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Section A.—Mathematical and Physical Sciences.

The Zeeman Effect and Spherical Harmonics.

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1. The chief object of the present paper is to present a simple system of equations which are competent to determine the frequencies and intensities of the lines in the standard Zeeman effect. By the standard Zeeman effect is meant the type where the terms are given by Landé's "g" and "γ" formulæ, and where the multiplicity of the two sets of terms is the same. It will probably be held that the theory of such multiplets has been fairly completely understood for the last two years owing to the works of Sommerfeld, Heisenberg, Landé and Pauli,* and the main new contribution of the present work is that, whereas these writers gave formulæ valid only either in weak or strong field (except for doublets, where Heisenberg and Jordan† give the value for any strength), here we have complete formulæ from which the intensity of any component in any strength of field can be obtained merely from the solution of rather simple algebraic equations.

The proper attack on this problem would undoubtedly be by way of the recent work of Heisenberg‡ on the helium spectrum, and his still more recent work on complex spectra; but this theory is still in the making, so that it has not been practicable to apply it here, and to this extent our results are unverified. Their validity rests firstly on a complete verification of all known facts connected with both weak and strong fields (and intermediate fields for doublets), and also on a conformity with the general features of wave mechanics. The work of Heisenberg and Jordan could readily have been adapted to give all the results of the present paper; but it would have been harder to follow because the matrix methods are not so easy for most readers as are spherical harmonics.

If the wave mechanics are applied to a rotating body, in the formulation as originally given by Schrödinger, they lead to rotations which must have integers

* See for instance Andrade, 'The Structure of the Atom,' 3rd edition, Chapter XV.

† 'Z. f. Physik,' vol. 37, p. 263 (1926).

‡ 'Z. f. Physik,' vol. 39, p. 499 (1926); vol. 41, p. 239 (1927).

for their quantum numbers, and so are not directly applicable for the half quantum number that the spinning electron requires. If nevertheless we persist in the calculation of the problem of the spinning electron, we are led to a system of equations which exactly corresponds to the standard triplet. This fact furnished the starting point of the present investigation. A rotating body moving in an orbit can be made to give the complete system of any odd multiplicity.

For even multiplicities this is not so, since they seem to require solutions of the wave equation which are inadmissible if the characteristic functions ψ are to be one-valued. This is certainly a severe difficulty; a tentative way of meeting it has been suggested by Heisenberg, London,* and Dennison,† in proposing that $|\psi^2|$ is the quantity that should be one-valued. This certainly permits of what we may call half-harmonics for the rotating body, but it may be doubted if the matter ends there, for we have no assigned reason why these half-harmonics should not also apply for the revolution of the electron about the nucleus, and so such a rule at any rate wants safeguarding in order to ensure that the orbital motion shall always be of whole harmonic type, for otherwise the Balmer series would have members in $R/(n+\frac{1}{2})^2$. In fact the proposed modification implies that Schrödinger's principle is inadequate to decide between two sets of alternatives as the permissible states of a mechanical system. It is not our intention to enter into this matter, and we can deal with even multiplicities without doing so to a considerable extent, for when the equations as determined for odd multiplicities are set down it appears that they are also applicable in every respect for even, the only change being not from whole to half numbers, but merely from even numbers to odd.‡

We shall therefore give a development of the theory of an avowedly rather crude model, taking as its justification the fact that it gives all the observed results. The development of the work goes in the form of tesseral spherical harmonics, and this is an essentially anisotropic procedure. The consequence is that one of the laws of spectra—the law of combination of the quantum number j—is rather concealed. In § 7 we sketch a different development which brings out the meaning of j with full force.

* 'Z. f. Physik,' vol. 40, p. 193 (1926), footnote on p. 209.

† 'Nature,' vol. 119, p. 316 (1927).

‡ [*Added April*, 1927.—Since writing the paper I have had the advantage of discussing "half-harmonics" with Dr. Dennison. By making an insignificant alteration in the definition of the function $P_r^{s,t}$ (incorporated in the text) the present work is directly applicable to even multiplicities, when r, s and t are simultaneously all half-numbers. But the questions raised above remain outstanding and the method of § 7 is still not available.]

2. Our model consists of a charged spinning spherical body moving in a central field of force. Let $-e$, m, be the charge and mass, x, y, z the position of the centre, and $\mathrm{V}(r)$ the potential energy at distance r. Then the motion of revolution contributes terms

$$\tfrac{1}{2}m(\dot{x}^2+\dot{y}^2+\dot{z}^2)+e\mathrm{V}(r)$$

to the Lagrangian function. Next take a set of Eulerian angles χ, λ, μ, and let the moment of inertia be I. This gives a contribution

$$\tfrac{1}{2}\mathrm{I}(\dot{\chi}^2+\dot{\lambda}^2+\dot{\mu}+2\dot{\lambda}\dot{\mu}\cos\chi)=\tfrac{1}{2}\mathrm{I}(\omega_x^2+\omega_y^2+\omega_z^2),$$

where ω_x, ω_y, ω_z are the components of spin about x, y, z. For an isotropic body it is possible to drop one of the three co-ordinates (μ), but perhaps the most convincing way of seeing this is to carry through the work without doing so, and to show that in fact it has no effect. Next we have the contribution arising from the magnetic field H along z. The orbital motion gives a contribution $-\mathrm{H}\dfrac{e}{2c}(x\dot{y}-\dot{x}y)$. The spin gives $-\mathrm{HI}\dfrac{e}{mc}\omega_z$ when we take e/mc for the ratio of magnetic moment to mechanical momentum, the hypothesis of Uhlenbeck and Goudsmit. Lastly, we have the interaction of the spin and the motion. The electric force has components $-\mathrm{V}'(x/r)$, etc., so that according to Uhlenbeck and Goudsmit we should take a term

$$-\mathrm{I}\frac{e}{mc^2}\frac{\mathrm{V}'}{r}\{\omega_x(y\dot{z}-\dot{y}z)+\omega_y(z\dot{x}-\dot{z}x)+\omega_z(x\dot{y}-\dot{x}y)\}.$$

This overlooks Thomas's correction, but as we do not intend to study the absolute value of the multiplet separation, we shall simply take the outside factor as $-\mathrm{I}m\,\mathrm{U}(r)$.

