

## Application of quantum mechanics to the problem of the anomalous Zeeman effect

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**Uhlenbeck** and **Goudsmit** invoked **Compton**'s hypothesis of a rotating electron in order to explain the anomalous Zeeman effect. The present paper examines the quantum-mechanical behavior of the atomic model that is characterized by that hypothesis. The result is that the Zeeman effect and the fine structure of the double spectra can be explained completely by the aforementioned hypothesis.

An examination of the magnetic behavior of atomic systems teaches us that according to the laws of quantum mechanics atomic systems that are composed of point charges must also always exhibit the normal Zeeman effect.

In order to explain the anomalous Zeeman effect, **Uhlenbeck** and **Goudsmit** called upon the hypothesis <sup>(1)</sup> that every individual electron should be the carrier of a magnetic moment  $m$  and a corresponding mechanical angular impulse of  $s$ . Moreover,  $m$  and  $s$  should be coupled by the relation:

$$m = \frac{e}{mc} s. \quad (1)$$

The quotient of the magnetic and mechanical moments should then differ from the value  $e / 2mc$  that is valid for atomic systems with point charges by the factor of 2. We shall not go into the question of which arguments can be cited for and against this hypothesis from the standpoint of electrodynamics here. Rather, in what follows, the quantum-mechanical behavior of the **Uhlenbeck-Goudsmit** model shall be investigated, and the result will be compared with experiment. It is known that the application of the previously-commonplace quantum rules to that model will lead to contradictions with experiments.

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<sup>(1)</sup> The hypothesis of a rotating electron already went back to A. **Compton**, Journ. Frankl. Inst. **192** (1921), 145. The application of that hypothesis to the problem that is of interest to us here – namely, the Zeeman effect – was first given by **G. E. Uhlenbeck** and **S. Goudsmit**, Naturwiss. **13**, Heft 47, 1925.

§ 1. **The Hamiltonian function of the model.** – In the sequel, we shall assume that the electron of charge  $-e$ , magnetic moment  $m$ , and angular impulse  $\mathfrak{s}$  (<sup>1</sup>)  $\left( m = \frac{e}{mc} \mathfrak{s} \right)$  circles a  $Z$ -fold positively-charged massive nucleus; the angular impulse of that motion will be called  $\mathfrak{k}$ . An external magnetic field  $\mathfrak{H}$  might perturb the motion of an electron. Magnetically, this model obviously behaves precisely like the one that was proposed by **Pauli** and **Landé**, which has been of such great service in the formal organization of the complicated spectra. In most cases, the fine structure and Zeeman effect that can appear by the combined effect of several valence electrons can be traced back to the fine structure and Zeeman effect of the simple model that is described above.

If one ignores the influence of relativity, the effect of the external field, and the effect of  $m$ , then the motion of the electron will be given by the **Pauli-Dirac** (<sup>2</sup>) theory of the hydrogen atom.

The additional perturbing energy decomposes into three parts:

$$H = H_1 + H_2 + H_3 .$$

1. The part that originates in the external field  $\mathfrak{H}$  is given by:

$$H_1 = \mathfrak{H} \cdot \left( \frac{e}{2mc} \mathfrak{k} \right) + \mathfrak{H} \cdot \left( \frac{e}{2mc} \mathfrak{s} \right) = \frac{e}{2mc} \mathfrak{H} (\mathfrak{k} + 2\mathfrak{s}) \quad (2)$$

using known rules.

2. If one considers the center of mass of the electron to be at rest and the nucleus as orbiting around the electron then the nucleus will generate the magnetic field:

$$\mathfrak{H}_i = \frac{eZ}{c} \frac{[\mathfrak{r} \mathfrak{v}]}{r^3} = \frac{eZ}{mc} \frac{\mathfrak{k}}{r^3}$$

at the location of the electron.

That field will correspond to a Larmor precession of the impulse  $\mathfrak{s}$  of magnitude  $\frac{e}{mc} \bar{\mathfrak{H}}_i$ . According to **Thomas** (<sup>3</sup>), we then have to observe that this is the Larmor precession only in the system that was just considered, in which the center of mass of the electron was at rest. In order to get the precession in the system in which the nucleus – or even better, the center of mass of the entire atom – is at rest, a Lorentz transformation

(<sup>1</sup>) From the **Compton-Uhlenbeck-Goudsmit** hypothesis, the individual electron must be endowed with an entirely well-defined  $\mathfrak{s}$ -impulse, namely, the quantum-mechanical  $\mathfrak{s}^2 = \left( \frac{h}{2\pi} \right)^2 s(s+1)$ ,  $s = 1/2$ . Here, however, we shall leave  $s$  undetermined in order to be able to also deal with several multiplets (i.e., triplets, quadruplets, etc.) that arise from coupling to electron magnets.

(<sup>2</sup>) **W. Pauli, Jr.**, Zeit. Phys. **36** (1926), 336; **P. Dirac**, Proc. Roy. Soc. London **110**, March 1926.

(<sup>3</sup>) **L. H. Thomas**, Nature **117** (1926), 514.

must still be performed. **Thomas** then got the value of  $\frac{e^2 Z}{2m^2 c^2} \frac{\bar{l}}{r^3} \mathfrak{k}$  for the Larmor precession in this latter system, which is actually of interest to us. That value obviously corresponds to a term:

$$H_2 = \frac{e^2 Z}{2m^2 c^2} \frac{\bar{l}}{r^3} \mathfrak{k} \mathfrak{s} \quad (3)$$

in the Hamiltonian function.

