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THE INFLUENCE OF A MAGNETIC FIELD ON THE DIELECTRIC CONSTANT OF A DIATOMIC DIPOLE GAS

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ABSTRACT

The investigation of the motion of a diatomic dipole molecule in crossed magnetic and electric fields shows that according to the old quantum theory there will be spatial quantization practically with respect to the direction of the magnetic field for experimentally realizable values of the field strengths. As a result of this the old quantum theory definitely requires that the application of a strong magnetic field to a gas such as hydrogen chloride produce a very large change in the dielectric constant of the gas. The theory of the dielectric constant of a diatomic dipole gas according to the new quantum mechanics, on the other hand, requires the dielectric constant not to depend upon the direction characterizing the spatial quantization, so that no effect of a magnetic field would be predicted. The effect is found experimentally not to exist; so that it provides an instance of an apparently unescapable and yet definitely incorrect prediction of the old quantum theory.

I. TREATMENT BY THE OLD QUANTUM THEORY

IN THE present paper we calculate the dielectric constant of a diatomic dipole gas in a magnetic field. We shall defer application of the new quantum dynamics until §II, and commence by employing the old quantum theory even though it is now obsolete. We include treatments by both theories because the difference in the results is very interesting and furnishes additional evidence for the new mechanics, inasmuch as in the old theory the dielectric constant is materially influenced by a magnetic field. This effect, which is absent in the new theory, arises from the fact that with sufficiently strong magnetic fields the direction characterizing the spatial quantization of the rotating molecules will be the direction of the magnetic field instead of that of the electric field. In order to determine the field strengths with which this transition occurs, it is necessary to determine the motion of the gas molecules in crossed electric and magnetic fields. The motion of a diatomic dipole molecule in an electric field has been treated by Hettner[1] and by W. Pauli, Jr.[2] The equations of motion can in this case be solved by means of the separation of variables. This procedure can also be followed for the motion of the molecule in a magnetic field alone, and in both a magnetic

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[1] G. Hettner, Zeits. f. Physik **2**, 349 (1920).

[2] W. Pauli, Jr., *ibid.* **6**, 319 (1921).

and an electric field when the two fields are parallel; it cannot be used for crossed fields, however. The treatment given the problem of crossed fields in this paper is based on the methods of Bohr,[3] and is somewhat similar to that given the problem of the hydrogen atom in crossed electric and magnetic fields by Klein[4] and by Lenz.[5]

We shall for simplicity consider a diatomic molecule without resultant electronic angular momentum as a rigid assemblage of charged mass-points along a line. For our purposes it can be characterized by three quantities, the moment of inertia $A=\Sigma m_i r_i^2$, the electric moment $\mu=\Sigma \epsilon_i r_i$, and the electric moment of inertia or quadrupole moment $\kappa=\Sigma \epsilon_i r_i^2$, in which ϵ_i is the charge and m_i the mass of the ith mass-point, and r_i its distance from the center of mass of the molecule. The detailed consideration of the quantum-allowed states of motion of the molecule given in the appendix of this paper leads to the result that except for terms of the order of magnitude of ω/ω_M the spatial quantization in crossed electric and magnetic fields is the same as for the magnetic field alone; namely, the total angular momentum vector $\boldsymbol{P}$, of magnitude $p=jh/2\pi$, has a component in the direction of the magnetic field vector $\boldsymbol{H}$ of magnitude $mh/2\pi$, and $\boldsymbol{P}$ further undergoes precessional motion about $\boldsymbol{H}$ with uniform angular velocity. ω and ω_M are given by the equations

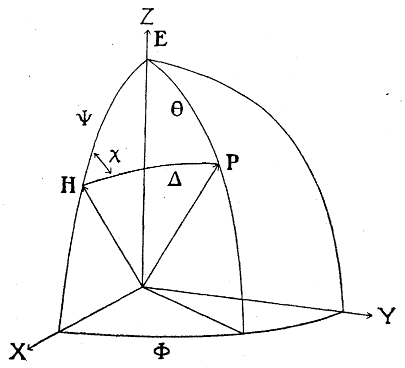

Fig. 1.

$$\omega=3\mu^2E^2A/2p^3, \tag{1a}$$

$$\omega_M=\kappa H/2Ac, \tag{1b}$$

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[3] N. Bohr, "On the Quantum Theory of Line Spectra," Part II, Det Kgl. Danske Vid. Selsk. **8,** IV, 1 (1918).

[4] O. Klein, Zeits. f. Physik **22,** 109 (1924).

[5] W. Lenz, *ibid.* **24,** 197 (1924).

in which E and H are the electric and magnetic field strengths respectively; $-\omega_M$ is the angular velocity of precession of $\boldsymbol{P}$ about $\boldsymbol{H}$ in the presence only of the magnetic field, and $-\omega\cos\Theta$, in which Θ is the angle between $\boldsymbol{P}$ and the electric field vector $\boldsymbol{E}$, is the angular velocity of the precessional motion of $\boldsymbol{P}$ about $\boldsymbol{E}$ in the presence only of the electric field.