We take all these terms together and convert into Hamiltonian form, neglecting the squares of the last two terms. The result, expressed in polar co-ordinates r, θ, ϕ, is

$$\begin{aligned}
&\frac{1}{2m}\Big(\mathrm{P}_r^2+\frac{1}{r^2}\mathrm{P}_\theta^2+\frac{1}{r^2\sin^2\theta}\mathrm{P}_\phi^2\Big)-e\mathrm{V}\\
&\quad+\frac{1}{2\mathrm{I}}\Big\{\mathrm{P}_\chi^2+\frac{1}{\sin^2\chi}(\mathrm{P}_\lambda^2+\mathrm{P}_\mu^2-2\mathrm{P}_\lambda\mathrm{P}_\mu\cos\chi)\Big\}\\
&\quad+\frac{e\mathrm{H}}{2mc}(\mathrm{P}_\phi+2\mathrm{P}_\lambda)\\
&\quad+\mathrm{U}(r)\Big\{(-\mathrm{P}_\theta\sin\phi-\mathrm{P}_\phi\cot\theta\cos\phi)\Big(-\mathrm{P}_\chi\sin\lambda+\frac{\mathrm{P}_\mu-\mathrm{P}_\lambda\cos\chi}{\sin\chi}\cos\lambda\Big)\\
&\quad+(\mathrm{P}_\theta\cos\phi-\mathrm{P}_\phi\cot\theta\sin\phi)\Big(\mathrm{P}_\chi\cos\lambda+\frac{\mathrm{P}_\mu-\mathrm{P}_\lambda\cos\chi}{\sin\chi}\sin\lambda\Big)+\mathrm{P}_\phi\mathrm{P}_\lambda\Big\}
\end{aligned}\tag{2.1}$$

The next stage is to form the wave equation. In doing so it is not of course sufficient just to write $P_\theta = \frac{h}{2\pi i}\frac{\partial}{\partial\theta}$, etc., but the variational method of Schrödinger provides an unambiguous answer. The method is not strictly applicable for the linear terms in H, and for these we do write $P_\phi = \frac{h}{2\pi i}\frac{\partial}{\partial\phi}$, etc. (it has been shown by Epstein* how the external magnetic field can be replaced by an electric current so as to make them quadratic). The result is

$$\begin{aligned}
W\psi = &-\frac{h^2}{8\pi^2 m}\left\{\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}\psi - eV\psi \\
&-\frac{h^2}{8\pi^2 I}\left\{\frac{1}{\sin\chi}\frac{\partial}{\partial\chi}\sin\chi\frac{\partial}{\partial\chi}+\frac{1}{\sin^2\chi}\left(\frac{\partial^2}{\partial\lambda^2}+\frac{\partial^2}{\partial\mu^2}-2\cos\chi\frac{\partial^2}{\partial\lambda\,\partial\mu}\right)\right\}\psi \\
&+\frac{eHh}{4\pi mci}\left(\frac{\partial}{\partial\phi}+2\frac{\partial}{\partial\lambda}\right)\psi \\
&-\frac{h^2}{8\pi^2}U(r)\left\{e^{i(\phi-\lambda)}\left(\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right)\left(\frac{\partial}{\partial\chi}+\frac{i}{\sin\chi}\left[\frac{\partial}{\partial\mu}-\cos\chi\frac{\partial}{\partial\lambda}\right]\right)\right. \\
&\left.+e^{-i(\phi-\lambda)}\left(\frac{\partial}{\partial\theta}-i\cot\theta\frac{\partial}{\partial\phi}\right)\left(\frac{\partial}{\partial\chi}-\frac{i}{\sin\chi}\left[\frac{\partial}{\partial\mu}-\cos\chi\frac{\partial}{\partial\lambda}\right]\right)+2\frac{\partial^2}{\partial\phi\,\partial\lambda}\right\}\psi.
\end{aligned} \tag{2.2}$$

3. We have to find the characteristic values and functions for this equation, and must start with the nul approximation which disregards the small terms. The orbital motion is solved by

$$W = W_{nk}, \qquad \psi = f_{nk}(r)\,P_k^u(\cos\theta)\,e^{iu\phi} \tag{3.1}$$

—the degeneracy in k that occurs in the hydrogen spectrum will not arise unless $V(r)$ is of the form $1/r$. The last two factors are the ordinary tesseral spherical harmonics, but it is rather convenient to make a slightly unusual definition for P_k^u; it is one which could advantageously be introduced generally. We define

$$P_k^u(z) = (k-u)!\,(1-z^2)^{\frac{u}{2}}\left(\frac{d}{dz}\right)^{k+u}\frac{(x^2-1)^k}{2^k k!}. \tag{3.2}$$

This is the usual form multiplied by $(k-u)!$ but the definition holds for negative values of u as well as positive, and the values are symmetrical about u zero. u admits of all integral values between $-k$ and k inclusive. The advantage of the introduction of the extra factor $(k-u)!$ is that all the scales of relation, etc., hold valid running right through $u=0$, which is not

* 'Proc. Nat. Acad.,' vol. 12, p. 634 (1926).

the case if it is omitted. We have not normalised the functions; indeed it is hardly ever an advantage to do so except in general theorems.

The following easily proved relations will be used later.

$$\left.\begin{aligned}\left(\frac{\partial}{\partial\theta} - i\cot\theta\,\frac{\partial}{\partial\phi}\right)\mathrm{P}_k^u(\cos\theta)\,e^{iu\phi} &= (k+u)\,\mathrm{P}_k^{u-1}e^{iu\phi}\\ \left(\frac{\partial}{\partial\theta} + i\cot\theta\,\frac{\partial}{\partial\phi}\right)\mathrm{P}_k^u(\cos\theta)\,e^{iu\phi} &= -(k-u)\,\mathrm{P}_k^{u+1}e^{iu\phi}\end{aligned}\right\} \tag{3.3}$$

Note that these relations automatically bar expressions like P_k^{k+1} and P_k^{-k-1}. We also have the normalizing relation

$$\int_0^\pi\!\!\int_0^{2\pi}\sin\theta\,d\theta\,d\phi\,|\mathrm{P}_k^u(\cos\theta)\,e^{iu\phi}|^2 = \frac{4\pi}{2k+1}(k+u)!\,(k-u)! \tag{3.4}$$

and the orthogonal relation

$$\int_0^\pi\!\!\int_0^{2\pi}\sin\theta\,d\theta\,d\phi\,\mathrm{P}_k^u(\cos\theta)\,e^{iu\phi}\,\mathrm{P}_{k'}^{u'}(\cos\theta)\,e^{-iu'\phi} = 0$$

unless both $k' = k$ and $u' = u$. Further if X stands for either $\sin\theta e^{-i\phi}$, $\cos\theta$ or $\sin\theta e^{i\phi}$

$$\int_0^\pi\!\!\int_0^{2\pi}\sin\theta\,d\theta\,d\phi\,\mathrm{P}_k^u e^{iu\phi}\,\mathrm{P}_{k'}^{u'}e^{-iu'\phi}\,.\,\mathrm{X}$$

vanishes always unless $k' = k \pm 1$. If $k' = k - 1$, the only integrals of this type that do not vanish are

$$\left.\begin{aligned}\int_0^\pi\!\!\int_0^{2\pi}\sin\theta\,d\theta\,d\phi\,\mathrm{P}_k^u e^{iu\phi}\cdot\mathrm{P}_{k-1}^{u-1}e^{-i(u-1)\phi}\cdot\sin\theta e^{-i\phi} &= \frac{4\pi\,(k+u)!\,(k-u)!}{(2k+1)\,(2k-1)}\\ \int_0^\pi\!\!\int_0^{2\pi}\sin\theta\,d\theta\,d\phi\,\mathrm{P}_k^u e^{iu\phi}\,\mathrm{P}_{k-1}^u e^{-iu\phi}\cos\theta &= \frac{4\pi\,(k+u)!\,(k-u)!}{(2k+1)\,(2k-1)}\\ \int_0^\pi\!\!\int_0^{2\pi}\sin\theta\,d\theta\,d\phi\,\mathrm{P}_k^u e^{iu\phi}\,\mathrm{P}_{k-1}^{u+1}e^{-(u+1)\phi}\sin\theta e^{i\phi} &= -\frac{4\pi\,(k+u)!\,(k-u)!}{(2k+1)\,(2k-1)}\end{aligned}\right\} \tag{3.5}$$

