Note on Diamagnetism: Clarification of Relations between Fundamental Molecular Theories

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This paper gives a brief discussion of Weber's theory of diamagnetism and of the relations between it and the more recent theory of Langevin, as well as a composite theory involving ideas from both and sometimes confused with that of Langevin.

IN the last 100 years two fundamental theories of diamagnetism have been published, *viz.*, those of Wilhelm Weber and Langevin. Although Weber's theory is the older and is the primary basis of the other, some of its important details appear still to be but little known. Moreover, there exists in magnetic literature, and in the minds of some physicists, a certain amount of confusion with regard to these theories and the relations between them. It is with the hope of aiding in the clarification of this situation that this note is written.

WEBER'S THEORY

It will be conducive to clearness to present Weber's theory in detail, and very nearly as it was presented by him. However, trouble will be avoided by using only one set of units, the electromagnetic system, instead of the three sets (in effect) which Weber used; in a number of cases it will be advisable to use equations where Weber used only verbal statements; and in a few cases it will be desirable to add additional equations which Weber clearly had in mind.

In 1847 Weber[1] set forth his general ideas on the nature of the fundamental elements which are involved in magnetism and diamagnetism:

In a *magnetic* body the elements consist of molecules, *around* which or *in* which are closed paths or orbits carrying electric charges in permanent and steady motion and which thus have permanent magnetic moments. When a magnetic field is applied, the elements *turn* and align their magnetic axes more or less completely with the direction of the field. Weber thus adheres to the idea of Ampère, but makes it somewhat more precise.

In *diamagnetic* bodies are similar closed paths *around* or *in* the molecules in which the electricity is at rest when no extraneous magnetic field is present. When a magnetic field is applied, the elements maintain their orientations fixed in space, but the electricity in the orbits is set into steady motion by electromagnetic induction in accordance with the Faraday-Neumann law. Thus the elements acquire magnetic moments, which persist as long as the field is maintained, but vanish when it is destroyed.

In *magnetic bodies also*, electromagnetic induction acts in exactly the same way to *change* the velocities of the charges in permanent motion in the orbits, but the change in the moment of any orbit is very small in comparison with the original moment.

In 1852,[2] in his work on *Electrical Measurements*, Weber developed in detail his molecular theory of magnetism and diamagnetism. It is with the latter only that this paper is concerned.

The immediate object of the mathematical theory is to calculate the magnetic moment of any quantity, such as the unit mass or unit volume, of a diamagnetic substance containing any number N of circular molecular paths or orbits each with the same radius r and the same electric charge E when in a magnetic field with intensity X.

If such a circle is introduced into the magnetic field with its axis normal to the intensity X, and

[1] W. Weber, *Werke*, J. Springer, Berlin, 1892ff., Vol. III, p. 255.

[2] See reference 1, and also, and especially, pp. 527–530.

then, in a time t, has the orientation of the axis changed from normal to X to parallel with X, or if, in the time t, while the axis is maintained parallel with X the intensity of the field is changed from 0 to X, the magnetic flux through the circle will be changed from 0 to $\pi r^2 X$. In accordance with the Faraday-Newmann law an electromotive force ψ around the circle will result such that

$$\int_0^t \psi dt = -\pi r^2 X. \tag{1}$$

If the axis of the orbit makes an angle φ with X we must replace (1) by the more general relation

$$\int_0^t \psi dt = -\pi r^2 X \cos\varphi. \tag{2}$$

For ψ we may write

$$\psi = 2\pi r R, \tag{3}$$

where R is the electric intensity around the circle.