The dielectric constant of a diatomic dipole gas. Under the influence of an electric field a gas becomes electrically polarized in the direction of the field, the amount of polarization per unit volume being

$$P=\frac{3}{4\pi}\,\frac{\epsilon-1}{\epsilon+2}E=N\bar{\bar{\mu}}+N\alpha E, \tag{2}$$

in which ϵ is the dielectric constant of the gas, N the number of molecules in unit volume, and α the deformation coefficient or coefficient of induced polarization of the gas. $\bar{\bar{\mu}}$ is the average value of $\bar{\mu}$ for all molecules in the gas, where $\bar{\mu}$ is the time-average of $\mu\cos\theta$ for one molecule in a given state of motion. An expression for $\bar{\bar{\mu}}$ applicable to polyatomic molecules in general was obtained by Debye[6] with the use of classical statistical mechanics; namely,

$$\bar{\bar{\mu}}=\mu^2E/3kT. \tag{3}$$

The interpretation of the oscillation-rotation[7] and the pure rotation[8] band spectra of hydrogen chloride required that this result be abandoned; for with the old quantum theory these spectra showed that the rotational energy of the molecule was restricted to the series of values $W=(j^2h^2)/8\pi^2A$, with $j=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots \infty$. The expression for the dielectric constant of a diatomic dipole gas according to the old quantum theory was derived by W. Pauli, Jr.,[2] in the following way. For a given molecule the average value of $\mu\cos\theta$ is

$$\bar{\mu}=\frac{\mu}{\tau}\int_0^\tau \cos\theta dt,$$

On substituting for dt its value given in Eq. (32) of the appendix, expanding in powers of $\mu E/\alpha_1$, and evaluating the resultant integrals by contour integration, one obtains the approximate result

$$\bar{\mu}=\frac{2\pi^2A\mu^2E}{h^2}\cdot\frac{1}{j^2}(3\cos^2\Theta-1), \tag{4}$$

[6] P. Debye, Physik. Zeits. **13,** 97 (1912).

[7] Colby, Astrophys. J. **58,** 303 (1923).

[8] Czerny, Zeits. f. Physik **34,** 227 (1925).

in which Θ represents as before the angle between $\boldsymbol{P}$ and $\boldsymbol{E}$. Assigning equal *a priori* probabilities to all of the possible quantum states characterized by the quantum numbers j and m, we have for the probability of a given state

$$w(j,m)=\frac{e^{-W/kT}}{\sum_j \sum_m e^{-W/kT}}, \tag{5}$$

and for $\bar{\mu}$ we have

$$\bar{\bar{\mu}}=\sum_j \sum_m w(j,m)\cdot\bar{\mu}(j,m). \tag{6}$$

When the electric field alone is present this expression can be easily evaluated, for then $\cos\Theta$ is equal to m/j, and

$$\bar{\mu}(j,m)=\frac{2\pi^2A\mu^2E}{h^2j^2}\left(3\frac{m^2}{j^2}-1\right), \tag{7}$$

and

$$\bar{\bar{\mu}}=\mu^2EC/kT, \tag{8}$$

with

$$C=\frac{\sum_j \sum_m \frac{1}{j^2}\left(3\frac{m^2}{j^2}-1\right)e^{-\sigma j^2}}{4\sigma\sum_j \sum_m e^{-\sigma j^2}}, \tag{9}$$

in which $\sigma=h^2/8\pi^2AkT$.

This is the result given by Pauli, who evaluated C by giving j and m integral values and assuming σ to be very small. Values of C as a function of σ have also been published by the writer,[9] assuming the values $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\cdots$ ∞ for j and $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, $\pm\frac{5}{2}$, $\cdots$ $\pm j$ for m.

The influence of a strong magnetic field on the dielectric constant. If in addition to the electric field a strong magnetic field is present, the average value of $\mu\cos\theta$ for a molecule in a given state of motion will no longer be given by Eq. (4). We prove in the appendix that if the magnetic field is so strong that the ratio ω/ω_M is small compared with unity, the spatial quantization is relative to the direction of the magnetic field, about which $\boldsymbol{P}$ undergoes a uniform precession. Accordingly the cosine of the angle Δ between $\boldsymbol{P}$ and $\boldsymbol{H}$ will be equal approximately to m/j. We now have the trigonometric relation

$$\cos\Theta=\cos\psi\cos\Delta+\sin\psi\sin\Delta\cos\chi,$$

in which χ, as shown in the figure, increases uniformly from 0 to 2π during the precessional motion of $\boldsymbol{P}$ about $\boldsymbol{H}$. From this relation we find

$$\frac{1}{2\pi}\int_0^{2\pi}(3\cos^2\Theta-1)d\chi=\left(\frac{3}{2}\cos^2\psi-\frac{1}{2}\right)\left(3\cos^2\Delta-1\right),$$

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[9] L. Pauling, Proc. Nat. Acad. Sci. **12**, 32 (1926); Phys. Rev. **27**, 568 (1926).

and from this on substituting for $\cos\Delta$ its value m/j

$$(3\cos^2\Theta-1)_{average}=\left(\frac{3}{2}\cos^2\psi-\frac{1}{2}\right)\left(3\frac{m^2}{j^2}-1\right). \tag{10}$$