The wave equation for a rotating body with two equal moments has been solved by Reiche* and shown to depend on hypergeometric functions. We here have a specially simple case on account of the equality of all the moments, but the solution is practically the same. We give it in a form which shows the close resemblance of the characteristic functions to spherical harmonics. The characteristic values are $\mathrm{W} = \dfrac{h^2}{8\pi^2\mathrm{I}}\,r\,(r+1)$ with $r = 0, 1, 2, \ldots$, and the

* 'Z. f. Physik,' vol. 39, p. 444 (1926).

associated functions are $P_r^{s,t}$ $(\cos\chi)$ $e^{i(s\lambda+t\mu)}$ where $P_r^{s,t}$ (z) satisfies the equation

$$\frac{d}{dz}(1-z^2)\frac{dP}{dz}+\left[r(r+1)-\frac{s_2+t^2-2stz}{1-z^2}\right]P=0.$$

We take as the solution,

$$P_r^{s,t}(z)=(r-s)!\,(1-z)^{(s-t)/2}(1+z)^{(s+t)/2}\left(\frac{d}{dz}\right)^{r+s}(1-z)^{r+t}(1+z)^{r-t}. \quad (3.6)$$

Both s and t admit of all integral values between $-r$ and r inclusive, and the definition applies for both positive and negative values.*

If $t=0$, $P_r^{s,0}=(-2)^r r!\,P_r^s$. The following relations are easily proved

$$\left[\frac{\partial}{\partial\chi}+\frac{i}{\sin\chi}\left(\frac{\partial}{\partial\mu}-\cos\chi\frac{\partial}{\partial\lambda}\right)\right]P_r^{s,t}(\cos\chi)\,e^{i(s\lambda+t\mu)}=(r+s)\,P_r^{s-1,t}(\cos\chi)\,e^{i(s\lambda+t\mu)},$$

$$\left[\frac{\partial}{\partial\chi}-\frac{i}{\sin\chi}\left(\frac{\partial}{\partial\mu}-\cos\chi\frac{\partial}{\partial\lambda}\right)\right]P_r^{s,t}(\cos\chi)\,e^{i(s\lambda+t\mu)}=-(r-s)P_r^{s+1,t}(\cos\chi)e^{i(s\lambda+t\mu)} \quad (3.7)$$

We shall also require the normalising relation

$$\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\sin\chi\,d\chi\,d\lambda\,d\mu\,|P_r^{s,t}(\cos\chi)\,e^{i(s\lambda+t\mu)}|^2 = \frac{2^{2r+3}\pi^2}{2r+1}(r-s)!\,(r+s)!\,(r-t)!\,(r+t)! \quad (3.8)$$

4. We now merely have to follow Schrödinger's method of approximation as applied to nearly degenerate systems. Write

$$\psi_{nku}^{rst}=f_{nk}(r)\,P_k^u(\cos\theta)\,e^{iu\phi}P_r^{s,t}(\cos\chi)\,e^{i(s\lambda+t\mu)}.$$

Then in (2.2)

$$\left(\frac{\partial}{\partial\phi}+2\frac{\partial}{\partial\lambda}\right)\psi_{nku}^{rst}=i(u+2s)\,\psi_{nku}^{rst},$$

and

$$\left[e^{i(\phi-\lambda)}\left\{\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\phi}\right\}\left\{\frac{\partial}{\partial\chi}+\frac{i}{\sin\chi}\left(\frac{\partial}{\partial\mu}-\cos\chi\frac{\partial}{\partial\lambda}\right)\right\}\right.$$
$$\left.+e^{-i(\phi-\lambda)}\left\{\frac{\partial}{\partial\theta}-i\cot\theta\frac{\partial}{\partial\phi}\right\}\left\{\frac{\partial}{\partial\chi}-\frac{i}{\sin\chi}\left(\frac{\partial}{\partial\mu}-\cos\chi\frac{\partial}{\partial\lambda}\right)\right\}+2\frac{\partial^2}{\partial\phi\,\partial\lambda}\right]\psi_{nku}^{rst}$$
$$=-(k-u)(r+s)\,\psi_{n,k,u+1}^{r,s-1,t}-(k+u)(r-s)\,\psi_{n,k,u-1}^{r,s+1,t}-2us\psi_{nku}^{rst}.$$

Any characteristic function is approximately of the form

$$\psi=\sum_{u,s}a_{us}\psi_{nku}^{rst}.$$

Strictly speaking there should also be a subscript t in a_{us} and a summation

* [*Added in proof.*—This definition applies also when r, s and t are half numbers, and this extends the work to even multiplicities, though of course in these cases the characteristic functions are double-valued.]

for t, but we shall soon see that this is unnecessary. The summations for u and s are restricted to values where both $|u| \leqslant k$ and $|s| \leqslant r$.

Let the associated energy be

$$W = W_{nk} + \frac{h^2}{8\pi^2 I} r(r+1) + \overline{W}.$$

Substituting in (2.2) we get†

$$\overline{W} \sum_{u,s} a_{us} \psi_{nku}^{rst} = \frac{eHh}{4\pi mc} \sum_{u,s} (u + 2s) a_{us} \psi_{nku}^{rst}$$

$$+ \frac{h^2}{8\pi^2} U(r) \sum_{u,s} a_{us} [(k-u)(r+s) \psi_{n,k,u+1}^{r,s-1,t} + (k+u)(r-s) \psi_{n,k,u-1}^{r,s+1,t} + 2us \psi_{nku}^{rst}].$$

Multiply by $\psi_{nku}^{rst}{}^*$ and integrate over the whole co-ordinate space. We write $\omega = \frac{eHh}{4\pi mc}$ so that ω is the normal Zeeman effect in energy units. Also put

$$\beta = \int \frac{h^2}{8\pi^2} U(r) \{f_{nk}(r)\}^2 r^2 dr \Big/ \int \{f_{nk}(r)\}^2 r^2 dr,$$

β is the constant of the multiplet separation. Then we have

$$\overline{W} a_{us} = \omega (u + 2s) a_{us} + \beta [(k - u + 1)(r + s + 1) a_{u-1, s+1}$$
$$+ (k + u + 1)(r - s + 1) a_{u+1, s-1} + 2usa_{us}]. \quad (4.1)$$

This system of difference equations is that which gives the term levels in the Zeeman effect.

The equation (4.1) contains no mention of t, and if t had been added as a subscript to a_{us} we should have obtained identically the same system of equations in a_{ust} for each value of t. These would all give the same levels and same a-ratios, though the characteristic functions would have a very different appearance. We shall see later that this difference is without effect on intensities as well as levels. The apparent complication is only due to the possibility of choosing any arbitrary radius of the sphere as pole for the Eulerian angles.

The fact which simplifies the problem to manageable proportions is that when all equations of this type are set down they fall into "chains" of equations; in each chain the only a's that occur have the sum of their two subscripts a constant, which is in fact the m of the term (while the u and s are the quantities which in a strong field are called m_k and m_r). Examples are given below.