We shall assume (though this is quite unessential) that the charge is uniformly distributed around the circle, the charge e per unit length being

$$e = E/2\pi r, \tag{4}$$

and shall assume that each element of charge e has associated with it a mass m such that

$$m/e = \epsilon, \tag{5}$$

where ϵ is a constant. Thus the total mass,

$$M = 2\pi r m, \tag{6}$$

associated with the total charge E is connected therewith by the relation

$$M/E = \epsilon. \tag{7}$$

Under the intensity R each mass m will be acted upon by a force

$$f = Re, \tag{8}$$

and will receive an acceleration

$$a = f/m = R/\epsilon. \tag{9}$$

Hence in the time t each mass m and charge e will acquire the velocity

$$u = \int_0^t a dt. \tag{10}$$

[3] In a recent important publication the application of the Neumann-Faraday law to this case is attributed to Larmor.

Combining Eqs. (3)–(5) and (8)–(10) with (2), we obtain

$$\int_0^t \psi dt = -\pi r^2 X \cos\varphi = 2\pi r \epsilon u, \tag{11}$$

so that

$$u = -rX\cos\varphi/2\epsilon. \tag{12}$$

The motion of the charge with velocity u constitutes an electric current

$$i = eu = -erX\cos\varphi/2\epsilon \tag{13}$$

around the circle, and gives it a magnetic moment

$$\mu_0 = \pi r^2 i = -\pi r^3 eX\cos\varphi/2\epsilon, \tag{14}$$

which may be resolved into two rectangular components, one parallel to X, *viz.*,

$$_{11}\mu_0 = -\pi r^3 eX\cos^2\varphi/2\epsilon, \tag{15}$$

and one normal to X, *viz.*,

$$_{\perp}\mu_0 = -\pi r^3 eX\cos\varphi\sin\varphi/2\epsilon. \tag{16}$$

For all the N orbits together contained in the quantity of substance considered we get

$$_{11}\mu = -\pi r^3 eX/2\epsilon \cdot \sum \cos^2\varphi, \tag{17}$$

and

$$_{\perp}\mu = -\pi r^3 eX/2\epsilon \cdot \sum \cos\varphi\sin\varphi. \tag{18}$$

If N is very great and the axes of the orbits are orientated completely at random, as we shall assume,

$$\sum \cos^2\varphi = N\langle\cos^2\varphi\rangle_{Av} = \tfrac{1}{3}N, \tag{19}$$

and

$$\sum \cos\varphi\sin\varphi = \tfrac{1}{2}N\langle\sin 2\varphi\rangle_{Av} = 0. \tag{20}$$

The resultant moment of the N orbits is thus

$$\mu = {}_{11}\mu = -N\pi r^3 eX/6\epsilon. \tag{21}$$

This, in view of (5)–(7), may be written

$$\mu = -N\pi r^2 E^2 X/12\pi M. \tag{22}$$

From (12) and (7) the *angular velocity* imparted to the charge in the orbit, in revolutions per second, is

$$\nu(=u/2\pi r) = -EX/4\pi M, \tag{23}$$

when the axis of the orbit is parallel with X, and

$$\nu = -EX\cos\varphi/4\pi M, \tag{24}$$

when the angle between them is φ. In all cases it is independent of the radius. The frequency ν is identical with the *change* in the angular velocity in one of Weber's *magnetic* orbits, the *change* in whose orbital moment is given by the right side of (14).

In his papers of 1852 and earlier Weber did not explain how the charges, either fixed or moving, are maintained in their paths, though he sometimes refers to these as *channels* (Kanäle). In 1871[4] he introduced definitely the idea that the charge (now assumed to be *concentrated*) in one of his magnetic molecules was maintained in its orbit by the attraction of an equal and opposite charge at the center, essentially the idea we have today of an electron orbit (except that Weber's moving charge was positive and his central fixed charge negative).

LATER THEORIES

The theory published in 1905 by Langevin[5] is very closely related to that of Weber, but differs from it in important ways. In Weber's theory the diamagnetic molecule may contain any number of orbits or channels, and its moment is zero because the electric charge in each channel is at rest. In Langevin's theory the diamagnetic molecule always contains more than one orbit, each of them being of Weber's magnetic kind, with a fixed magnetic moment (out of the field). But the different orbits in each molecule have such moments and such orientations that their resultant moment vanishes.