This equation shows that the effective polarization due to one molecule in the state characterized by the quantum numbers j and m is equal to $(\frac{3}{2}\cos^2\psi-\frac{1}{2})$ times its value in the absence of the magnetic field; i.e.,

$$\bar{\mu}_\psi(j,m)=\left(\frac{3}{2}\cos^2\psi-\frac{1}{2}\right)\bar{\mu}(j,m). \tag{11}$$

Since this multiplicative factor is independent of j and m, we may substitute Eq. (10) in (4) and obtain the result

$$\bar{\bar{\mu}}_\psi=\left(\frac{3}{2}\cos^2\psi-\frac{1}{2}\right)\cdot\frac{\mu^2E}{kT}\cdot C, \tag{12}$$

in which C has the value given by Eq. (9). We can consequently state that *in the presence of a strong magnetic field making an angle* ψ *with the electric field the polarization due to permanent dipoles will according to the old quantum theory be* $(\frac{3}{2}\cos^2\psi-\frac{1}{2})$ *times its value in the absence of the magnetic field.*[10]

The old quantum theory accordingly definitely requires that with the magnetic field nearly at right angles to the electric field gases such as hydrogen chloride should show a *negative polarization*, and a *dielectric constant smaller than unity*; the absolute value of the negative polarization should be equal to one-half of the usual positive polarization, except for the relatively small and always positive contribution due to deformation.

In view of the fact that the band spectra do not directly determine the possible values of the quantum number m, it is to be especially emphasized that this result regarding the effect of a magnetic field is completely independent of the assumption of particular values for this quantum number. The value of C, as shown in Eq. (9), does depend on this choice, but the ratio of $\bar{\bar{\mu}}_\psi$ to $\bar{\bar{\mu}}$ (Eqs. 12 and 8) is simply $\frac{3}{2}\cos^2\psi-\frac{1}{2}$, and so is independent of C.

It is of interest to consider the magnitude of the magnetic field strength necessary to make ω/ω_M small and so produce this effect. Using for A its value as determined by Czerny[8] from the pure rotation absorption

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[10] This quantitatively predicted effect is not to be confounded with the effect qualitatively predicted by Ruark and Breit, Phil. Mag. **49**, 504 (1925), and found experimentally not to exist by Weatherby and Wolf, Phys. Rev. **27**, 769 (1926), for their effect involved molecules without a permanent electric moment, such as those of helium, oxygen, and air.

spectrum of hydrogen chloride, for μ the value found from its dielectric constant,[9] for p the expression $jh/2\pi$, and for κ the estimate -1×10^{-25} E.S.U.,[11] we find from (1*a*,*b*) that ω/ω_M becomes small when

$$H \gg F^2/10{,}000j^3$$

in which H is the field strength in gauss, and F the electric field strength in volts/cm. It is at once apparent that this condition can be easily achieved experimentally.

II. Treatment by the New Quantum Mechanics

According to the new quantum mechanics, the spatial rotator is characterized by two numbers j and m, such that j can assume the values $0, 1, 2, 3, \cdots \infty$, and m the values $0, \pm1, \pm2, \pm3, \cdots \pm j$. The corresponding energy values, in the absence of an external field, are

$$W(j,m) = j(j+1)h^2/8\pi^2A. \qquad (13)$$

The energy-levels thus differ from those of the old quantum theory with half quantum numbers only by a constant additive quantity, and are in complete agreement with the infra-red spectral data.

The new quantum mechanics leads to a formula for the dielectric constant of a diatomic dipole gas greatly different from that given by the old quantum theory, as has been shown both by L. Mensing and W. Pauli, Jr.,[12] and by J. H. Van Vleck.[13] The average polarization due to molecules with a given value of j not equal to zero vanishes, and only those molecules with $j=0$ produce any polarization under the influence of an external electric field. Hence the new quantum mechanics shows in this case much greater similarity to the classical theory than did the old quantum theory; for on the basis of the classical theory only those molecules with very small rotational energy, namely, less than μE, contributed to the polarization,[14] while the old quantum theory stated that no such molecules were present.

The dielectric constant of a diatomic dipole gas. As shown by Mensing and Pauli and by Van Vleck, the polarization excited in a molecule by a static external electric field can be calculated by means of the Ladenburg-Kramers dispersion formula, derived on the basis of the Heisenberg

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[11] This estimate is substantiated by the fact that Professor O. Stern has recently shown by a very sensitive adaptation of the experiment determining the bending of a molecular stream in a strong inhomogeneous magnetic field that a molecule of water vapor at around 0°C has a magnetic moment of the order of magnitude of 0.001 Bohr magnetons, which corresponds to a quadrupole moment of the order of that assumed for hydrogen chloride.

[12] L. Mensing and W. Pauli, Jr., Physik. Zeits. **27**, 509 (1926); also C. Manneback, *ibid.* **27**, 563 (1926).

[13] J. H. Van Vleck, Nature, August 14, 1926.