† In this formula r is used in two senses, as the radius in U (r) and elsewhere as a quantum number. It would cause more confusion to alter one of the symbols than to retain this ambiguity.

Each chain gives a determinantal equation of which the roots are the W's of the associated levels. We label each of these with an index j (the reason for choice of particular numbers for j only appears later), and then determine the ratios of all the a's for each j. Before exhibiting this and proving its correctness, we shall, however, return to the model and work out intensities.

Schrödinger has shown how this is to be done. Let ψ, ψ' be two characteristic functions, and X any component of electric moment. The associated intensity is

$$\mathrm{I} = \left|\int \psi\psi'^{*}\mathrm{X}\right|^2 \Big/ \int |\psi|^2 \int |\psi'|^2, \tag{4.2}$$

where ψ'^{*} is the complex quantity conjugate to ψ', the integrations being over the whole co-ordinate space. We shall here take the co-ordinates x, y, z of the centre of the body as determining the electric moment. Combining them in the appropriate way, we have to consider the three quantities $x + iy$, $2z$, $x - iy$, or $r \sin\theta\, e^{i\phi}$, $2r\cos\theta$, $r\sin\theta\, e^{-i\phi}$, corresponding respectively to $\perp r$ $\|$, $\perp l$, components. If we substitute in (4.2) any of our characteristic functions, the integration for the radius is always the same, so that it falls out of consideration as far as concerns relative intensity, and this is all we shall be concerned with.

Take as our two states those with functions

$$\psi = \sum_s a^{k,j}_{m-s,s}\, \psi^{r,s,t}_{n,k,m-s}$$

and

$$\psi' = \sum_{s'} a^{k',j'}_{m'-s,s}\, \psi^{r,s',t'}_{n',k',m'-s'}.$$

If we multiply ψ by ψ'^{*} and integrate for μ and λ, the only terms that will not vanish are those for which $t' = t$ and $s' = s$. If then we multiply by, say, $\mathrm{X} = r\sin\theta e^{-i\phi}$, the only terms that will not vanish are those for which $m' = m - 1$, and even these will do so unless $k' = k \pm 1$ (see § 3). Similarly if we take $\mathrm{X} = 2r\cos\theta$, we must have $m' = m$, $k' = k \pm 1$, and if $\mathrm{X} = r\sin\theta e^{i\phi}$, $m' = m + 1$, $k' = k \pm 1$. We thus have three formulæ for intensity, of which the first is

$$k \rightarrow k - 1,\ m \rightarrow m - 1,\ j \rightarrow j'$$

$$\frac{\left|\int \sum_s a^{k,j}_{m-s,s}\, a^{k-1,j'}_{m-1-s,s}\, \psi^{rst}_{n,k,m-s}\, \psi^{rst*}_{n',k-1,m-1-s} \sin\theta e^{-i\phi}\right|^2}{\int \sum_s (a^{k,j}_{m-s,s})^2 \left|\psi^{rst}_{n,k,m-s}\right|^2 \int \sum_s (a^{k-1,j'}_{m-1-s,s})^2 \left|\psi^{rst}_{n',k-1,m-1-s}\right|^2}. \tag{4.3}$$

The integration for μ gives a factor $(r + t)!\,(r - t)!$ by (3.8) in every term of both numerator and denominator. This factor therefore cancels out, and

as the ratios of the $a_{\mu s}$'s are not affected by t we see that the intensities of the lines, as well as their frequencies, are independent of it. This completes the proof of the statement in § 2 that μ is without effect on the spectrum. Applying to (4.3) the integral formulæ of § 3, and dropping certain constant factors, we have

$$\frac{\left\{\sum_s a^{k,j}_{m-s,s}\, a^{k-1,j'}_{m-1-s,s}\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s)!\right\}^2}{\left[\left\{\sum_s (a^{k,j}_{m-s,s})^2\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s)!\right\}\times\left\{\sum_s (a^{k-1,j'}_{m-1-s,s})^2\,(r+s)!\,(r-s)!\,(k+m-s-2)!\,(k-m+s)!\right\}\right]}. \quad (4.4)$$

The other two components are

$$\frac{4\left\{\sum_s a^{k,j}_{m-s,s}\, a^{k-1,j'}_{m-s,s}\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s)!\right\}^2}{\left[\left\{\sum_s (a^{k,j}_{m-s,s})^2\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s)!\right\}\times\left\{\sum_s (a^{k-1,j'}_{m-s,s})^2\,(r+s)!\,(r-s)!\,(k+m-s-1)!\,(k-m+s-1)!\right\}\right]} \quad (4.5)$$

for the parallel component, and for the other perpendicular component,

$$\frac{\left\{\sum_s a^{k,j}_{m-s,s}\, a^{k-1,j'}_{m+1-s,s}\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s)!\right\}^2}{\left[\left\{\sum_s (a^{k,j}_{m-s,s})^2\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s)!\right\}\times\left\{\sum_s (a^{k-1,j'}_{m+1-s,s})^2\,(r+s)!\,(r-s)!\,(k+m-s)!\,(k-m+s-2)!\right\}\right]}. \quad (4.6)$$

These formulæ give the intensities observed in a direction at right angles to the magnetic field, not the energies emitted.

5. The formulæ (4.1) and (4.4, 5, 6) are all that is required for the complete statement of the standard Zeeman effect. Moreover, though our model fails, the equations derived from it are just as valid for even multiplicities as for odd. For these it is usual to use half quantum numbers, and it is interesting to observe that these half numbers do not occur in the equations at all, but arise in much the same way as does the energy $h\nu\,(n+\frac{1}{2})$ in the problem of a linear vibrator. It is in fact quite easy to formulate the equations without any halves in them at all; it is only necessary to sacrifice symmetry in order to do so, but the statement of conditions becomes somewhat clumsy on account of "end effects," that is, cases where the chain of equations is shorter than it is in general. On this account it is best to make use of half number suffixes for even multiplicities —the coefficients are still all integers. We now restate the rules for finding

the levels and intensities, then give examples, and finally outline the proof that our equations always lead to the observed results.

Take $k = 0, 1, 2 \ldots$ for $s, p, d \ldots$

$r = 0, \frac{1}{2}, 1 \ldots$ for singlets, doublets, triplets . . .

Let u be any integer between $-k$ and k inclusive, and let s be either an integer or half integer with r (*i.e.*, $r + s$ is an integer) and $-r \leqslant s \leqslant r$.

Take any of the permitted values of u and s, and write down the equation

$$-a_{u-1, s+1}\beta(k-u+1)(r+s+1) + a_{u,s}[\overline{\mathrm{W}} - \beta . 2us - \omega(u+2s)]$$
$$- a_{u+1, s-1}\beta(k+u+1)(r-s+1) = 0,$$

in which all the coefficients are integers, whatever r may be. Set down the corresponding equations in $a_{u-1,s+1}$, $a_{u+1,s-1}$, and carry on in both directions until stopped by either of the conditions $|u| \not> k$ or $|s| \not> r$. The determinant of this system of equations will give the values of $\overline{\mathrm{W}}$ corresponding to $m = u + s$. If the roots are arranged in decreasing order of magnitude, the greatest will have $j = k + r$, and the others are to be numbered by units downwards as far as the chain goes. u and s are themselves m_k and m_r in strong fields. The intensity of a line is given by applying the formulæ of § 4 (and we may again note that all the coefficients are integers there).