3. According to **Sommerfeld's** theory, the relativistic variation of mass gives rise to an additional energy of magnitude:

$$H_2 = - \frac{1}{2mc^2} \left[ W_0^2 + 2e^2 Z W_0 \frac{\bar{l}}{r} + e^4 Z^2 \frac{\bar{l}}{r^2} \right]. \quad (4)$$

The overbar on the  $r$  independent terms signifies the mean of the unperturbed motion. In what follows, we shall assume that the perturbing function  $H$  has the same form in quantum mechanics as in classical mechanics and electrodynamics. As the basis for that assumption, one can state that all of the quantities that enter into  $H$  commute, and thus, from the correspondence principle, no forms can come under consideration in  $H$  that deviate from the ones that are derived here essentially. An inevitable basis for the perturbing functions that are given here cannot be given as long as a concomitant rigorous quantum theory of electrodynamics is lacking.

**§ 2. Line of reasoning for the perturbation calculations.** In the quantum-mechanical calculations that will now follow, we can assume that the absolute values of  $\mathfrak{k}$  and  $\mathfrak{s}$  are quantized in the unperturbed system – i.e., they are diagonal matrices. That assumption can be regarded as unjustified for:

$$\mathfrak{k} \left[ \mathfrak{k}^2 = \left( \frac{h}{2\pi} \right) k(k+1) \right],$$

since the known degeneracy of  $k$  exists in the unperturbed system. However, since only  $\mathfrak{k}$ , but not the perihelion length that is conjugate to  $\mathfrak{k}$ , appears in the perturbing energy  $H$  itself, the assumed quantization of  $|\mathfrak{k}|$  will enter into the accounting for  $H$ . Physically, that means that the model of the Zeeman effect for hydrogen that will be examined here will be completely analogous to that of the alkali atoms. For the alkali atoms,  $|\mathfrak{k}|$  is already established by the interaction with the other electrons. An analogous consideration can be applied to the component  $M_z$  of the total impulse  $\mathfrak{M}$  of the atom in the direction of the field. The starting system indeed degenerates with regard to  $M_z = \frac{h}{2\pi} m$ . However, since only  $m$ , but not the angle variable that is conjugate to  $m$ , appears

in the perturbing energy  $H$ , the quantization of  $M_z$  will still enter into  $H$ . We will then be able to simplify our calculations by the assumption that in the initial system  $|\xi\rangle, |\varsigma\rangle, M_z$  will not degenerate, and therefore they can be based upon diagonal matrices for the sake of quantum theory.

The initial system is then degenerate in regard to one coordinate [cf., the completely analogous treatment of the model in classical mechanics <sup>(1)</sup>]. We can characterize that coordinate by the component  $s_z = \frac{h}{2\pi} m_z$  of the eigen-impulse  $\varsigma$  of the electron and the conjugate angle variable. However, we can also characterize it by the total impulse  $\mathfrak{M}$  and the variable that is conjugate to it.

The perturbation process in quantum mechanics for degenerate systems can be sketched out as follows <sup>(2)</sup>:

Let any solution  $p^0, q^0$  of the unperturbed problem be given, and furthermore, the dependency of the perturbing function upon the coordinates of the unperturbed problem. If the initial system did not degenerate then the additional energy  $W$  that corresponds to the perturbation would be given by the temporal mean  $H$  of the perturbing function over the unperturbed motion. That mean  $H$  would then itself be a diagonal matrix. However, if the initial system does degenerate – e.g., the energy values of the states  $n + 1, \dots, n + r$  coincide – then the mean value  $H$  of the perturbing energy will contain terms that correspond to the transitions between the states  $n + 1, \dots, n + r$ ; i.e., it would not be a diagonal matrix.

In that case, a canonical transformation of the  $p^0, q^0$ :

$$\left. \begin{aligned} p' &= S^{-1} p^0 S, \\ q' &= S^{-1} q^0 S \end{aligned} \right\} \quad (5)$$

shall be carried out in such a way that:

$$W = S^{-1} H S \quad (6)$$

becomes a diagonal matrix. Like  $H$ , the transformation matrix  $S$  in this contains only terms that correspond to the transitions between states of the sequence  $n + 1, n + 2, \dots, n + r$  and diagonal terms. The transformation function  $S$  can be found when one seeks to solve the  $r$  equations in  $r$  unknowns:

$$W S_k - \sum_l H_{kl} S_l = 0 \quad (k, l = n + 1, \dots, n + r). \quad (7)$$

These solutions exist for  $r$  different values of  $W$  – viz., the “eigenvalues” of the problem – at the same time as the additional energies of the perturbed system. If an  $*$  means the transition to the complex-conjugate quantities, and  $\sim$  means the exchange of indices then one will have:

<sup>(1)</sup> E. g., by **W. Pauli**, *Zeit. Phys.* **16** (1923), 155; **20** (1924), 371.

<sup>(2)</sup> **M. Born, W. Heisenberg, and P. Jordan**, *Zeit. Phys.* **35** (1926), 557. See, esp., Chap. 3, § 2.

$$\left. \begin{aligned} W_n S_{kn} - \sum_l H_{kl} S_{ln} &= 0, \\ W_n S_{kn}^* - \sum_l H_{kl}^* S_{ln}^* &= 0 \end{aligned} \right\} \quad (8)$$

for any two eigenvalues  $W_n, W_m$ , so:

$$(W_n - W_m) \sum_{k=n+1}^{n+r} S_{kn} S_{km}^* = 0.$$

If one then normalizes by way of:

$$\sum_{k=n+1}^{n+r} S_{kn} S_{kn}^* = 1 \quad (9)$$

then one will have  $S \cdot \tilde{S}^* = 1$ , and  $S$  will be the desired transformation matrix. By substituting this into (5), one will obtain the coordinates of the perturbed system in this approximation.