[14] Alexandrow, Physik. Zeits. **22**, 258 (1921).

quantum mechanics by Born and Jordan[15] and of the wave mechanics by Schrödinger,[16] by placing the frequency of the impressed disturbance equal to zero. Placing the Z-axis parallel to the electric lines of force, corresponding to spatial quantization with respect to the electric field, we obtain for the polarization of a molecule characterized by the quantum numbers j and m the expression

$$\bar{\mu}(j,m) = 2\mu^2 E \sum_{j',m'}{}' \frac{z^2(j,m\,;j',m')}{h\nu(j,m\,;j',m')}, \tag{14}$$

in which $z(j,m;j',m')$ represents the term in the matrix z corresponding to the transition $j \rightarrow j'$, $m \rightarrow m'$, and $\nu(j,m;j',m')$ represents the corresponding frequency, considered positive in absorption and negative in emission; the summation is to be extended over all values of j' and m' for which $z(j,m;j',m')$ does not vanish. The values

$$z^2(j,m\,;j',m') = \frac{(j-m)(j+m)}{(2j-1)(2j+1)} \text{ for } m'=m, j'=j-1 \tag{15a}$$

$$= \frac{(j-m+1)(j+m+1)}{(2j+1)(2j+3)} \text{ for } m'=m, j'=j+1 \tag{15b}$$

$$= 0 \text{ otherwise}$$

have been derived by Mensing[17] and by Dennison.[18] On substituting these values, together with the values of $h\nu$ obtained from the energy-levels given by Eq. (13), we find for $j \neq 0$ the equation

$$\bar{\mu}(j,m) = \frac{8\pi^2 A\mu^2 E}{h^2} \cdot \frac{1}{(2j-1)(2j+3)} \left(3\frac{m^2}{j(j+1)} - 1 \right). \tag{16}$$

For $j=0$, however, only the jump with absorption can occur; from (15b) we accordingly find

$$\bar{\mu}(0,0) = 8\pi^2 A\mu^2 E/3h^2\ . \tag{17}$$

Since m does not occur in the energy expression (13), the probability of every value of m, with j constant, is the same. We may consequently find the average contribution to the polarization of molecules in the jth state by simply averaging $\bar{\mu}(j,m)$ as given in Eq. (16) over all values of m. On doing this zero is obtained for every state with j not zero:

$$\bar{\mu}(j) = \frac{1}{2j+1} \sum_{m=-j}^{+j} \bar{\mu}(j,m) = 0,$$

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[15] Born and Jordan, Zeits. f. Physik **34,** 858 (1925).

[16] Schrödinger, Ann. d. Physik **81,** 109 (1926).

[17] L. Mensing, Zeits. f. Physik **36,** 814 (1926).

[18] Dennison, Phys. Rev. **28,** 318 (1926).

so that only molecules with $j=0$ are effective. From Eq. (5) the probability of this state is

$$w(0,0)=\left(\sum_{j=0}^{\infty}\ \sum_{m=-j}^{+j}e^{-\sigma j(j+1)}\right)^{-1}, \tag{18}$$

in which σ, as before, is $h^2/8\pi^2AkT$. We thus obtain the result that the total polarization of N molecules is

$$\bar{\mu}_z=N\cdot w(0,0)\cdot\bar{\mu}(0,0)=\frac{\mu^2E}{3kT}\cdot\frac{1}{\sigma\sum_{j=0}^{\infty}(2j+1)e^{-\sigma j(j+1)}}. \tag{19}$$

For small values of σ; i.e., for high temperatures, this reduces to the classical equation of Debye.

The dielectric constant in the presence of a magnetic field. We shall next calculate the polarization produced when the electric lines of force are parallel to the X- (or Y-) axis, and the characteristic direction Z of quantization is determined by some other influence, such as a strong magnetic field. We again use Eq. (14), except that for $z^2(j,m;\ j',m')$ we substitute $x^2(j,m;j',m')$ or $y^2(j,m;j',m')$, with the following values, given by Mensing and Dennison:

$$x^2(j,m\ ;j',m')=y^2(j,m\ ;j',m')=\frac{(j+m+1)(j+m+2)}{4(2j+1)(2j+3)} \tag{20a}$$

$$\text{for } m'=m+1,j'=j+1$$

$$=\frac{(j-m)(j-m-1)}{4(2j-1)(2j+1)} \tag{20b}$$

$$\text{for } m'=m+1,j'=j-1$$

$$=\frac{(j+m-1)(j+m)}{4(2j-1)(2j+1)} \tag{20c}$$

$$\text{for } m'=m-1,j'=j-1$$

$$=\frac{(j-m+1)(j-m+2)}{4(2j+1)(2j+3)} \tag{20d}$$

$$\text{for } m'=m-1,j'=j+1$$

$$=0 \text{ otherwise.}$$

From $20a$, b, c, and d we find for $j\neq 0$

$$\bar{\mu}_x(j,m)=\bar{\mu}_y(j,m)=-\frac{4\pi^2A\mu^2E}{h^2}\cdot\frac{1}{(2j-1)(2j+3)}\left(3\frac{m^2}{j(j+1)}-1\right), \tag{21}$$

and from $20a$ and d for $j=0$

$$\bar{\mu}_x(0,0)=\bar{\mu}_y(0,0)=8\pi^2A\mu^2E/3h^2. \tag{22}$$

The polarization resulting when $\boldsymbol{E}$ and $\boldsymbol{H}$ are inclined at an angle ψ to each other may be found by taking the resultant of the polarizations produced by the components of $\boldsymbol{E}$ parallel and perpendicular to $\boldsymbol{H}$, given by Eqs. (16), (17) and (21), (22). On doing this we find for all molecules with $j \neq 0$ the result