As it is easier to follow arithmetic than algebra, we shall give an example, and shall take $k < r$. To avoid having to write an enormous number of equations we shall take the p-levels of the quartet system.

Quartet system, p-terms. $k = 1, r = 3/2$.

The chains are

(1) $$a_{1,3/2}[\overline{\mathrm{W}} - 3\beta - 4\omega] = 0,$$

(2) $$a_{0,3/2}[\overline{\mathrm{W}} - 3, \omega] - a_{1,1/2}\beta . 2 . 1 = 0,$$
$$-a_{0,3/2}\beta . 1 . 3 + a_{1,1/2}[\overline{\mathrm{W}} - \beta - 2\omega] = 0,$$

(3) $$a_{-1,3/2}[\overline{\mathrm{W}} + 3\beta - 2\omega] - a_{0,1/2}\beta . 1 . 1 = 0,$$
$$-a_{-1,3/2}\beta . 2 . 3 + a_{0,1/2}[\overline{\mathrm{W}} - \omega] - a_{1,-1/2}\beta . 2 . 2 = 0,$$
$$-a_{0,1/2}\beta . 1 . 2 + a_{1,-1/2}[\overline{\mathrm{W}} + \beta] = 0,$$

(4) $$a_{-1,1/2}[\overline{\mathrm{W}} + \beta] - a_{0,-1/2}\beta . 1 . 2 = 0,$$
$$-a_{-1,1/2}\beta . 2 . 2 + a_{0,-1/2}[\overline{\mathrm{W}} + \omega] - a_{1,-3/2}\beta . 2 . 3 = 0,$$
$$-a_{0,-1/2}\beta . 1 . 1 + a_{1,-3/2}[\overline{\mathrm{W}} + 3\beta + 2\omega] = 0,$$

(5) $$a_{-1,-1/2}[\overline{\mathrm{W}} - \beta + 2\omega] - a_{0,-3/2}\beta . 1 . 3 = 0,$$
$$-a_{-1,-1/2}\beta . 2 . 1 + a_{0\,-3/2}[\overline{\mathrm{W}} + 3\omega] = 0,$$

(6) $$a_{-1,-3/2}[\overline{\mathrm{W}} - 3\beta + 4\omega] = 0.$$

If we form the determinant for each chain, we get an algebraic equation which determines one, two, or three of the levels, for any value of $\omega : \beta$. For the general case numerical solutions would have to be used; but if ω is much greater than β, we can immediately see that all the levels are approximately multiples of ω—the Paschen-Back effect. Though our formulæ are valid in all cases, general algebraic formulæ are not easy to follow, and we therefore discuss the extreme cases, which were the only ones treated by earlier writers. To order the levels for weak fields we approximate with ω small. For example, the chain (2) gives, for $m = 3/2$

$$(\overline{W} - 3\omega)(\overline{W} - \beta - 2\omega) = 6\beta^2$$

whence

$$\overline{W} = 3\beta + \frac{12}{5}\omega, \quad -2\beta + \frac{13}{5}\omega.$$

These solutions we label respectively $j = 5/2$, $j = 3/2$, according to our rule. Furthermore for no value of ω are the roots equal, so that as ω increases adiabatically the roots cannot cross, and we can associate together the solutions in weak and strong fields. The first here becomes 3ω, the second $2\omega + \beta$. The following table shows the whole solution :—

Chain.	$\overline{W}$ weak.	$\overline{W}$ strong.	m.	j.	Weak fields, "a" ratios.		
1	$3\beta + 4\omega$	$4\omega + 3\beta$	5/2	5/2	1		
2	$3\beta + \frac{12}{5}\omega$	3ω	3/2	5/2	2	3	
	$-2\beta + \frac{13}{5}\omega$	$2\omega + \beta$	3/2	3/2	1	-1	
3	$3\beta + \frac{4}{5}\omega$	$2\omega - 3\beta$	1/2	5/2	1	6	3
	$-2\beta + \frac{13}{15}\omega$	ω	1/2	3/2	1	1	-2
	$-5\beta + \frac{4}{3}\omega$	$-\beta$	1/2	1/2	1	-2	1
4	$3\beta - \frac{4}{5}\omega$	$-\beta$	$-1/2$	5/2	3	6	1
	$-2\beta - \frac{13}{15}\omega$	$-\omega$	$-1/2$	3/2	-2	1	1
	$-5\beta - \frac{4}{3}\omega$	$-2\omega - 3\beta$	$-1/2$	1/2	1	-2	1

Chain.	$\overline{\mathrm{W}}$ weak.	$\overline{\mathrm{W}}$ strong.	m.	j.	Weak fields, "a" ratios.
5	$3\beta - \frac{12}{5}\omega$	$-2\omega + \beta$	$-3/2$	$5/2$	3 2
	$-2\beta - \frac{13}{5}\omega$	-3ω	$-3/2$	$3/2$	-1 1
6	$3\beta - 4\omega$	$-4\omega + 3\beta$	$-5/2$	$5/2$	1

It may be well here to mention a few points about the chains which are not entirely obvious from the algebra, but which were in fact found most useful in constructing them. We can show that many of the coefficients are immediately determined simply by the existence of the chain type of equations. Take first the case of $k > r$. Then the first member of a chain will involve terms in a_{ur} $(\overline{\mathrm{W}} - \ldots)$ and $a_{u+1,\, r-1}$, and the second in a_{ur}, $a_{u+1,\, r-1}$ $(\overline{\mathrm{W}} - \ldots)$, $a_{u+2,\, r-2}$. Now if the coefficients are to be algebraic, they must be such that if we put $u = k$ we get a chain of one member, for the first equation is then reduced to the one term in a_{kr} $(\overline{\mathrm{W}} - \ldots)$. It follows that in the second equation the coefficient of a_{ur} must contain a factor $(k-u)$, in order that this equation may be satisfied identically for $u = k$. Similar considerations show that in the third equation the coefficient of $a_{u+1,\, r-1}$ must have a factor $k-u-1$, in order that it may vanish identically for the case $u = k - 1$, which is required so as to give the two-member chain. The argument continues all down the chain and determines a factor for each member lying on one side of the diagonal. By attacking the chain from the lower end, and putting $u = -k$, etc., similar factors can be deduced for the other side of the diagonal. The other factors in $r + s + 1$, etc., follow out of the consideration of cases where $k < r$, so that k and not r limits the length of the chain. This argument is of course not conclusive, but the process indicated was in fact found to be most useful in constructing the equations.

Our example of the quartet p-terms has shown how the chains go for $k < r$. When $k > r$ the corresponding arrangement of chains is rather similar. It starts with chains of 1, 2, 3 . . . members, increasing up to the maximum multiplicity, stays there, and then decreases back to 1. The j's of the end chains go from $k + r$ downwards; in the middle part they go down to $k - r$. Thus for example the chains of quartet d are of lengths 1, 2, 3, 4, 4, 3, 2, 1 members, while for quintet f they would be of 1, 2, 3, 4, 5, 5, 5, 4, 3, 2, 1 members.

