ON THE THEORY OF DIAMAGNETISM*

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Abstract

Relations between the Weber-Langevin theory and that of Pauli. The first theory gives a band for the Zeeman effect; the second, which is based on Larmor precession, gives sharp lines, as is known. The susceptibilities, K_1 and K_2, are different except when the orbits are normal to the intensity H of the magnetic field. When they are parallel to H, K_1 vanishes and K_2 is half that for the normal orbits, an extreme case. In the simplest case, viz., that of coplanar orbits, the ratio of the susceptibility K_R for random orientation of the orbits to that K_P for similar orientation with all orbital axes parallel to H is 1/3 by the first theory, and 2/3 by the second. In the general case of Pauli's theory $K_R/K_P = 2/3 \times$(ratio of total "quadrupolmoment" to quadrupolmoment normal to A), where A designates a principal atomic axis, which may be normal to no orbit, and K_P the susceptibility when A is parallel to H. In the general case of random orientation $K_2/K_1 = 2$. *Molecular magnetic orientation.* In 1910 Langevin showed that the magnetic field tends to orient unsymmetrical diamagnetic atoms, so as to make the magnitude of the extraneous flux through the orbits a minimum. The general law is similar to that for magnetic double-refraction, alignment approaching completeness and diamagnetic susceptibility approaching a minimum as H increases and temperature decreases. Thus this theory cannot explain the recent results of Glaser on the variation of susceptibility with pressure; it is suggested that these may possibly be due to a quantization resulting from the weak magnetic moment produced according to either theory in an intense field. *Larmor precession* of a diamagnetic atom is shown to be independent of orbital motions and due to the same cause as Weber's rotations.

1. This paper derives briefly some fundamental relations between the theories developed by W. Weber and Langevin,[1] which are almost identical, and the recent theory of Pauli.[2] These theories and the relations between them are often misunderstood. Thus it has been stated that the theories of Weber and Langevin give different results for the Zeeman effect, while those of Langevin and Pauli agree; also that the two latter give the same value for the susceptibility. All of these statements are quite incorrect. The paper also calls attention to an addition by Langevin to the theory which is of interest in connection with recent experiments and possible future experiments on diamagnetism and atomic structure, and it gives a simple theory of Larmor precession.

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[1] Langevin, Ann. de Chim. et de Phys., 1905.

[2] Pauli, Zeits. f. Phys. **2**, 201 (1920)

2. Consider a circular groove or electron orbit, with radius a, in which an electron with charge e and mass m can move (Weber 1852) or does move (Weber 1871, Langevin 1905) with frequency n revolutions per second. If the plane of the orbit remains fixed while there is impressed a magnetic field whose intensity H makes an angle θ with the axis of the orbit (and its magnetic moment M if there is originally motion), the frequency of the orbital motion will increase, as follows both from the equations of Weber and from those of Langevin, by the quantity

$$\Delta n = -(eH/4\pi mc)\cos\theta, \tag{1}$$

which is independent of the original frequency. This produces an increase ΔM in the magnetic moment of the orbit such that

$$\Delta M = -(e^2a^2/4mc^2)H\cos\theta, \tag{2}$$

whose component in the direction of H is

$$\Delta M_H = -(e^2a^2/4mc^2)H\cos^2\theta.$$

An atom for all of whose orbits together ΣM is initially zero is a diamagnetic atom. It is easy to conceive a diamagnetic atom such that $\Sigma\Delta M$ and $\Sigma\Delta M_H$ are independent of the orientation in the field. In general, however, the magnitude of $\Sigma\Delta M_H$ for either a magnetic or a diamagnetic atom will be a maximum when a definite atomic axis A is parallel to H.

If all the orbits in an atom are parallel (normal to A) and all the atoms oriented with A parallel to H, each orbit contributes to the resultant moment the maximum amount

$$\Delta M_0 = -e^2a^2H/4mc^2; \tag{3}$$

while, if all the orbits are parallel to H,

$$\Delta M_H = \Delta M = 0 \tag{4}$$

for each orbit.

If the atoms in any case are distributed at random, the average contribution of an orbit is

$$\Delta M = -\tfrac{1}{3}e^2\overline{a^2}H/4mc^2 \tag{5}$$

since the mean value of $\cos^2\theta$ is now $\frac{1}{3}$.

Thus the ratio of the susceptibility in the third case to that in the first is 1/3, as shown by both Weber and Langevin. If all the orbits in the atom are not parallel, the ratio of the susceptibility for random distribution to that when A for each atom is parallel to H is clearly greater than 1/3, and becomes unity when the atom is completely symmetrical.