$$\bar{\mu}_\psi(j,m) = \left(\frac{3}{2}\cos^2\psi - \frac{1}{2}\right)\bar{\mu}(j,m), \tag{23}$$

in complete agreement with the classical expression. For $j=0$, however, we find

$$\bar{\mu}_\psi(0,0) = \bar{\mu}(0,0). \tag{24}$$

The previous result regarding the influence of a magnetic field on the polarization does not follow, for on summing over m we find again that only those molecules in the lowest state, with $j=0$, contribute to the polarization. From the similarity of (17) and (22) it then follows immediately that the polarization μ_ψ is still given by the expression on the right-hand side of (19), and is consequently independent of the direction of quantization. Since for small values of electric and magnetic field strengths the only effect of applying a magnetic field to the gas will be to change the direction characteristic of the spatial quantization, we thus see that *on the basis of the new quantum mechanics a magnetic field should not influence the dielectric constant of a gas such as hydrogen chloride.*

Since this paper was submitted for publication, a note by Kronig[19] has appeared in which it is stated that according to the new quantum mechanics a magnetic field should be without effect on the dielectric constant of a diatomic dipole gas.

III. COMPARISON WITH EXPERIMENT

The experiment suggested by the foregoing considerations was undertaken by Dr. L. M. Mott-Smith and C. R. Daily[20] in the Norman Bridge Laboratory of Physics of the California Institute of Technology, with the following results, which have been published in detail in the PHYSICAL REVIEW. Measurements were made on hydrogen chloride at pressures varying from 2 to 350 cm, using a sensitive heterodyne beat method of measuring the dielectric constant, and using the gas-handling technique described by Zahn.[21] The magnetic field strength was about 4800 gauss, and the electric field strength only a few volts/cm, so that the quantization was very closely with respect to the magnetic field. At each pressure the dielectric constant was measured with the fields

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[19] Kronig, Proc. Nat. Acad. Sci. **12**, 488, 608 (1926).

[20] Mott-Smith and Daily, Phys. Rev. **28**, 978 (1926).

[21] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

both mutually parallel and mutually perpendicular. *In no case was any change in the dielectric constant detected,* within a limit of error of about one part in 100,000 in ϵ; i.e., about 2 percent in the polarization for a pressure of 20 cm. The same result was also obtained with nitric oxide, NO.

APPENDIX

The motion of a diatomic dipole molecule in crossed fields according to the old quantum theory. The equation of motion of the idealized diatomic dipole molecule in an electric field $\boldsymbol{E}$ and a magnetic field $\boldsymbol{H}$ may be written vectorially as

$$A\frac{d}{dt}[\boldsymbol{r}\boldsymbol{v}]=\mu[\boldsymbol{r}\boldsymbol{E}]+\frac{\kappa}{c}[\boldsymbol{r}[\boldsymbol{v}\boldsymbol{H}]], \tag{25}$$

in which $\boldsymbol{r}$ represents a unit vector in the direction of the axis of the molecule, and with the same sense as the electric moment. The velocity $d\boldsymbol{r}/dt$ is denoted by $\boldsymbol{v}$. By means of this equation we shall now determine the perturbing influence of the fields to the first approximation.

The unperturbed motion is characterized by four constants of integration. For our purposes it is desirable to choose as these constants the direction and magnitude of the total angular momentum vector (three constants) and the absolute phase of the motion. The perturbing fields produce changes in these quantities, the determination of which constitutes the perturbation problem. In order to find the perturbations for the angular momentum vector let us average each term of (25) through a length of time equal to the period of the unperturbed motion. If we define $\boldsymbol{P}$ as the angular momentum vector averaged through the period of the unperturbed motion, the left side of Eq. (25) becomes $d\boldsymbol{P}/dt$, and we have

$$\frac{d\boldsymbol{P}}{dt}=\mu\overline{[\boldsymbol{r}\boldsymbol{E}]}+\frac{\kappa}{c}\overline{[\boldsymbol{r}[\boldsymbol{v}\boldsymbol{H}]]}. \tag{26}$$

The effect of the magnetic field. In order to evaluate the magnetic term in Eq. (26) we note that on account of the identity

$$[\boldsymbol{r}[\boldsymbol{v}\boldsymbol{H}]]+[\boldsymbol{H}[\boldsymbol{r}\boldsymbol{v}]]+[\boldsymbol{v}[\boldsymbol{H}\boldsymbol{r}]]=0 \tag{27}$$

and the relation

$$\frac{d}{dt}[\boldsymbol{r}[\boldsymbol{H}\boldsymbol{r}]]=[\boldsymbol{v}[\boldsymbol{H}\boldsymbol{r}]]+[\boldsymbol{r}[\boldsymbol{H}\boldsymbol{v}]]$$

we may write

$$2[\boldsymbol{r}[\boldsymbol{v}\boldsymbol{H}]]=-[\boldsymbol{H}[\boldsymbol{r}\boldsymbol{v}]]-\frac{d}{dt}[\boldsymbol{r}[\boldsymbol{H}\boldsymbol{r}]].$$

