviations from COULOMB's law. They may be described in terms of an effective nuclear radius but no definite physical meaning can be given to that quantity, since it is not to be expected that the interaction can be described as the interaction of two charge densities; at present, however, any other hypothesis concerning this interaction (such as the hypothesis used by BREIT and ROSENTHAL (*5*)) is rather arbitrary.

Nevertheless it is satisfactory that the effective radii for the different isotopes of one element increase with increasing atomic weight. The case of SAMARIUM (*38*) is of special interest. Here the isotope shifts depend irregularly on the atomic weight and one can infer that there must exist an irregularity in the structure of the nuclei.

Let us now consider the values of the angular momentum derived from the study of hyperfine structure (and partly from the study of band spectra). The most essential feature of these values is that they are not in contradiction with the assumption that the nucleus is built of protons and neutrons, both particles having a spin $\frac{1}{2}$. There seem to exist certain other regularities but no general rules for predicting the angular momentum of an arbitrary nucleus can be given.

No satisfactory theory has been given for the values of the magnetic moments. One has tried to arrive at an understanding of these values in terms of a vector model, but the number of theoretical possibilities is so large and the values of the moments are so uncertain, that we do not believe that definite results can be obtained in this way.

Let us now consider some of the light nuclei in more detail. The simplest nucleus is the proton. The angular momentum determined from the band spectrum is $\frac{1}{2}$. The magnetic moment was determined by STERN, FRISCH (*18*) and ESTERMANN (*13*), as well as by RABI, KELLOG and ZACHARIAS (*31*), by means of measurements on atomic or molecular beams. The factor γ is not two (as would follow from DIRAC's theory) but about thrice as large. It follows that the proton cannot be described by DIRAC's equation. This is probably connected with FERMI's theory, according to which a proton can be transformed into neutron, positron + neutrino.

The deuteron (heavy hydrogen nucleus) consists of a proton and a neutron. The angular momentum is 1. This value can be explained by assuming that there is no orbital angular momentum and that the spin of proton and neutron are parallel. The magnetic moment can be estimated from the influence of paramagnetic gases on the velocity of the reaction ortho-hydrogen→para-hydrogen. One obtains the value $\gamma = 0{,}7$. This leads to the supposition that the neutron has a negative magnetic moment (i.e. a moment opposite to the angular momentum). Various hypotheses have been made concerning the neutron proton interaction. Of these the hypothesis of MAJORANA (*27*) has been most succesful in explaining the values of the nuclear binding energies.

According to MAJORANA the interaction is of the exchange type and independent of the orientation of the spins. The only interaction between the spins would then be the magnetic interaction. Because of this magnetic interaction the state with parallel spins would be the state of lowest energy but there would exist an other state in which the spins are opposite to each other. An estimation of the energy difference of these states leads to a value of $10^4 - 10^5$ eV. From an experimental point of view, no objection can be made to this value but theoretical investigations of WEIZSÄCKER (*42*) and a discussion of the capture of neutrons by protons by FERMI (*15*) seem to show that the exchange forces are not completely independent of the orientation of the spins, so that there will exist a spin-spin interaction which is much larger than the magnetic interaction. However this may be, the structure of the deuteron does not offer essential difficulties.

For the α-particle $i = 0$; it can be interpreted as a highly symmetric system of two protons and two neutrons.

Let us now consider Li_6 and N_{14}. For these nuclei $i = 1$; and the magnetic moment is certainly small. This would be in agreement with the view that these nuclei consist of a deuteron and a number (one or three) of α particles. According to SCHÜLER (*47*) the magnetic moment of Li_6 is of the same order of magnitude as that of the deuteron but BACHER (*1*) gives $\gamma < 0{,}2$ for N_{14} and this would mean that an application of the vector model in its usual form is impossible. SCHÜLER and SCHMIDT have tried to explain the situation by assuming that the magnetic moment of the proton depends on the mass of the nucleus. Though it cannot be excluded a priori that one might arrive at a satisfactory description of magnetic moments by means of a vector model with varying moment of the proton, one must not forget that such a vector model would be fundamentally different from the usual one; moreover in the author's opinion such a satisfactory theory of magnetic moments has not yet been given, nor does a discussion of other magnetic moments lead to a convincing argument against WEIZSÄCKER's conclusion according to which the spin-spin and spin-orbit interactions in the nucleus are so large, that an application of the usual vector model is out of question.