**§ 3. Performing the calculation.** The application of this process to the problem that is being treated here leads to the following general calculation:

1. Since it does not contain the degenerate coordinates, the part  $H_3$  of the perturbing energy can be ignored at first, and then added in later as an additive constant.

2. From the general rules of quantum mechanics (*loc. cit.*), one has the following relations for the impulse  $\mathfrak{k}$  and  $\mathfrak{s}$  (<sup>1</sup>):

$$\left. \begin{aligned} \mathfrak{k}^2 &= \left( \frac{h}{2\pi} \right)^2 k(k+1), \quad \mathfrak{s}^2 = \left( \frac{h}{2\pi} \right)^2 s(s+1), \\ k_x k_y - k_y k_x &= -\varepsilon k_z \quad \left( \varepsilon = \frac{h}{2\pi i} \right), \\ \text{or, more simply :} \\ [\mathfrak{k} \mathfrak{k}] &= -\varepsilon \mathfrak{k}, \quad [\mathfrak{s} \mathfrak{s}] = -\varepsilon \mathfrak{s} \end{aligned} \right\} \quad (10)$$

(the square brackets mean the vectorial product). Any component of  $\mathfrak{k}$  commutes with any component of  $\mathfrak{s}$ .

If one sets:

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(<sup>1</sup>) In the aforementioned paper, the angular impulse was defined with the opposite sign, so one will have:

$$M_x M_y - M_y M_x = \varepsilon M_z$$

there.

$$k_z = m_k \frac{h}{2\pi}, \quad s_z = m_s \frac{h}{2\pi}$$

then one will have:

$$\left. \begin{aligned} (k_x + ik_y)(k, m_k - 1; k, m_k) &= \frac{h}{2\pi} \sqrt{k(k+1) - m_k(m_k - 1)}, \\ (k_x - ik_y)(k, m_k; k, m_k - 1) &= \frac{h}{2\pi} \sqrt{k(k+1) - m_k(m_k - 1)}, \\ (s_x + is_y)(s, m_s - 1; s, m_s) &= \frac{h}{2\pi} \sqrt{s(s+1) - m_s(m_s - 1)}, \\ (s_x - is_y)(s, m_s; s, m_s - 1) &= \frac{h}{2\pi} \sqrt{s(s+1) - m_s(m_s - 1)}. \end{aligned} \right\} \quad (11)$$

If one now introduces the variable  $m$  in place of  $m_k$  by way of the equation  $m = m_k + m_s$  then  $m_s$  will now be canonically-conjugate to the difference between the “nodal lengths” (*Knotenlängen*) (cf., the calculation in classical mechanics that was cited above) that were canonically-conjugate to  $m_k$  and  $m_s$  up to now. One will then have:

$$H_1 + H_2 = \frac{e}{2mc} \mathfrak{H}(\mathfrak{k} + 2\mathfrak{s}) + \frac{e^2 Z}{2m^2 c^2} \frac{\bar{\Gamma}}{r^3} \cdot \mathfrak{k} \mathfrak{s}. \quad (12)$$

With the abbreviations:

$$\frac{e}{2mc} |\mathfrak{H}| \frac{h}{2\pi} = \mu$$

and

$$\frac{1}{2} \frac{e^2 Z}{m^2 c^2} \frac{\bar{\Gamma}}{r^3} \left( \frac{h}{2\pi} \right)^2 = \lambda,$$

it follows that:

$$H_1 + H_2 = m (k_z + 2s_z) + \lambda [k_z s_z + \frac{1}{2} (k_x + i k_y) (s_x - is_y) + \frac{1}{2} (k_x - i k_y) (s_x + is_y)]$$

and

$$\left. \begin{aligned} (H_1 + H_2)(m_s, m_s) &= \mu(m + m_s) + \lambda m_s (m - m_s), \\ (H_1 + H_2)(m_s, m_s - 1) &= \frac{1}{2} \lambda \sqrt{[s(s+1) - m_s(m_s - 1)][k(k+1) - (m - m_s)(m - m_s + 1)]}, \\ (H_1 + H_2)(m_s - 1, m_s) &= \frac{1}{2} \lambda \sqrt{[s(s+1) - m_s(m_s - 1)][k(k+1) - (m - m_s)(m - m_s + 1)]}. \end{aligned} \right\} \quad (13)$$

The indices  $m, k, s$  can be omitted as constants on the left-hand sides of these equations.