With a view to illustrating the matter further, and also to calculating some intensities, we will give one of the four-chains of quartet d. Take that for which $m = \frac{1}{2}$ (and of course $k = 2$, $r = 3/2$)

$$a_{-1,\frac{3}{2}}[\overline{\mathrm{W}} + 3\beta - 2\omega] - a_{0,\frac{1}{2}}\beta\,.\,2\,.\,1 = 0,$$

$$-a_{-1,\frac{3}{2}}\beta\,.\,3\,.\,3 + a_{0,\frac{1}{2}}[\overline{\mathrm{W}} - \omega] - a_{1,-\frac{1}{2}}\beta\,.\,3\,.\,2 = 0.$$

$$-a_{0,\frac{1}{2}}\beta\,.\,2\,.\,2 + a_{1,-\frac{1}{2}}[\overline{\mathrm{W}} + \beta] - a_{2,-\frac{3}{2}}\beta\,.\,4\,.\,3 = 0.$$

$$-a_{1,-\frac{1}{2}}\beta\,.\,1\,.\,1 + a_{2,-\frac{3}{2}}[\overline{\mathrm{W}} + 6\beta + \omega] = 0.$$

For weak fields the roots are

$$\overline{\mathrm{W}} = 6\beta + \tfrac{5}{7}\omega, \quad -\beta + \tfrac{24}{35}\omega, \quad -6\beta + \tfrac{3}{5}\omega, \quad -9\beta.$$

So as to give an example of the calculation of intensities, we may note that for the first solution ($j = 7/2$)

$$a_{-1,\frac{3}{2}} = 4, \quad a_{0,\frac{1}{2}} = 18, \quad a_{1,-\frac{1}{2}} = 12, \quad a_{2,-\frac{3}{2}} = 1.$$

In applying the formulæ for intensities, we have to remember that they are all relative, so that we shall have to work out two. Now of the whole multiplet *line*—and this is true of all cases—two members have specially simple behaviour, and these are the lines connecting respectively the two first and the two last chains, each of which has only one member. These lines behave as though the Zeeman effect had no anomaly; they keep their intensity constant, and their shift increases uniformly with the magnetic field according to the strict Larmor theorem. We shall call them the leading members of the multiplet. For quartet d the leading chain gives

$$k = 2,\ r = \tfrac{3}{2},\ m = \tfrac{7}{2},\ j = \tfrac{7}{2},\ \overline{\mathrm{W}} = 6\beta + 5\omega,\ a_{2,\frac{3}{2}} = 1,$$

so the intensity of the leading member of the pd lines is

$$\{3\,!\ 0\,!\ 4\,!\ 0\,!\}^2 / \{3\,!\ 0\,!\ 4\,!\ 0\,!\}\ \{3\,!\ 0\,!\ 2\,!\ 0\,!\} = 12.$$

Compare with this the intensity in a weak field of the line

$$k,\ 2 \to 1\,; \quad j,\ \tfrac{7}{2} \to \tfrac{5}{2}\,; \quad m,\ \tfrac{1}{2} \to -\tfrac{1}{2}.$$

Our formula gives

$$\{0 + 18\,.\,3\,.\,2\,!\ 1\,!\ 2\,!\ 2\,! + 12\,.\,6\,.\,1\,!\ 2\,!\ 3\,!\ 1\,! + 1\,.\,1\,.\,0\,!\ 3\,!\ 4\,!\ 0\,!\}^2$$
$$\div[\{4^2\,.\,3\,!\,0\,!\,1\,!\,3\,! + 18^2\,.\,2\,!\,1\,!\,2\,!\,2\,! + 12^2\,1\,!\,2\,!\,3\,!\,1\,! + 1^2\,.\,0\,!\,3\,!\,4\,!\,0\,!\}$$
$$\times\{3^2\,.\,2\,!\ 1\,!\ 0\,!\ 2\,! + 6^2\,.\,1\,!\ 2\,!\ 1\,!\ 1\,! + 1^2\,.\,0\,!\ 3\,!\ 2\,!\ 0\,!\}] = \tfrac{24}{7},$$

i.e., 2/7 of the leading line.

We will also verify an example of the fact that in weak fields lines involving $j \to j - 2$ give no intensity, a result by no means obvious with the present method. Take the line

$$k,\ 2 \to 1\,;\ j,\ \tfrac{7}{2} \to \tfrac{3}{2}\,;\ m,\ \tfrac{1}{2} \to -\tfrac{1}{2}.$$

We only need the numerator. It is

$$\{18\,(-2)\,.\,2!\;1!\;2!\;2! + 12\,.\,1\,.\,1!\;2!\;3!\;1! + 1\,.\,1\,.\,0!\;3!\;4!\;0!\}^2$$
$$= \{-288 + 144 + 144\}^2 \qquad = 0.$$

6. There are a good many end cases that would have to be treated to construct the complete proof that we have really got the standard multiplet. We shall, however, be content to treat here only of the "complete" chains, which are those where $k \geqslant r$, while $m \leqslant k - r$. The reader can deal with the other cases for himself by similar methods.

Since the sum of the suffixes in a chain is always the same, we shall drop one of them, retaining s, which for the case we consider runs from r to $-r$. We shall set down the chain for m. It is

$$a_r\,[\overline{W} - \beta\,.\,2r\,(m - r) - \omega\,(m + r)] - a_{r-1}\,\beta\,(k + m - r + 1)\,.\,1 \qquad = 0$$

$$- a_r\,\beta\,(k-m+r)\,2r + a_{r-1}\,[\overline{W} - \beta\,(2r-2)\,(m - r + 1) - \omega\,(m + r - 1)]$$
$$- a_{r-2}\,\beta\,(k + m - r + 2)\,.\,2 \qquad = 0$$

$$\cdots\cdots \qquad \cdots\cdots \qquad \cdots\cdots$$

$$- a_{s+1}\,\beta\,(k - m + s + 1)\,(r + s + 1) + a_s\,[\overline{W} - \beta\,.\,2s\,(m - s) - \omega\,(m + s)]$$
$$- a_{s-1}\,\beta\,(k + m - s + 1)\,(r - s + 1) \qquad = 0$$

$$\cdots\cdots \qquad \cdots\cdots \qquad \cdots\cdots$$

$$- a_{-r+1}\,\beta\,(k - m - r + 1)\,.\,1 \quad + a_{-r}\,[\overline{W} + \beta\,.\,2r\,(m + r) - \omega\,(m - r)] = 0$$

The form that the solution takes in weak fields is best shown by introducing new variables. Numbering the equations from the top (1), (2), (3) . . , form the following sums

$$(1) + (2) + (3) + (4) + \ldots\ldots$$
$$(2) + 2(3) + 3(4) + \ldots\ldots$$
$$(3) + 3(4) + 6(5) + \ldots$$
$$(4) + 4(5) + \ldots$$