We will now consider the large positive quadrupole moments of Cp and Eu. For Cp we have $\overline{(3z^2 - r^2)} \sim 5{,}6 \times 10^{-24}$. If we assume a value $0{,}7 \times 10^{-12}$ for the radius of the nucleus and if we take into account that for one particle the mean value of $(3 \cos^2 \vartheta - 1)$ is certainly smaller than 2 (while this value can only be approximated by making very improbable assumptions) then one is led to the conclusion that the quadrupole moment cannot possibly be due to one proton. So it is necessary to assume that it is caused by a group of particles. It might even be that the nucleus as a whole has a prolate shape and that the nucleus as a whole is rotating about its major axis. In this connection there may be some point in remarking that for heavy nuclei the rotational energy estimated by means of the elementary formula $E = \hbar^2/2I (I =$ moment of inertia$)$ is small compared with the binding energy. In any case the existence of large quadrupole moments seems to offer an argument in favour of the idea that the nucleus must be treated as a whole and that its properties are not determined by the behaviour of one particle.

We turn now to the discussion of the results obtained by the investigation of internal conversion which were mentioned in § 24. If it were possible to speak of an excited state of one proton or of one neutron (or perhaps of one α-particle) then one should expect the radiation to be almost exclusively dipole radiation. Quadrupole radiation would only be emitted with a measurable intensity in those cases in which a nucleus is in an excited state from which transitions by means of dipole radiation are forbidden by the selection rules, and the frequent occurrence of quadrupole radiation would force us to make very artificial assumptions concerning the level scheme. We are inclined to believe that the existence of quadrupole radiation is a consequence of the very strong binding forces between the particles in the nucleus. Quadrupole radiation would be emitted by a rotating nucleus with a large quadrupole moment but also by a vibrating nuclear „drop".

Finally it is of interest to consider in some detail the possibility of magnetic dipole radiation. In the case of atomic spectra magnetic dipole radiation will rarely occur. In zero approximation this radiation will always vanish. It can only occur as a consequence of spin-orbit interaction.

But let us now consider the two hypothetical states of the deuteron with $i = 1$ and $i = 0$. In this case a transition with emission of magnetic dipole radiation is possible. FERMI (*15*) has explained the large cross section for the capture of neutrons by protons by assuming that in this process magnetic dipole radiation is emitted. This explanation is only possible when the spin-spin interaction is not exclusively magnetic. An argument for the existence of spin-spin interaction may be derived from a discussion of the data on the elastic scattering of neutrons by protons. FERMI has even succeeded in deriving a definite value for the capture cross section which is in satisfactory agreement with experiment.

More general in any transition which corresponds to a change of direction of a spin magnetic dipole radiation will be emitted. If the transition corresponds to a change of the relative orientation of a spin and an orbital momentum, the radiation field will be a superposition of magnetic dipole radiation and quadrupole radiation. The results of WEIZSÄCKER and FERMI seem to show that in such transitions a rather large amount of energy may be emitted.

Our conclusion is, that the assumption that the very large conversion coefficients for the soft γ-rays of RaC are due to magnetic dipole radiation, is probably correct[1]; on the other hand the existence of these large coefficients offers a further argument in favour of the existence of rather large spin-spin and spin-orbit interactions.

Since our paper was written there appeared an article by Bohr (*44*) on nuclear structure. It seems to us that our speculations concerning the structure of the nucleus fit in very well in the general scheme put forward by Bohr.

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[1] Added in proof: In a recent paper (Proc. roy. Soc. London A *155*, 315, 1936.) Hulme, Mott, Oppenheimer and Taylor arrive at a similar conclusion.

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