3. The number of values of  $m_s$  that belongs to a given system of values  $k, s, m$  are determined by the conditions:

$$\left. \begin{array}{l} -s \leq m_s \leq +s \\ \text{and} \\ -k \leq m - m_s \leq +k \\ \text{or} \\ k + m \geq m_s \geq -k + m. \end{array} \right\} \quad (14)$$

One obtains the transformation function  $S$  from (7) by solving the linear equations:

$$W S_r - \sum H_{rl} S_l = 0, \quad (15)$$

in which the indices  $r l$  run through all values of  $m_s$  that are possible for a given system of values  $k, s, m$ . The eigenvalues of  $W$  are obtained by setting the determinant whose terms are  $\delta_{rl} W - H_{rl}$  equal to zero. If one lets  $m_1$  denote the smallest value of  $m_s$  that is possible for given  $k, s, m$ , and lets  $m_2$  denote the smallest one then that will yield equation (16) (<sup>†</sup>):

$$0 = \begin{vmatrix} W - \mu(m + m_1) - \lambda m_1(m - m_1) & \tilde{H}_{12} & 0 & 0 & \dots & 0 \\ \tilde{H}_{12} & W - \mu(m + m_1 + 1) - \lambda(m_1 + 1)(m - m_1 - 1) & \tilde{H}_{23} & 0 & \dots & 0 \\ 0 & \tilde{H}_{23} & W - (\dots) & \tilde{H}_{34} & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{vmatrix}, \quad (16)$$

in which:

$$\begin{aligned} \tilde{H}_{12} &= -\frac{1}{2} \lambda \sqrt{[s(s+1) - m_1(m_1+1)][k(k+1) - (m-m_1)(m-m_1-1)]}, \\ \tilde{H}_{23} &= -\frac{1}{2} \lambda \sqrt{[s(s+1) - (m_1+1)(m_1+2)][k(k+1) - (m-m_1-1)(m-m_1-2)]}, \\ \tilde{H}_{34} &= \text{etc.} \end{aligned}$$

We thus have an algebraic equation of degree  $m_2 - m_1 + 1$  for  $W$  with rational coefficients in  $k, s, m$ . The sum of the roots is equal to the negative coefficients of the second terms, and is then given by:

$$\sum_{n=m_1}^{m_2} W_n = \sum_{n=m_1}^{m_2} \mu(m + m_1) + \lambda m_1(m - m_1). \quad (17)$$

The fact that the sum  $\sum_{n=m_1}^{m_2} W_n$  is linear in  $\lambda$  and  $\mu$  is a statement of the so-called “summation principle” of the Zeeman effect.

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[<sup>†</sup>] Translator’s note: The original equation (16) was displayed in landscape mode, not portrait mode, so it was reset.

4. In order to be able to pursue the result of the quantum-mechanical calculation in all of its details, it will be preferable to examine a special example. We choose the *doublet* model; i.e.,  $s = 1/2$ .

The possible values of  $m_s$  here are  $\pm\frac{1}{2}$ , in general, so for  $m = k + \frac{1}{2}$ ,  $m_s$  will be capable of assuming only the value  $+\frac{1}{2}$ , while for  $m = k - \frac{1}{2}$ ,  $m_s$  will be capable of assuming only the value  $-\frac{1}{2}$ . In general, the equation:

$$\begin{vmatrix} W - \mu(m - \frac{1}{2}) + \lambda(m + \frac{1}{2})\frac{1}{2} & -\frac{1}{2}\lambda\sqrt{k(k+1) - (m + \frac{1}{2})(m - \frac{1}{2})} \\ -\frac{1}{2}\lambda\sqrt{k(k+1) - (m + \frac{1}{2})(m - \frac{1}{2})} & W - \mu(m + \frac{1}{2}) - \lambda(m - \frac{1}{2}) \end{vmatrix} = 0 \quad (18)$$

will then enter in place of (16), or:

$$W^2 - \left(2\mu m - \frac{\lambda}{2}\right)W + \mu^2(m^2 - \frac{1}{4}) - \mu\lambda \cdot m - \frac{\lambda^2}{4}k(k+1) = 0, \quad (19)$$

$$W = \mu m - \frac{\lambda}{4} \pm \frac{1}{2}\sqrt{\mu^2 + 2\mu\lambda \cdot m + \lambda^2(k + \frac{1}{2})^2}. \quad (20)$$

By contrast, for  $m = k + \frac{1}{2}$ , one gets  $m_s = \frac{1}{2}$  and:

$$W = \mu(m + \frac{1}{2}) + \frac{\lambda}{2}(m - \frac{1}{2}), \quad (21)$$

while for  $m = -k - \frac{1}{2}$ , it will follow that  $m_s = -\frac{1}{2}$  and:

$$W = \mu(m - \frac{1}{2}) - \frac{\lambda}{2}(m + \frac{1}{2}). \quad (22)$$

If one introduces the abbreviation:

$$v = \frac{\lambda}{\mu}(k + \frac{1}{2})$$

then one will have:

$$\left. \begin{aligned}
 W &= \mu \left( m - \frac{v}{k + \frac{1}{2}} \pm \sqrt{1 + 2 \frac{m}{k + \frac{1}{2}} v + v^2} \right), \\
 W_{m=k+1/2} &= \mu \left[ m \left( 1 + \frac{v}{2k+1} \right) - \frac{v}{k + \frac{1}{2}} + \frac{1}{2} \right] \\
 &= \mu \left[ k + 1 + v \left( \frac{1}{2} - \frac{1}{k + \frac{1}{2}} \right) \right], \\
 W_{m=-k-1/2} &= \mu \left[ m \left( 1 - \frac{v}{2k + \frac{1}{2}} \right) - \frac{v}{k + \frac{1}{2}} - \frac{1}{2} \right] \\
 &= \mu \left[ -k - 1 + v \left( \frac{1}{2} - \frac{1}{k + \frac{1}{2}} \right) \right].
 \end{aligned} \right\} \quad (23)$$

Equations (23) agree with the doublet formulas in **Voigt's** well-known theory of coupling <sup>(1)</sup>.