When a molecule of this kind is introduced into the magnetic field either of two things may be conceived to happen.

I. WEBER-LANGEVIN THEORY

If through the action of intramolecular and intermolecular forces the orientations of the molecule and its orbits remain fixed in space, the orbital velocities, as seen by a fixed observer, change. The *increment* $\Delta\nu$ of frequency, or angular velocity in revolutions per second, is given by the formula

$$\Delta\nu = -EX\cos\varphi/4\pi M \qquad (24)$$

for an orbit whose axis makes the angle φ with X, just as in Weber's theory the frequency *created* is given by this same formula. Similarly, for i, u, and μ_0 in (12)–(16) we must substitute Δi, Δu, and $\Delta\mu_0$. The original moment being zero, Eqs. (17)–(22) give the values of the total moment of the material considered, and its components.

This theory is neither exactly the Weber theory nor the Langevin theory proper, with which it is sometimes confused, but may perhaps be designated as the *Weber-Langevin* theory.

Equations (17) and (18) give exactly the results which Weber would have obtained if he had taken the trouble to write down the calculation for the diamagnetic effect in the case of a magnetic substance.

II. LANGEVIN'S THEORY

In adopting the second alternative mentioned, Langevin proceeds in a general manner by using the Maxwell-Hertz equations to find what happens to a system of diamagnetic molecules symmetrical about their centers, and each free to move in any way as a whole, when a magnetic field is created in the region which they occupy. He shows that a molecule of the kind considered acquires, when the field is created, the mean magnetic moment

$$\mu = \sum\pi\langle a^2\rangle_{Av}E^2X/4\pi M \qquad (25)$$

parallel with X, where a is the instantaneous perpendicular distance between an electron in its complex motion and a straight line L in the direction of X through the nucleus, the summation being made with regard to the time and extending to all the orbits.

The same formula gives the moment of any number of molecules, the summation now extending over the whole number N of orbits.

Assuming that theorem of Larmor according to which a symmetrical electronic system in such a molecule as we have been considering when placed in a magnetic field undergoes no internal change whatever, but, to a fixed observer, acquires an angular velocity

$$\nu = -EX/4\pi M \qquad (23), (26)$$

about the line through the nucleus parallel to X which we have just considered, he interprets his result in accordance with this theorem.

Thus consider again one of the orbits, with the straight line L, representing the vector X, passing through the nucleus and making an angle ϕ with the normal to the plane of the orbit. At a certain instant the electron occupies a point P in the orbit distant a from L and, as always, distant r, the radius of the orbit, from the nucleus. The whole molecule rotates about L with the frequency given by (26). The moment of the orbit due to this rotation when the

[4] See reference 1, Vol. VII, p. 257.
[5] P. Langevin, Ann. Chim. Phys. 5, 70 (1905).

electron is at P is thus

$$\mu_P = \pi a^2 E\nu \tag{27}$$

along L, and the mean value of the moment is

$$\langle\mu_P\rangle_{Av} = \pi\langle a^2\rangle_{Av} E\nu. \tag{28}$$

If there are any number N or orbits in the quantity of matter under consideration, the total moment is thus

$$\mu = \sum\langle\mu_P\rangle_{Av} = \sum\pi\langle a^2{}_{Av}\rangle_{Av} E\nu \tag{29}$$

which, in view of (26), is identical with (25).

For any orbit with angle ϕ

$$\langle a^2\rangle_{Av} = \tfrac{1}{2}r^2(1+\cos^2\varphi). \tag{30}$$

Thus, if N is very great and all the N orbits have the same radius r and are orientated at random, so that $\langle\cos^2\varphi\rangle_{Av} = \frac{1}{3}$, we get

$$\langle a^2{}_{Av}\rangle_{Av} = \tfrac{2}{3}r^2 \equiv r^2\langle\sin^2\varphi\rangle_{Av}. \tag{31}$$

In this case (25) becomes

$$\mu = -N\cdot\pi r^2\cdot E^2X/6\pi M, \tag{32}$$

which is just twice as great as μ on each of the two theories considered above.