The rule is to multiply the equation in $a_s\overline{W}$ by the binomial coefficient $\binom{r - s}{k + r - j}$ and sum, j being $k + r$, $k + r - 1$, etc., in turn. The resulting equations are then readily expressed in terms of

$$b_r \quad = a_r + a_{r-1} + \ldots\ldots + a_{-r}$$
$$b_{r-1} = \qquad a_{r-1} + 2\,a_{r-2}\ldots\ldots + 2ra_{-r}$$
$$b_{j-k} = \Sigma_{-r}^{j-k} \binom{r - s}{k + r - j}\,a_s$$

and are

$$b_r\{\overline{\mathrm{W}} - \beta \, . \, 2kr - \omega\,(m + r)\} + b_{r-1}\omega \qquad = 0$$

$$-b_r\beta\,(k - m + r)\,2r + b_{r-1}\{\overline{\mathrm{W}} - \beta \, . \, 2\,(kr - k - r) - \omega\,(m + r - 1)\} + b_{r-2} \, . \, 2\omega = 0$$

$$\cdots\cdots\cdots \qquad \cdots\cdots\cdots \qquad \cdots\cdots\cdots$$

$$-b_{j-k+1}\beta(j-m+1)(j-k+r+1) + b_{j-k}\{\overline{\mathrm{W}} - \beta[j(j+1) - k(k+1) - r(r+1)] - \omega(m+j-k)\} + b_{j-k-1}(k+r-j+1)\omega = 0$$

$$\cdots\cdots\cdots \qquad \cdots\cdots\cdots \qquad \cdots\cdots\cdots$$

From these equations it is evident that if $\omega = 0$, we have Landé's γ formula because the determinant will have no members on one side of the diagonal. If we put $\beta = 0$, we have the Paschen-Back effect as all the members on the other side of the diagonal now vanish, but of course our transformation was unnecessary in order to show this.

It remains to prove Landé's g-formula, and to do this we solve first for the b's with $\omega = 0$ and a given j. It then appears that all the b's with index greater than $j - k$ vanish, while the rest are easily expressed as products of two binomial coefficients. When ω is not quite zero, the upper b's no longer quite vanish, but it is easy to see that each bears to the next a ratio of order ω. Let the characteristic required be

$$\overline{\mathrm{W}} = \beta\,[\,j\,(j + 1) - k\,(k + 1) - r\,(r + 1)\,] + q\omega.$$

Then the value of q will be obtained from the three equations

$$b_{j-k+1}\{\beta j\,(j + 1) - \beta\,(j + 1)\,(j + 2)\} + b_{j-k}\,(k + r - j)\,\omega \qquad = 0$$

$$-b_{j-k+1}\,\beta\,(j - m + 1)\,(j - k + r + 1) + b_{j-k}\,(q - m - j + k)\,\omega + b_{j-k-1}\,(k + r - j + 1)\,\omega = 0.$$

$$-b_{j-k}\,\beta\,(j - m)\,(j - k + r) + b_{j-k-1}\{\beta j\,(j + 1) - \beta\,(j - 1)j\} \qquad = 0.$$

The determinant of these equations reduces to Landé's g-formula,

$$q = m\left\{1 + \frac{j\,(j + 1) - k\,(k + 1) + r\,(r + 1)}{2j(j+1)}\right\}$$

If the algebra of the transformation is examined, it appears that at no stage of it is it necessary to assume how many members the chain of equations has. Consequently the proof is valid for the incomplete end chains as well as for the middle ones. It would only require trivial modifications to make it applicable for $k < r$.

The connection of the roots with those in the Paschen-Back effect is obvious, for we can order them together from the top of the chain in each case. This

rests on the fact that for no value of ω can the determinant of a chain have equal roots, as may easily be shown by a Sturmian method, so that as ω increases adiabatically, the root which starts as, say, p^{th} in order must end as p^{th} too. For example, the first solution, which for small fields is $\beta \,.\, 2kr + m\left(1 + \dfrac{r}{k+r}\right)\omega$, becomes in strong fields $(m+r)\,\omega + \beta \,.\, 2r\,(m-r)$. In tracing out the connections in general, it must be remembered that there is an essential asymmetry between the top and bottom of the chain system.

It is easy to solve for the ratios of the b's for zero field with a given j, and thence to deduce the corresponding a's; but the expressions are not very simple. They are required in order to determine intensities in weak fields. I have, as a matter of fact, examined the general case sufficiently to see that it is only a matter of heavy algebraic manipulation, without inherent difficulty, to simplify these intensity formulæ; but it seemed sufficient to be content with actually calculating them only for a number of cases (*e.g.*, quintet system, arbitrary k and m). Wherever this has been done, the values given by Kronig* are verified.

In this connection, however, there is one very important consideration that cannot be neglected—the combination rule for j. This also is of course verified where it has been tried, but the type of calculation required to do so is so intricate that it is not in the least suggestive of a general principle, but rather of a sort of accident; so that even if we gave a proof starting from the formulæ of § 4 it would not be very convincing. The plain fact is that we have been treating of all field strengths indifferently, and except in the case of zero field j is nothing more than a name. To fit in with the familiar notation, we have adopted numeration by j, instead of numbering from say 0 to $2r$, and the consequence is merely a slight simplification of the algebra. To bring out the force of j we shall outline a new attack on the whole problem, omitting entirely the terms introduced on account of the magnetic field.

7. The quantum number j only has a real meaning in the absence of the external magnetic field, so that we may say that it depends on considerations involving the isotropy of the atom. Now this isotropy could hardly be better concealed than by spherical harmonics in the form in which we have used them. To exhibit it we must adopt a different method of expressing them, and this is not hard, at any rate in the case of odd multiplicities. We saw that the characteristic functions were of the form

$$f_{nk}(r)\, \mathrm{P}_k^m(\cos\theta)\, e^{im\phi}\, \mathrm{P}_r^{s,\,t}(\cos\chi)\, e^{i(s\lambda+t\mu)},$$

* 'Z. f. Physik,' vol. 31, p. 885 (1925).

and that all the results were unaffected by t. Put $t = 0$, and we have simply another ordinary spherical harmonic $P_r^s(\cos\chi)\, e^{is\lambda}$.

Now any spherical harmonic in x, y, z can be written as a combination of terms

$$r^{a+b+c+1}\left(\frac{\partial}{\partial x}\right)^a\left(\frac{\partial}{\partial y}\right)^b\left(\frac{\partial}{\partial z}\right)^c\frac{1}{r}, \tag{7.1}$$

and in this form the isotropy can be made explicit. We also introduce three co-ordinates ξ, η, ζ, with radius ρ and replace $P_r^s(\cos\chi)\, e^{is\lambda}$ by

$$\rho^{a'+b'+c'+1}\left(\frac{\partial}{\partial \xi}\right)^{a'}\left(\frac{\partial}{\partial \eta}\right)^{b'}\left(\frac{\partial}{\partial \zeta}\right)^{c'}\frac{1}{\rho}. \tag{7.2}$$