5. We now go on to the calculation of the intensities. In order to determine the transformation function  $S$ , we solve the equation:

$$W S_{-1/2} - (H_1 + H_2) \left( -\frac{1}{2}, -\frac{1}{2} \right) S_{-1/2} - (H_1 + H_2) \left( -\frac{1}{2}, +\frac{1}{2} \right) S_{+1/2} = 0. \quad (24)$$

That yields:

$$\left. \begin{aligned}
 S_{+1/2} &= C \cdot \left( W - \mu \left( m - \frac{1}{2} \right) + \frac{\lambda}{2} \left( m + \frac{1}{2} \right) \right), \\
 S_{-1/2} &= C \cdot \frac{\lambda}{2} \sqrt{k(k+1) - \left( m^2 - \frac{1}{4} \right)},
 \end{aligned} \right\} \quad (25)$$

in which  $C$  represents an arbitrary constant, at first. If one again distinguishes between the two values of  $W$ :

$$\text{“}W_{+1/2}\text{”} \quad \text{and} \quad \text{“}W_{-1/2}\text{”}$$

then it will follow that:

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<sup>(1)</sup> Cf., e.g., **A. Sommerfeld**, *Zeit. Phys.* **8** (1922), 257.

$$\left. \begin{aligned}
 S_{+\frac{1}{2},+\frac{1}{2}} &= C_{+\frac{1}{2}} \cdot \left( W_{+\frac{1}{2}} - \mu(m - \frac{1}{2}) + \frac{\lambda}{2}(m + \frac{1}{2}) \right) \\
 &= \frac{1}{2} C_{+\frac{1}{2}} \left( \mu + \lambda m + \sqrt{\mu^2 + 2\lambda\mu m + \lambda^2(k + \frac{1}{2})^2} \right), \\
 S_{+\frac{1}{2},-\frac{1}{2}} &= C_{+\frac{1}{2}} \frac{\lambda}{2} \sqrt{k(k+1) - (m^2 - \frac{1}{4})}, \\
 S_{-\frac{1}{2},-\frac{1}{2}} &= \frac{1}{2} C_{-\frac{1}{2}} \cdot \left( \mu + \lambda m - \sqrt{\mu^2 + 2\lambda\mu m + \lambda^2(k + \frac{1}{2})^2} \right), \\
 S_{-\frac{1}{2},+\frac{1}{2}} &= C_{-\frac{1}{2}} \frac{\lambda}{2} \sqrt{k(k+1) - (m^2 - \frac{1}{4})}.
 \end{aligned} \right\} \quad (26)$$

If finally follows from the normalization condition (9) that:

$$\left. \begin{aligned}
 |C_{+\frac{1}{2}}| &= \frac{1}{\sqrt{\frac{1}{2}(\mu + \lambda m + \sqrt{\mu^2 + 2\lambda\mu m + \lambda^2(k + \frac{1}{2})^2}) \cdot \sqrt{\mu^2 + 2\lambda\mu m + \lambda^2(k + \frac{1}{2})^2}}}, \\
 |C_{-\frac{1}{2}}| &= \frac{1}{\sqrt{\frac{1}{2}(-\mu - \lambda m + \sqrt{\mu^2 + 2\lambda\mu m + \lambda^2(k + \frac{1}{2})^2}) \cdot \sqrt{\mu^2 + 2\lambda\mu m + \lambda^2(k + \frac{1}{2})^2}}}.
 \end{aligned} \right\} \quad (27)$$

For the special case  $m = \pm(k + \frac{1}{2})$ , that will naturally yield [cf., (21) and (22)]:

$$\left. \begin{aligned}
 S_{+\frac{1}{2},+\frac{1}{2}} &= 1, & S_{+\frac{1}{2},-\frac{1}{2}} &= 0, \\
 S_{-\frac{1}{2},-\frac{1}{2}} &= 1, & S_{-\frac{1}{2},+\frac{1}{2}} &= 0,
 \end{aligned} \right\} \quad (28)$$

since no degeneracy is present here.

The actual calculation of the intensities now comes about by substituting (26), (27), (28) in the transformation (5). The solutions of the unperturbed system are to be used for  $p^0$ ,  $q^0$ . In that, we must observe that the coordinates  $q^0$  of the electron are diagonal matrices relative to  $m_s$ .

Moreover, it suffices to consider the transition  $k \rightarrow k - 1$ , since the transition  $k \rightarrow k + 1$  will give nothing new.

We deduce from the work of **Born, Heisenberg, and Jordan** [*loc. cit.*, Chap. 4, eq. (33)] that:

$$\left. \begin{aligned}
 q_z^0(k, m, m_s; k-1, m, m_s) &= A(k) \sqrt{k^2 - (m - m_s)^2}, \\
 (q_x^0 + iq_y^0)(k, m-1, m_s; k-1, m, m_s) &= A(k) \sqrt{(k - m + m_s)(k - m + m_s + 1)}, \\
 (q_x^0 - iq_y^0)(k, m, m_s; k-1, m-1, m_s) &= A(k) \sqrt{(k + m - m_s)(k + m - m_s - 1)}.
 \end{aligned} \right\} \quad (29)$$

$A(k)$  means a quantity that depends upon only  $k$ .