To the first order of approximation we may now take the average value of these quantities through a period of the osculating unperturbed motion. The second term then becomes zero; and on substituting for $\overline{[\mathbf{r}\mathbf{v}]}$ its value $\mathbf{P}/A$ we obtain the equation

$$\frac{\kappa}{c}\,\overline{[\mathbf{r}[\mathbf{v}\mathbf{H}]]} = -\frac{\kappa}{2Ac}[\mathbf{H}\mathbf{P}]. \tag{28}$$

On substituting this result in (26) we observe that the effect of the magnetic field is to produce precessional motion of $\mathbf{P}$ about $\mathbf{H}$, with the angular velocity $-\kappa H/2Ac$, in which $H = |\mathbf{H}|$.

It can further be shown, by determining the Hamiltonian function in the way given by Schwarzschild, that the energy added by the magnetic field as it is increased adiabatically from zero to $\mathbf{H}$ is

$$\Psi_M = -\kappa(\mathbf{H}\mathbf{P})/2Ac. \tag{29}$$

The effect of the electric field. It is found that the average value of $[\mathbf{r}\mathbf{E}]$ taken through a period of the osculating field-free motion is zero; for the electric field produces only a second-order effect. In order to determine the perturbations due to the electric field it is accordingly necessary to consider not the osculating motion in the absence of both the electric and the magnetic field, but rather that in the presence of the electric field and the absence of the magnetic field.[22] In this case the Hamiltonian function is

$$\mathcal{H} = \frac{1}{2A}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \mu E\cos\theta, \tag{30}$$

in which ϕ and θ are the polar coordinates of the axis of the molecule, θ being measured with reference to $\mathbf{E}$ and ϕ with reference to an arbitrary zero-point. E is equal to $|\mathbf{E}|$. The coordinate ϕ is cyclic; hence we may write

$$p_\phi = A\sin^2\theta\dot{\phi} = \alpha_2, \text{ a constant.} \tag{31}$$

Substituting this result in (30), and placing $p_\theta = A\dot{\theta}$ and $\mathcal{H} = \alpha_1$, the energy constant, we obtain

$$dt = A\{2A\alpha_1 - \alpha_2^2\operatorname{cosec}^2\theta + 2A\mu E\cos\theta\}^{-\frac{1}{2}}d\theta. \tag{32}$$

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[22] I am indebted to Prof. J. H. Van Vleck for the observation that the justification for this procedure may be deduced by a different method developed by Bohr, Born, and others for perturbed degenerate systems. The electric term in the Hamiltonian function is much larger than the magnetic one, and so the former may be considered of the first order and the latter of the second. The former, however, gives only a second-order effect because its average value is zero to a first approximation. Born notes on p. 302 of his *Atommechanik* that in such cases it is possible to determine the secular perturbations by first averaging over the rapidly fluctuating first-order terms in the absence of the second-order perturbing terms, and hence it is legitimate for us to use the Hettner expression (36) even in the presence of a magnetic field.

Inasmuch as the old quantum theory required that the energy of the lowest quantum state be $h^2/32\pi^2A$ in order to account for the pure rotation spectrum of hydrogen chloride, the quantity $\mu E/\alpha_1$ can be treated as very small in comparison with unity. It is accordingly permissible to expand the radical in the denominator and neglect higher powers of $\mu E/\alpha_1$.

We may use for the period τ of the variable θ the value corresponding to zero field; namely,

$$\tau=\pi(2A/\alpha_1)^{\frac{1}{2}} \tag{33}$$

In order to determine the motion of the vector $\boldsymbol{P}$, we note that from Eqs. (31) and (32) we may write

$$d\phi=(\alpha_2/A\ \sin^2\theta)dt$$

In the time τ in which θ goes through a complete libration ϕ progresses from ϕ_0 to ϕ_τ, an angle given by the equation

$$\phi_\tau-\phi_0=\frac{\alpha_2}{A}\int_0^\tau\frac{dt}{\sin^2\theta}=\alpha_2\oint\frac{d\theta}{\sin^2\theta\{2A\alpha_1-\alpha_2{}^2\text{cosec}^2\theta+2A\mu E\cos\theta\}^{\frac{1}{2}}},$$

or, to the first approximation,

$$\phi_\tau-\phi_0=2\pi-\frac{3\pi\mu^2E^2\alpha_2}{8\alpha_1{}^2}\left(\frac{2}{A\alpha_1}\right)^{\frac{1}{2}}. \tag{34}$$

The system has undergone a pseudo-regular precession about the electric field, with a velocity which to the first approximation is found from Eq. (34), using the value of τ given by (33) and introducing for α_1 the value $p^2/2A$ and for α_2 the value $p\cos\Theta$, we thus find the velocity of precession to be $-(3\mu^2E^2A/2p^3)\cos\Theta$. Since in the absence of the magnetic field this angular velocity provides a measure of the magnitude of $d\boldsymbol{P}/dt$, and hence of $\mu\overline{[\boldsymbol{rE}]}$, we are now able to write

$$\mu\overline{[\boldsymbol{rE}]}=3\mu^2A(\boldsymbol{PE})[\boldsymbol{PE}]/2p^4 \tag{35}$$