The operator occurring in the last line of (2.2) is then

$$-\frac{h^2}{4\pi^2}U(r)\left\{\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\left(\eta\frac{\partial}{\partial \zeta}-\zeta\frac{\partial}{\partial \eta}\right)+\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\left(\zeta\frac{\partial}{\partial \xi}-\xi\frac{\partial}{\partial \zeta}\right)\right.$$
$$\left.+\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\left(\xi\frac{\partial}{\partial \eta}-\eta\frac{\partial}{\partial \xi}\right)\right\},$$

or say $\left(\left[r\cdot\frac{\partial}{\partial r}\right]\left[\rho\cdot\frac{\partial}{\partial \rho}\right]\right)$ in vector notation. This operator commutes with r and ρ, and as before we can omit consideration of the radius while ρ is purely auxiliary, and plays no part in the integrations. We can drop out the factors $r^{a+b+c+1}$ and $\rho^{a'+b'+c'+1}$ from (7.1) and (7.2) as of no interest, and can take as the equation to determine the characteristic values,

$$\overline{W}\psi = -2\beta\left(\left[r\cdot\frac{\partial}{\partial r}\right]\left[\rho\cdot\frac{\partial}{\partial \rho}\right]\right)\psi,$$

where in order to satisfy the nul approximation ψ must be a sum of products of harmonics in x, y, z of degree k and in ξ, η, ζ of degree r. Now the operator in this equation is invariant for a change of axes, provided that the transformation is applied simultaneously to x, y, z, and ξ, η, ζ. Hence any solution that can be obtained must be of tensor form. We shall show that *j is the rank of the tensor solution.*

The present section does not pretend to completeness, and indeed we shall only give a few examples to bring out this interpretation of j. It will be convenient to use a tensor notation, so we shall write x_a for x, y, or z, and ξ_a for ξ, η, ζ. We follow the tensor notation in omitting the summation sign when duplicated indices are to be summed; but there is here no distinction between co- and contravariance, so that all the indices are written below. We shall make use of the notation of vector products with suffix for the component.

Thus $[x\xi]_1 = x_2\xi_3 - x_3\xi_2$. Any spherical harmonic, *e.g.*, $\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\frac{\partial}{\partial x_\gamma}\cdot\frac{1}{r}$ we write simply as $d_\alpha\, d_\beta\, d_\gamma$. Similarly for $\frac{\partial}{\partial \xi_\alpha}\frac{\partial}{\partial \xi_\beta}\frac{\partial}{\partial \xi_\gamma}\cdot\frac{1}{\rho}$ we write $\mathrm{D}_\alpha\,\mathrm{D}_\beta\,\mathrm{D}_\gamma$.

The equation for the characteristic functions is then

$$\overline{\mathrm{W}}\psi = -2\beta\left[x\frac{\partial}{\partial x}\right]_\alpha\left[\xi\frac{\partial}{\partial \xi}\right]_\alpha\psi$$
$$= -\beta\left\{\left(x_\beta\frac{\partial}{\partial x_\gamma} - x_\gamma\frac{\partial}{\partial x_\beta}\right)\left(\xi_\beta\frac{\partial}{\partial \xi_\gamma} - \xi_\gamma\frac{\partial}{\partial \xi_\beta}\right)\right\}\psi.$$

The appropriate solution will be a sum of products each of which has k d's and r D's.

Consider the triplet p terms. The permissible forms of solution are $\psi = d_\alpha \mathrm{D}_\beta$, and we have to find what combination gives an actual solution. Solving out in detail (either directly or by transformation of the work of § 4), we find the following solutions

$$\overline{\mathrm{W}} = -4\beta \qquad j = 0 \qquad \psi = \mathrm{C}\, d_\alpha\, \mathrm{D}_\alpha$$
$$\overline{\mathrm{W}} = -2\beta \qquad j = 1 \qquad \psi = \mathrm{C}_\alpha\, [d\mathrm{D}]_\alpha$$
$$\overline{\mathrm{W}} = 2\beta \qquad j = 2 \qquad \psi = \mathrm{C}_{\alpha\beta}\, d_\alpha\, \mathrm{D}_\beta$$
$$\text{with} \quad \mathrm{C}_{\alpha\beta} = \mathrm{C}_{\beta\alpha}, \quad \text{and} \quad \mathrm{C}_{\alpha\alpha} = 0.$$

The C's here are arbitrary constants, and the conditions attached to the last, which reduce them from 9 to 5, are just those that exclude terms corresponding to the previous solutions. If we do the same work for the triplet d terms, the typical solution must depend on $d_\alpha\; d_\beta\; \mathrm{D}_\gamma$, and it is possible to build three tensors out of this, one of the third rank, one of the second, by what we may call curl-contraction, and one of the first by complete contraction. The solutions are

$$\overline{\mathrm{W}} = -6\beta \qquad j = 1 \qquad \psi = \mathrm{C}_\alpha d_\alpha d_\beta \mathrm{D}_\beta$$
$$\overline{\mathrm{W}} = -2\beta \qquad j = 2 \qquad \psi = \mathrm{C}_{\alpha\beta} d_\alpha\, [d\mathrm{D}]_\beta$$
$$\text{with} \quad \mathrm{C}_{\alpha\beta} = \mathrm{C}_{\beta\alpha}, \qquad \mathrm{C}_{\alpha\alpha} = 0.$$
$$\overline{\mathrm{W}} = 4\beta \qquad j = 3 \qquad \psi = \mathrm{C}_{\alpha\beta\gamma} d_\alpha d_\beta \mathrm{D}_\gamma$$
$$\text{with} \quad \mathrm{C}_{\alpha\beta\gamma} = \mathrm{C}_{\beta\alpha\gamma} = \mathrm{C}_{\alpha\gamma\beta} \quad \text{and} \quad \mathrm{C}_{\alpha\beta\beta} = 0.$$

It is easy to enumerate the numbers of independent solutions that these give. They are of course 3, 5, 7.

Such examples can be multiplied indefinitely, but perhaps the above will suffice. For a complete discussion it would be necessary to elaborate somewhat

the notation and method of this section, and this would open a wider field than the present paper contemplates. In any particular case it is fairly easy to verify the combination law of j, exhibiting it as dependent on the tensor-ranks of the two characteristic functions. We shall not go further into the matter here.

In conclusion we may note a few points of general interest. We have succeeded in giving to j a very clear physical meaning, but only for odd multiplets. There seems no simple way of extending the idea to even—to do so would require the invention of tensors of half rank! So here again we come to the difficulty of the half quantum number of the spinning electron.

The model that we have used gives, of course, only a very abbreviated account of the interactions of a group of electrons, and it is doubtful how far its extension is legitimate. For instance, consider the case of a triplet-singlet intercombination line. To give such a line with our model it is only necessary to extend the idea of electric moment. It is easy to show that every feature of the intercombination* is given by replacing the vector x_a in the electric moment by $[x\xi]_a$. We may observe that the presence of ξ in the quasi-moment seems natural, for Heisenberg has explained that singlet and triplet in helium would not combine at all but for the magnetism in the electron, and so we should expect the intensity of an intercombination line to involve the spin.

Summary.

The problem of a spinning electrified body moving in a central orbit in a magnetic field is solved by the method of the wave mechanics in spherical harmonics. It is shown to lead to a set of simple arithmetical equations which exactly give all the features of the standard Zeeman effect in all strengths of field. The model only yields strictly the odd multiplicities, but the same system of equations is just as competent to give the even. Formulæ are given for the intensity of any line at any strength of field. A few examples are worked out. The development in spherical harmonics brings out strongly the meaning of the quantum numbers k, m, r, m_k, m_r, but much more obscurely, j; and an alternative development is sketched which brings out the full force of j.

I must express my thanks to Dr. R. Schlapp for his help in working out several of the details.

* Except the *absolute* values of the intensities.