One will obtain the desired intensities by substituting (26) to (29) into (5) and elementary computations. However, the general formulas are rather complicated. In

what follows, we will give the result for the special case of the  $D$  line type, and thus consider the transition  $k = 1 \rightarrow k = 0$ . From (5), that will yield:

$$\left. \begin{aligned}
 |q'_z|^2(1, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}) &= \frac{1}{2} |A^2(1)| \left( 1 + \frac{\mu + \frac{1}{2}\lambda}{\sqrt{\mu^2 + \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_z|^2(1, \frac{1}{2}, -\frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}) &= \frac{1}{2} |A^2(1)| \left( 1 - \frac{\mu + \frac{1}{2}\lambda}{\sqrt{\mu^2 + \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_z|^2(1, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}) &= \frac{1}{2} |A^2(1)| \left( 1 + \frac{\mu + \frac{1}{2}\lambda}{\sqrt{\mu^2 + \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_z|^2(1, -\frac{1}{2}, -\frac{1}{2}; 0, -\frac{1}{2}, -\frac{1}{2}) &= \frac{1}{2} |A^2(1)| \left( 1 - \frac{-\mu + \frac{1}{2}\lambda}{\sqrt{\mu^2 - \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_x + iq'_y|^2(1, -\frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}; \frac{1}{2}) &= |A^2(1)| \left( 1 + \frac{\mu - \frac{1}{2}\lambda}{\sqrt{\mu^2 - \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_x + iq'_y|^2(1, -\frac{1}{2}, -\frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}) &= |A^2(1)| \left( 1 - \frac{\mu - \frac{1}{2}\lambda}{\sqrt{\mu^2 - \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_x + iq'_y|^2(1, -\frac{3}{2}, \frac{1}{2}; 0, -\frac{1}{2}, -\frac{1}{2}) &= |A^2(1)| \cdot 2, \\
 |q'_x - iq'_y|^2(1, \frac{3}{2}, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}) &= |A^2(1)| \cdot 2, \\
 |q'_x - iq'_y|^2(1, \frac{1}{2}, \frac{1}{2}; 0, -\frac{1}{2}, -\frac{1}{2}) &= |A^2(1)| \left( 1 - \frac{\mu + \frac{1}{2}\lambda}{\sqrt{\mu^2 + \lambda\mu + \frac{9}{4}\lambda^2}} \right), \\
 |q'_x - iq'_y|^2(1, +\frac{1}{2}, -\frac{1}{2}; 0, +\frac{1}{2}, -\frac{1}{2}) &= |A^2(1)| \left( 1 + \frac{\mu + \frac{1}{2}\lambda}{\sqrt{\mu^2 + \lambda\mu + \frac{9}{4}\lambda^2}} \right).
 \end{aligned} \right\} \quad (30)$$

These intensity formulas also agree with the ones that are derived in **Voigt's** theory (cf., **A. Sommerfeld**, *loc. cit.*, pp. 286).

**§ 4. Special treatment of the limiting cases  $\lambda \ll \mu$  and  $\mu \ll \lambda$ .** In order to ease the comparison of the empirical results with the theory, it will be convenient to derive the results of the theory for the special cases  $\lambda \ll \mu$  and  $\lambda \gg \mu$ , especially. The limiting case  $\lambda \ll \mu$  can be obtained from the calculations of the previous section with no further assumptions. For example, in the first approximation (up to quantities of order  $\lambda^2$ ), the determinant (16) will decompose into the product of diagonal terms, and one will have:

$$W = (H_1 + H_2) (m_s, m_s).$$

However, in order to calculate the limiting case  $\mu \ll \lambda$ , some new analysis will be necessary. We next set  $\mu = 0$ ; we will then have  $H_1 = 0$ , and a term that is proportional to  $\mathfrak{k} \mathfrak{s}$  will remain in  $H_2$ . It will now be convenient to introduce the total impulse  $\mathfrak{M}$  of the atoms:

$$\mathfrak{M} = \mathfrak{k} + \mathfrak{s}.$$

Due to the commutability of  $\mathfrak{k}$  and  $\mathfrak{s}$ , one will then have:

$$\mathfrak{M}^2 = \mathfrak{k}^2 + \mathfrak{s}^2 + 2 \mathfrak{k} \mathfrak{s}. \quad (31)$$

Since, on the other hand:

$$\mathfrak{M}^2 = \left( \frac{h}{2\pi} \right)^2 j(j+1),$$

one will have:

$$\left. \begin{aligned} \left( \frac{2\pi}{h} \right)^2 \mathfrak{k} \mathfrak{s} &= \frac{1}{2} [j(j+1) - k(k+1) - s(s+1)], \\ \text{and} \\ H_2 &= \frac{1}{2} \lambda [j(j+1) - k(k+1) - s(s+1)]. \end{aligned} \right\} \quad (32)$$

$H$  is a diagonal matrix as a function of  $j$ .

For small values of  $\mu$ , we can now consider the system that is characterized by (32) to be “unperturbed.” In the unperturbed system, the atom will then exhibit a precession around the axis of the total impulse. The energy values of the perturbed system are given by the temporal mean of  $H_1$  over the unperturbed motion. If one thinks of  $\mathfrak{k}$  and  $\mathfrak{s}$  as having been decomposed into a component that is parallel to  $\mathfrak{M}$  and one that is perpendicular to it then the latter will drop out, because of precisely that precession, and only the former will contribute to  $H_1$ .

We can adapt this line of reasoning, which is borrowed from classical mechanics, to quantum mechanics, since all of the quantities that come under consideration commute.