Like Weber, Langevin calls attention to the fact that in *magnetic* bodies there is superposed on the *magnetic* effect, because of the changes in the orientation of the molecules, the *diamagnetic* effect caused by the changes of velocity in the orbits (or the Larmor rotation).

In converting operation (25) to the formula for the case in which the number N of orbits is very large and they are orientated at random, Langevin wrote $\langle a^2{}_{Av}\rangle_{Av} = \frac{1}{3}\cdot r^2$ instead of $\langle a^2{}_{Av}\rangle_{Av} = \frac{2}{3}\cdot r^2$ and in this way obtained exactly the value of μ (Eq. (22)) resulting from the Weber and Weber-Langevin theories, instead of the correct result in (32) which is twice as great. This accident was noticed for the first time, apparently, fifteen years later by Pauli,[6] who has given a more extensive discussion of (29) and its applicability.

Equation (22) was used by Langevin to calculate the mean magnitude of r^2 in water, in which and in other liquids and in solids (22) would be expected to hold better than (32), which applies strictly only to free and symmetrical molecules, such as krypton, xenon, neon, etc., in the gaseous state. Equation (32) has been applied to many other cases where it certainly cannot hold on account of the inapplicability of Larmor's theorem.

[6] W. Pauli, Zeits. f. Physik 2, 201 (1920).

It is an interesting fact that since ν is independent of the orbital velocity, Eq. (32), like (22), applies equally well whether the individual orbits are magnetic or, like Weber's in diamagnetic molecules, non-magnetic—a result also easy to see otherwise:

It is instructive to demonstrate (32) also in the following two ways:

(1) We resolve the angular velocity ν of an orbit in Larmor rotation about the line L into two rectangular components, one $\nu_z \equiv \nu\cos\phi$ about the normal Z—which would be the total increment in the electron velocity if the orbit were to remain fixed in space—and the other $\nu_D \equiv \nu\sin\phi$, the velocity of the orbit about a diameter D in the plane containing L and Z.

The first gives rise to a mean moment

$$\mu_z = E\nu\cos\varphi\pi r^2$$

in the direction Z; the second to a mean moment

$$\mu_D = E\nu\sin\varphi\tfrac{1}{2}\pi r^2$$

in the positive direction of D.

Resolving these two moments parallel and perpendicular to L, we get

$$_{\parallel}\mu_z = E\nu\pi r^2\cos^2\varphi \qquad {}_{\perp}\mu_z = E\nu\pi r^2\cos\varphi\sin\varphi$$
$$_{\parallel}\mu_D = E\nu\tfrac{1}{2}\pi r^2\sin^2\varphi \qquad {}_{\perp}\mu_D = -E\nu\tfrac{1}{2}\pi r^2\sin\varphi\cos\varphi$$

The normal components (for each orbit) cancel; and the mean values of the parallel components for a great number N of orbits and random distribution are equal, each being $E\nu\pi r^2/3$. Thus their sum is

$$\mu \equiv N(\mu_L)_{Av} = N\tfrac{2}{3}E\nu\pi r^2$$

in agreement with (32).

(2) The mean moment, along L, of any orbit due to the Weber, or Larmor, rotation is the same as if the charge of the electron were at rest in the orbit and uniformly distributed over the circle. The total moment of the N orbits distributed at random is the same as it would be if all the orbits were superposed, with their nuclei coincident. The assemblage is thus equivalent to a sphere with radius r and charge NE uniformly distributed over its surface and in rotation with the angular velocity ν. This, as is well known, has the magnetic moment $NE\cdot\frac{2}{3}\pi r^2\cdot\nu$, again in agreement with (32).

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