The contribution of the perturbing field to the energy function can be shown, as has been done by Hettner, to have the value

$$\psi_E=\frac{\mu^2E^2A}{4p^2}(1-3\cos^2\Theta). \tag{36}$$

The combined effect of an electric and a magnetic field. Substituting (28) and (35) in (26), we obtain the result

$$\frac{d\boldsymbol{P}}{dt}=\frac{3\mu^2A}{2p^4}(\boldsymbol{PE})[\boldsymbol{PE}]-\frac{\kappa}{2Ac}[\boldsymbol{HP}], \tag{37}$$

which shows that the average angular momentum vector ***P*** undergoes simultaneously precession about both the electric and the magnetic field, with the indicated velocities. The magnetic term of this equation differs from that of Klein and Lenz only in the replacement of $-e$ and m by κ and A; the electric term is, however, completely different. For the first-order effect of the electric field is in our problem zero, and we have used the second-order term, corresponding in the case of the hydrogen atom to the quadratic Stark effect, which was neglected by Klein and Lenz.

Our differential equation is easily soluble in the scalar form. The Z-axis is chosen along ***E***, and the X-axis in such a way that ***H*** lies in the XZ plane, making the angle ψ with ***E***. Purely kinematically the following equations are then obtained from Eq. (37):

$$d\Phi/dt = -\omega\cos\Theta - \omega_z + \omega_x\cot\Theta\cos\Phi, \tag{38}$$

and

$$d\Theta/dt = \omega_x\sin\Phi, \tag{39}$$

in which

$$\omega_x = \omega_M \sin\psi \text{ and } \omega_z = \omega_M \cos\psi.$$

As shown in Fig. 1 the angles Θ and Φ are the polar coordinates of the vector ***P***. Dividing (38) by (39), we obtain

$$\cos\Theta\cos\Phi - \sin\Theta\sin\Phi\, d\Phi/d\Theta = (\omega/\omega_x)\cos\Theta\sin\Theta + (\omega_z/\omega_x)\sin\Theta,$$

which on integration gives the equation

$$\cos\Phi\sin\Theta = -(\omega_z/\omega_x)\cos\Theta - (\omega/2\omega_x)\cos^2\Theta + B, \tag{40}$$

showing the relation between Θ and Φ during the perturbed motion. On substituting the value for $\cos\Phi$ given by this equation in (39) and integrating, we obtain

$$-\omega_x(t-t_0) = \int_{x_0}^{x} (a_0\xi^4 + 4a_1\xi^3 + 6a_2\xi^2 + 4a_3\xi + a_4)^{-\frac{1}{2}} d\xi \tag{41}$$

in which $x = \cos\Theta$

and

$$a_0 = -\omega^2/4\omega^2{}_x \qquad a_3 = \frac{\omega_z}{2\omega_x} B$$

$$a_1 = -\omega\omega_z/4\omega_x{}^2$$

$$a_2 = -\frac{1}{6}\left(1 - \frac{\omega}{\omega_x}B + \frac{\omega_z{}^2}{\omega_x{}^2}\right) \qquad a_4 = 1 - B^2.$$

Here x_0 is one of the roots of the equation

$$a_0\xi^4 + 4a_1\xi^3 + 6a_2\xi^2 + 4a_3\xi + a_4 = 0\ ; \tag{42}$$

namely, it is the smaller of the two real roots lying between -1 and $+1$, between which x performs librations.

If we now make the substitution

$$\sigma=\frac{A_2}{2}+\frac{A_3}{\xi-x_0},\quad s=\frac{A_2}{2}+\frac{A_3}{x-x_0},$$

Eq. (41) becomes

$$-\omega_x(t-t_0)=\int_s^\infty(4\sigma^3-g_2\sigma-g_3)^{-\frac{1}{2}}d\sigma, \tag{43}$$

in which g_2 and g_3 are the invariants of Eq. (42) and have the values

$$g_2=a_0a_4-4a_1a_3+3a_2^2$$

$$g_3=a_0a_2a_4+2a_1a_2a_3-a_2^3-a_0a_3^2-a_1^2a_4,$$

while

$$A_2=a_0x_0^2+2a_1x_0+a_2$$

$$A_3=a_0x_0^3+3a_1x_0^2+3a_2x_0+a_3.$$

Now let e, e', e'' be the roots of the equation $4\sigma^3-g_2\sigma-g_3=0$, and such that $e<e'<e''<S<\infty$. We can then write

$$4\sigma^3-g_2\sigma-g_3=4(\sigma-e)(\sigma-e')(\sigma-e'').$$

If we now make the substitution

$$\sin^2\psi=\frac{e''-e}{\sigma-e},\quad \sin^2\phi=\frac{e''-e}{s-e},\quad k^2=\frac{e'-e}{e''-e},$$

Eq. (43) becomes the following:

$$-\omega_x(t-t_0)=(e''-e)^{-\frac{1}{2}}\int_0^\phi(1-k^2\sin^2\psi)^{-\frac{1}{2}}d\psi.$$

This is the Legendre normal form of the elliptical integral of the first kind. We may accordingly write as the solution of our problem

$$-\omega_x(t-t_0)=(e''-e)^{-\frac{1}{2}}F(\phi,k).$$

This last equation gives the relation between ϕ and t, and hence between Θ and t, for ϕ was obtained from Θ by means of the transformations given above. On substituting this expression for Θ in Eq. (40), a similar equation giving the relation between Φ and t is obtained.