In the direction of  $\mathfrak{M}$ , one takes the:

$$(\text{component of } \mathfrak{k}) = \frac{(\mathfrak{M} \cdot \mathfrak{k})}{\mathfrak{M}^2} \cdot \mathfrak{M}$$

and the

$$(\text{component of } \mathfrak{s}) = \frac{(\mathfrak{M} \cdot \mathfrak{s})}{\mathfrak{M}^2} \cdot \mathfrak{M},$$

so

$$\left. \begin{aligned}
 \bar{H}_1 &= \frac{e}{2mc} \mathfrak{H} \cdot \mathfrak{M} \left( \frac{(\mathfrak{M}_x)}{\mathfrak{M}^2} + 2 \frac{(\mathfrak{M}_s)}{\mathfrak{M}^2} \right) \\
 &= \frac{e}{2mc} \mathfrak{H} \cdot \mathfrak{M} \left( 1 + \frac{(\mathfrak{M}_s)}{\mathfrak{M}^2} \right) \\
 &= \mu \cdot m \left( 1 + \frac{j(j+1) - k(k+1) + s(s+1)}{2j(j+1)} \right),
 \end{aligned} \right\} \quad (33)$$

so finally, one will generally have for  $\mu \ll \lambda$ :

$$\overline{H_1 + H_2} = \mu \cdot m \left( 1 + \frac{j(j+1) - k(k+1) + s(s+1)}{2j(j+1)} \right) + \frac{1}{2} \lambda (j(j+1) - k(k+1) - s(s+1)). \quad (34)$$

Equation (34) agrees with the **Landé** formula (the values of  $g$  and  $\gamma$  are “interval proportions”).

**§ 5. Calculation of the fine structure with no field.** The calculations up to now have generally provided the proof that the **Uhlenbeck-Goudsmi**t hypothesis will lead to the Zeeman effect, as well as the interval proportions that agree with experiments.

In order to resolve the question of whether the hypothesis that we have established also leads to the correct absolute values of the intervals, the values of  $\lambda$  and  $H_3$  will still need to be calculated.

One then deals with the mean values:

$$\frac{\bar{l}}{r}, \quad \frac{\bar{l}}{r^2}, \quad \frac{\bar{l}}{r^3},$$

in the calculations. We will base that calculation on the two-dimensional hydrogen atom <sup>(1)</sup>; one then has:

$$H_0 = \frac{1}{2m} (p_x^2 + p_y^2) - \frac{e^2 Z}{r}$$

for the energy of the unperturbed atom and:

$$\left. \begin{aligned}
 p_x x - x p_x &= \frac{h}{2\pi i}, & p_y y - y p_y &= \frac{h}{2\pi i}, \\
 xy - yx &= 0, & p_x p_y - p_y p_x &= 0.
 \end{aligned} \right\} \quad (35)$$

If one introduces polar coordinates by way of the formulas:

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<sup>(1)</sup> The exact calculations of the mean values for the three-dimensional case were carried out by **W. Pauli** and gave the same result as the calculations above.

$$\left. \begin{aligned} r^2 = x^2 + y^2, \quad p_r = m\dot{r}, \quad \varphi = \arctan \frac{y}{x}, \\ p_\varphi = m(x\dot{y} - y\dot{x}) = mr^2\dot{\varphi} \end{aligned} \right\} \quad (36)$$

then one will have:

$$\left. \begin{aligned} H_0 = \frac{1}{2m} \left[ p_r^2 + \frac{1}{r^2} \left( p_\varphi^2 - \frac{1}{4} \left( \frac{h}{2\pi} \right)^2 \right) \right] - \frac{e^2 Z}{r}, \\ p_r r - r p_r = \frac{h}{2\pi i}, \quad p_\varphi \varphi - \varphi p_\varphi = \frac{h}{2\pi i}, \\ r\varphi - \varphi r = 0, \quad p_r p_\varphi - p_\varphi p_r = 0. \end{aligned} \right\} \quad (36a)$$

According to the repeatedly-cited paper “Quantenmechanik II” [pp. 600, equation (17)],  $p_\varphi$  is quantized:

$$p_\varphi = m_0 \frac{h}{2\pi},$$

in which we assume that  $m_0$  is a half-integer, in order to come into harmony with **Pauli**'s results (*loc. cit.*), and in fact  $m_0 - \frac{1}{2}$  will be identical with the  $k$  that was introduced above. Namely, for **Pauli**, the Hamiltonian function for the three-dimensional problem has the form:

$$H_0 = \frac{1}{2m} \left( p_r^2 + \frac{1}{r} \hbar^2 \right) - \frac{e^2 Z}{r}. \quad (37)$$

If one would like to bring (36a) and (37) into agreement then it will follow that:

$$k^2 = \left( \frac{h}{2\pi} \right)^2 k(k+1) = p_\varphi^2 - \frac{1}{4} \left( \frac{h}{2\pi} \right)^2 = \left( \frac{h}{2\pi} \right)^2 \left( m_0^2 - \frac{1}{4} \right).$$

The mean value  $\overline{\frac{1}{r}}$  next gives from the equation [“Quantenmechanik II,” pp. 577, equation (17)]:

$$-\frac{\overline{Ze^2}}{r} = \overline{E_{\text{pot}}} = -2\overline{E_{\text{kin}}} = 2W_0. \quad (38).$$

In this, one has:

$$W_0 = H_0 = -\frac{R h Z^2}{n^2},$$

in which  $n$  means a whole number. Furthermore, according to **Pauli**, one concludes from the equations of motion that:

$$\frac{d}{dt} p_r = -\frac{\partial H_0}{\partial r} = -\frac{1}{mr^3} \left[ p_\phi^2 - \frac{1}{4} \left( \frac{h}{2\pi} \right)^2 \right] + \frac{e^2 Z}{r^2}; \quad (39)$$

hence, in the temporal mean:

$$\frac{\overline{e^2 Z}}{r^2} = \frac{1}{mr^3} \cdot \left[ \overline{p_\phi^2} - \frac{1}{4} \left( \frac{h}{2\pi} \right)^2 \right]. \quad (40)$$