3. The theory of Pauli, unlike that of Weber and Langevin, is based on Larmor precession, of the simplest type, and therefore is applicable only to monatomic gases. According to Larmor's theorem, an atom with any number of electron orbits when placed in a magnetic field precesses

around an axis B through the nucleus and parallel to the field intensity, with the angular velocity, in revolutions per second,

$$\Delta n = -eH/4\pi cm. \tag{6}$$

The moment $\Delta M_H = \Delta M$ contributed by the electron orbit of Section 2 can be found, on this theory, as follows. Let ρ denote the perpendicular distance from the electron to the axis B. Then the mean areal velocity of e about B is

$$\tfrac{1}{2} \cdot 2\pi\Delta n \cdot \overline{\rho^2},$$

whose product by e gives the mean value of the moment, viz.,

$$\Delta M = -e^2H\overline{\rho^2}/4mc^2. \tag{7}$$

This is identical with the moment which would be produced by distributing the charge e uniformly over the orbit and rotating the circle about B with the velocity Δn.

When $\theta = 0$, $\rho^2 = a^2$, and

$$\Delta M = \Delta M_0, \tag{8}$$

the value given by the Weber-Langevin theory.

When $\theta = \pi/2$, $\overline{\rho^2} = a^2/2$. Thus in this case

$$\Delta M = \tfrac{1}{2} \cdot \Delta M_0. \tag{9}$$

For random distribution, the mean moment produced is the same as if the charge e were uniformly distributed over the sphere of radius a and the sphere rotated about B with the velocity Δn. Thus in this case

$$\Delta M = \tfrac{2}{3} \cdot \Delta M_0 \tag{10}$$

4. In order to proceed to more general results, let us now, with Pauli, assume three rectangular axes X', Y', Z', fixed in the atom, the origin coinciding with the nucleus; let us assume Z' to coincide with the axis A, and X' and Y' with the principal axes normal to A. Let the coordinates of an electron with reference to these axes be denoted by x', y', z'. Then, by definition, Debye's principal "quadrupolmoments" of the atomic electron system are

$$\theta_1 = \Sigma\overline{ex'^2}\,,\ \theta_2 = \Sigma\overline{ey'^2}\,,\ \theta_3 = \Sigma \cdot \overline{ez'^2}\,. \tag{11}$$

Further, let X, Y, Z be a rectangular coordinate system fixed in space in which the nucleus is at the origin and Z coincides in direction with H. In this system let x, y, z denote the electron coordinates. Let the direction cosines of X', Y', Z' with respect to Z be denoted by α, β, γ, and let the distance of an electron from the origin be denoted by R. Then we have, with Pauli,

$$z = x'\alpha + y'\beta + z'\gamma\ ,\quad \Sigma e\overline{R^2} = \theta_1 + \theta_2 + \theta_3 = \theta\ ,$$

and

$$\Sigma e\overline{\rho^2} = \theta - \Sigma e\overline{z^2} = \theta - (\theta_1\alpha^2 + \theta_2\beta^2 + \theta_3\gamma^2)$$

where ρ has the same significance as in Section 3.

(1) Suppose the atoms all aligned in such a way that A is parallel to H ($\alpha=\beta=0$, $\gamma=1$). In this case

$$\Sigma\overline{e\rho^2}=\theta-\theta_3=\theta_1+\theta_2 \tag{12}$$

(2) Suppose the atoms oriented at random ($\overline{\alpha^2}=\overline{\beta^2}=\overline{\gamma^2}=\frac{1}{3}$). Then (Pauli)

$$\Sigma\overline{e\rho^2}=\theta-\tfrac{1}{3}\theta=\tfrac{2}{3}\theta\ . \tag{13}$$

Thus the ratio σ of the susceptibility for random distribution to that for alignment is

$$\sigma=\tfrac{2}{3}\theta/(\theta_1+\theta_2)=\tfrac{2}{3}(\theta_1+\theta_2+\theta_3)/(\theta_1+\theta_2). \tag{14}$$

For coplanar orbits $\theta_3=0$, so that

$$\sigma=\tfrac{2}{3} \tag{15}$$

as in the simple case considered in Section 3. This is evidently the minimum possible value of σ on this theory. The maximum value, attained when the atom is completely symmetrical ($\theta_1=\theta_2=\theta_3$), is unity.

From what precedes it is also evident that for circular orbits and random distribution the susceptibility according to Pauli is twice that according to Weber and Langevin.