Since the same elliptic function is thus shown to occur in the relations between both Θ and Φ and t, these two variables have the same period. Accordingly the secular perturbations are characterized by only one period, and the entire system by two, that of the unperturbed system and that due to the perturbing forces. If we represent by τ' the time required for one cycle in the precessional motion of $\boldsymbol{P}$, we can evidently write

$$-\omega_x(e''-e)^{\frac{1}{2}}\cdot\tau'=2F(\pi/2,k)=2K,$$

in which K is the complete elliptical integral of the first kind. The corresponding frequency of precession is

$$\nu = 1/\tau' = -\omega_x(e''-e)^{\frac{1}{2}}/2K. \qquad (44)$$

The determination of the quantum-allowed states of motion. The perturbed system is now non-degenerate, and two quantum conditions are required to determine a given state of motion. Bohr has shown that to the first order of small quantities one of these conditions is that characterizing the unperturbed motion; in this case

$$W_0 = I^2/8\pi^2 A = j^2h^2/8\pi^2 A\,.$$

Moreover, he has remarked that to the same approximation the average contribution Ψ of the perturbing forces to the energy function must remain constant throughout the secular motion.

Reference to the kinematical relation between Φ and Θ (Eq. 40) verifies that Ψ is not a function of the time, for from (29) and (36) we find

$$\Psi = \Psi_E + \Psi_M = \tfrac{1}{6}\omega p - \omega_x pB\,. \qquad (45)$$

The second quantum condition can now be obtained; for the second action variable I_2 must satisfy the relation

$$\delta\Psi = \nu\delta I_2\,.$$

There are, however, only two constants which determine the secular perturbations; one is the quantity B given by (40), and the other is a constant fixing the absolute phase of the motion of $\boldsymbol{P}$. The second constant is of no significance with regard to the quantum conditions; so that the only variation that I_2 can experience must result from a variation in B. Hence we can write

$$\delta\Psi = \nu(dI_2/dB)\delta B\,,$$

or, collecting terms involving B and integrating,

$$I_2 = \int \frac{\partial\Psi}{\partial B}\cdot\frac{dB}{\nu} + \text{constant}.$$

The constant can be included in the quantity I_2, which can then assume only the values allowed in case either the electric or the magnetic field is present alone. We are thus led, with the use of (44) and (45), to the following equation giving the second quantum condition:

$$2p\int (e''-e)^{-\frac{1}{2}}K\,dB = I_2 = mh\,, \qquad (46)$$

in which I_2 has been placed equal to its quantum-allowed value mh, m being the directional quantum number.

It can easily be shown that in case only one field is present or the fields are parallel or anti-parallel this equation leads to the spatial quantization obtained in the usual way by the separation of variables.

The system in the presence of an electric field small relative to the magnetic field. If the electric field is so small relative to the magnetic field that the quantity ω/ω_M is small compared with unity, the expression determining the action variable I_2 may be evaluated. In this case the two quantities a_0 and a_1 may be treated as small, and it is then possible to determine the three roots e, e', and e'' of the equation $4\sigma^3 - g_2\sigma - g_3 = 0$ by the method of successive approximations. On doing this there result as a second approximation the expressions

$$e = \frac{a_2}{2} - \frac{4a_1a_3 - a_0a_4 - (12a_0a_2(3a_2a_4 - 2a_3^2))^{\frac{1}{2}}}{12a_2}$$

$$e' = \frac{a_2}{2} - \frac{4a_1a_3 - a_0a_4 + (12a_0a_2(3a_2a_4 - 2a_3^2))^{\frac{1}{2}}}{12a_2}$$

$$e'' = -a_2 + \frac{6a_1a_2a_3 - a_0a_3^2}{9a_2^2}\,.$$

By substituting these values in (46), using the well known series development for K, and integrating, neglecting powers higher than linear in ω/ω_M, there is obtained the equation

$$2\pi p B \sin\psi = mh\left[1 + \frac{\omega}{\omega_M}\left\{3\sin^3\psi - \frac{mh}{8\pi p}\sin^2\psi + \frac{mh}{4\pi p}\cos^2\psi + \frac{m^2h^2}{16\pi^2p^2}\sin\psi\cos^2\psi - \frac{m^2h^2}{8\pi^2p^2}\sin^3\psi\right\}\right]. \tag{47}$$

Furthermore, the quantity $B \sin \psi$ is given by the relation

$$B\sin\psi = \cos\Delta + (\omega/2\omega_M)\cos^2\Theta, \tag{48}$$

in which Δ is the angle between $\boldsymbol{P}$ and $\boldsymbol{H}$. Hence we have proved that except for corrections proportional to and of the order of magnitude of the first power of ω/ω_M the spatial quantization with crossed fields is the same as with the magnetic field alone; namely, that the component of angular momentum in the direction of the magnetic field must be equal to $mh/2\pi$.

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