Finally, from (36), one has:

$$\left. \begin{aligned} mr^2 \dot{\phi} &= p_\phi, \\ \frac{p_\phi}{mr^2} &= \dot{\phi}. \end{aligned} \right\} \quad (41)$$

If one now introduces the angle variable that is conjugate to the principal quantum number (to the corresponding angle variable  $J = n h$ , resp.) <sup>(1)</sup> then, analogous to the classical theory, one will have:

$$\dot{\phi} = 2\pi \dot{w} = -2\pi \frac{\partial H_0}{\partial J} = + \frac{4\pi RZ^2}{n^3}. \quad (42)$$

Finally, equations (38), (40), (41), and (42), with the use of the relation  $p_\phi = \frac{h}{2\pi} (k + \frac{1}{2})$ , yield:

$$\left. \begin{aligned} \frac{1}{r} &= \frac{1}{e^2} \cdot \frac{2RhZ}{n^2}, \\ \frac{1}{r^2} &= \frac{m}{p_\phi} \cdot \dot{\phi} = \frac{m}{\frac{h}{2\pi} (k + \frac{1}{2})} \cdot \frac{4\pi RZ^2}{n^3} = \frac{8\pi^2 RZ^2}{h(k + \frac{1}{2})n^3}, \\ \frac{1}{r^3} &= \frac{1}{r^2} \cdot \frac{e^2 Z m}{p_\phi^2 - \frac{1}{4} \left( \frac{h}{2\pi} \right)^2} = \frac{m^2 e^2 RZ^3 \cdot 32\pi^4}{k(k + \frac{1}{2})(k + 1)n^3 h^3}. \end{aligned} \right\} \quad (43)$$

In the absence of an external magnetic field, from (2) to (4), (34), and (43), the total perturbing energy will be given by:

<sup>(1)</sup> The justification for the introduction of such a variable is proved in the paper of **Born and Wiener** [Zeit. Phys. **36** (1926), 174] and the paper by **Dirac** that was cited above.

$$\left. \begin{aligned}
 H_2 + H_3 &= \frac{1}{2} \frac{e^2 Z}{m^2 c^2} \cdot \frac{4\pi^2 m^2 e^2 R Z^3 (j(j+1) - k(k+1) - s(s+1))}{hk(k + \frac{1}{2})(k+1)n^3} \\
 &\quad - \frac{1}{2mc^2} \left( -\frac{3R^2 h^2 Z^4}{n^4} + \frac{8\pi^2 m e^4 R Z^4}{h(k + \frac{1}{2})n^3} \right) \\
 &= \frac{2R^2 h^2 Z^4}{n^3 m c^2} \left( \frac{j(j+1) - k(k+1) - s(s+1)}{2k(k + \frac{1}{2})(k+1)} - \frac{1}{k + \frac{1}{2}} + \frac{3}{4n} \right).
 \end{aligned} \right\} \quad (44)$$

A precise, empirical test of this formula is possible for doublet atoms ( $s = 1 / 2$ ) – e.g., for the hydrogen, alkali, and Röntgen spectrum: Experimentally, (if one neglects the mutual interaction of the electrons), two energy levels with *different*  $k$ , but *equal*  $j$  will coincide. The distance between two levels of equal  $k$  and different  $j$  will be given by the **Sommerfeld** fine structure formula.

The values  $s = \frac{1}{2}$ ,  $j = k \pm \frac{1}{2}$  must be substituted in equation (44); that will yield:

$$\left. \begin{aligned}
 &\text{for } k = j - \frac{1}{2}: \\
 H_2 + H_3 &= \frac{2R^2 h^2 Z^4}{n^3 m c^2} \left( \frac{1}{2j(j + \frac{1}{2})} - \frac{1}{j} + \frac{3}{4n} \right) \\
 &= \frac{2R^2 h^2 Z^4}{n^3 m c^2} \left( -\frac{1}{j + \frac{1}{2}} + \frac{3}{4n} \right), \\
 &\text{for } k = j + \frac{1}{2}: \\
 H_2 + H_3 &= \frac{2R^2 h^2 Z^4}{n^3 m c^2} \left( -\frac{1}{2(j + \frac{1}{2})(j+1)} - \frac{1}{j+1} + \frac{3}{4n} \right) \\
 &= \frac{2R^2 h^2 Z^4}{n^3 m c^2} \left( -\frac{1}{j + \frac{1}{2}} + \frac{3}{4n} \right).
 \end{aligned} \right\} \quad (45)$$

Thus, in general, for  $s = \frac{1}{2}$ :

$$H_2 + H_3 = \frac{2R^2 h^2 Z^4}{n^3 m c^2} \left( -\frac{1}{j + \frac{1}{2}} + \frac{3}{4n} \right). \quad (46)$$

Formula (46) reproduces the facts of experiment completely. In particular, it follows from the absence of  $k$  in equation (46) that the “screening doublets” can be explained by the **Uhlenbeck-Goudsmit** theory. Moreover, the splitting of the magnetic doublet agrees with the one that is obtained from the **Sommerfeld** fine structure formula.

Whether or not the question of how far the basic assumptions (2) to (4) in the theory is presented here are free of arbitrariness can still not be decided, but one can still regard the results of our calculations as important support for the **Compton-Uhlenbeck-Goudsmit** hypothesis, on the one hand, and quantum mechanics, on the other.