5. In a recent paper[3] A. Glaser has obtained the very interesting result, if his interpretation of his experimental work is correct, that the molecular susceptibilities of certain diamagnetic gases at somewhat reduced pressures become three times as great as at atmospheric pressure. This result could not be predicted on the unmodified theory of Pauli, which applies only to monatomic gases, and could be accounted for on the Weber-Langevin theory only by assuming coplanar orbits, which are far from probable, and complete alignment, a reason for which is not manifest.

6. It is of interest to consider whether alignment could not be produced by the action of the magnetic field on diamagnetic atoms which are not completely symmetrical and in which there is an axis A (Section 2). If the magnetic moment is M_1H when a field is impressed with H parallel to A, and M_2H (for simplicity assumed identical for all directions normal to A) when H is normal to A, it is easily shown that when the axis A makes an angle θ with H there is a torque

$$T=-\tfrac{1}{2}(M_1-M_2)H^2\sin 2\theta \tag{16}$$

tending to set A normal to H, or to make the magnitude of the extraneous magnetic flux through the atom as small as possible. The equations are quite similar to those for the magnetic torque upon a paramagnetic or diamagnetic crystal sphere, and the general law for the action of the

[3] A. Glaser, Ann. der Phys. **75**, 459 (1924)

field toward producing alignment is similar to that developed by Langevin[4] to account for magnetic and electric double-refraction. The alignment approaches completeness, and the susceptibility a minimum (in magnitude) as the strength of the field increases and the temperature decreases. The expression derived by Langevin for the alteration of susceptibility with alignment indicates, however, that even in the most intense fields available the effect must be extremely minute except at temperatures very close to absolute zero. From the standpoint of this theory, experiments on the susceptibility of diamagnetic substances, gases in particular, as a function of the temperature and magnetic intensity may yield important information on the arrangement and constitution of the electron orbits only under extreme conditions. The theory evidently cannot account, even qualitatively, for the results of Glaser.

It is perhaps possible that alignment might be produced as the result of a spatial quantization due to the weak magnetic moment given to the atom according to the theory of Weber and Langevin or that of Pauli in an intense magnetic field.

7. For $\theta=0$ or 2π, Eq. (1) gives

$$\Delta n = \mp eH/4\pi mc \tag{17}$$

which, as Langevin points out, corresponds to the normal Zeeman effect. He does not point out, however, that, with random distribution, Δn has all values between this maximum and zero, on account of the presence of the factor $\cos\theta$ in the general expression, so that a band occurs instead of sharp lines. This fact has doubtless been noticed by many others, but I have seen no statement of it in the literature, and I have recently been assured by one distinguished physicist that the Langevin theory gives sharp lines, while the Weber theory does not. As a matter of fact, Eqs. (1) and (17) are common to both theories. Pauli's theory, based on Larmor precession, of course gives sharp lines.

8. It may be of interest to consider further the theorem on atomic precession first stated by Larmor, and established in a different way by Lorentz.[5] If we consider a diamagnetic atom, as defined in Section 2, and divide the torque produced on the atom by the magnetic field by the angular momentum in order to obtain the velocity of precession, we obtain the indeterminate expression 0/0. We may, however, start with an atom whose orbits are so arranged that it has a definite magnetic moment, and imagine the arrangement to be distorted gradually until the moment vanishes. Since the magnetic moment of each orbit is pro-

[4] Langevin, C. R. **151,** 475 (1910); Le Radium **7,** 249 (1910)

[5] Lorentz, The Theory of Electrons, section 104 (1909)

portional to its angular momentum, the precessional velocity remains constant and equal to that given by Larmor. It is especially interesting to see that the Larmor rotation is exactly the rotation which would be produced by impressing the magnetic field on the atom with the arrangement of its orbits unchanged, but with the charge in each orbit at rest and located at any point of the orbit or distributed in any way along the orbit (the ratio of e to m being assumed unchanged). For if we consider such an orbit in which the electron is distant ρ from the axis B, and apply the magnetic field parallel to B, the electron will acquire the angular velocity $\Delta n = -eH/4\pi mc$ and will move in the circle of radius ρ around the axis B, in accordance with Eq. (1). The result is independent of ρ. Thus the electron may occupy any position in its orbit, or the charge may be distributed along the orbit in any way. The Larmor rotation in a diamagnetic atom is due to the momentum given to the charge by the creation of the field, as in Weber's theory, not to the torque arising from the action of the steady field on the moving electrons—which vanishes for the complete atom in which the resultant torque on each orbit also vanishes.

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[6] Received February 3, 1925— Ed.