The Theory of the Faraday Effect in Molecules

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In treating the Faraday effect two cases may be distinguished, depending upon whether the frequency of the incident light is near resonance or well removed from resonance with absorption lines of the molecule.

Frequency of incident light well removed from resonance with any absorption lines. In this case it is imperative to include the perturbation of the intensities by the magnetic field, as well as the perturbation of the energies. A general expression is obtained for the rotation by molecules (poly-, di-, or monatomic), of the form

$$V = \sum_{n'} \left\{ \frac{\nu^2 A(nn')}{(\nu(n'n)^2 - \nu^2)^2} + \frac{\nu^2 B(nn')}{\nu(n'n)^2 - \nu^2} + \frac{\nu^2 C(nn')}{T(\nu(n'n)^2 - \nu^2)} \right\},$$

where V is the Verdet constant. This formula contains dia- and paramagnetic terms of the usual type, but augmented by terms arising from perturbation of the intensities. It contains, in addition, other diamagnetic terms which have the same frequency dependence as the paramagnetic terms. For atoms this expression reduces to that given by Rosenfeld. However for diatomic molecules our results differ from Kronig's, since we include the effects of the components of magnetic moment perpendicular to the axis of figure. The terms arising in this way were omitted by Kronig, although generally they are of the same order of magnitude as the contribution of the parallel component of the moment.

Independence of spin. When the over-all spin-multiplet width is small compared to kT/h the rotation is completely independent of spin. As a consequence the paramagnetic terms vanish for nonlinear polyatomic molecules, and for linear polyatomic and diatomic molecules in Σ states.

Magnitude of the rotation and comparison with experiment. The classical Becquerel formula for the Verdet constant is $V = \gamma (e/2mc^2)\nu\partial n/\partial\nu$, with $\gamma = 1$. It is shown that the rotations, in the visible and near ultraviolet, of the gases for which data are available should be approximately representable by a formula of this form, provided γ is given the proper value. The γ value should lie between zero and one. This conclusion, in all cases but one, agrees with the known facts. The exception is oxygen, but the data are probably in error because of polymerization effects which seriously alter the absorption at high pressures.

Frequency of incident light near resonance with an absorption line. Here only the perturbation of the energies by the magnetic field need be considered. It is shown that the rotation in iodine vapour, observed by Wood, is due to rotational distortion of the excited ${}^{3}\Pi_{0}$ level, which partially uncouples the spin moment from the figure axis. The magnetic rotation spectrum of the alkalis, observed by Wood and Loomis, is also explained, in particular the quenching of lines of large rotational quantum number.

TWO different experimental procedures have been employed in measuring the Faraday rotation in gaseous molecules. One method uses a continuous band of incident frequencies, and a low gas pressure; rotation is then observed only in the immediate neighborhood of an absorption line. The other uses monochromatic incident radiation, and high pressures; it serves to mea-

sure the rotation in "transparent" regions of the spectrum. The first method is exemplified by Loomis's measurements of the magnetic rotation spectrum of the alkalis, the second by Siertsema's work on the rotation of hydrogen in the visible.

Correspondingly, the theory must distinguish two cases:

- (I) Incident light near resonance with an absorption line of the molecule.
- (II) Incident light well removed from resonance with any absorption line.

Anticipating our later results, we may remark that (I) is the simpler of the two, as here the rotation is caused by the Zeeman effect alone. In case (II) it is essential to include, in addition, the effect of the perturbation of the amplitudes (i.e., intensities) by the magnetic field.

§§1 to 5 of this paper deal with case (II). §1 discusses, in a non-mathematical way, the theoretical attack, the general conclusions, and the experimental data. §§2, 3, and 4 give the mathematical development of the theory. §5 is concerned with the magnitude of the rotation and with the application of the theory to a number of simple examples.

§6 treats case (I), in particular, the rotation of iodine as observed by Wood, and the work of Loomis mentioned above.

§1. DISCUSSION OF THEORY AND EXPERIMENT

The theory of the Faraday effect in atoms has been treated by Rosenfeld¹ and others. Rosenfeld found, for the case of multiplet widths small compared to kT/h, that when the frequency of the incident light is not near any absorption line the rotation can be expressed as a sum of terms of two types: the diamagnetic, characterized by independence of temperature, and the paramagnetic, proportional to 1/T. The diamagnetic terms are given by

$$V = \frac{4\pi e N \nu^2}{3 hmc^2} \sum_{n'} \frac{\nu(n'n) |P(nn')|^2}{(\nu(n'n)^2 - \nu^2)^2},$$
(1)

where V, the Verdet constant, is the rotation per gauss per cm, the P(nn') are the matrix elements of the resultant electric moment, and ν is the frequency of the incident light. Eq. (1) can also be written in the Becquerel form

$$V = \frac{e}{2mc^2} \nu \frac{\partial n}{\partial \nu},$$

in which n is the index of refraction, as given by the Kramers dispersion formula.² This value of V will be called the normal Verdet constant.

The purpose of the present paper will be to extend the theory to molecules. A start in this direction has already been made by Kronig,³ who, under the same condition that ν is not too near the frequency of any line, finds a Verdet

³ R. de L. Kronig, Zeits. f. Physik **45**, 458 and 508 (1927).

¹ L. Rosenfeld, Zeits. f. Physik 57, 835 (1930).

² See, for example, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 362.

constant of only one-third the normal value.⁴ This result seems unsatisfactory, for it does not agree with Rosenfeld's calculation in the limiting case of a central field. It will be shown that the error lies in Kronig's neglect of the components of magnetic moment perpendicular to the axis of figure of the diatomic molecule. Since in a central field the components of magnetic moment along any three orthogonal axes contribute equally to the rotation, neglect of two of these components will naturally lead to Kronig's result.

We shall suppose throughout that ν is well outside the Zeeman pattern of any line, i.e., that $\nu - \nu(n'n)$ is large compared to the Zeeman displacements. When only this restriction is made the rotation of any molecule⁵ is found to be given by a formula of the form

$$V = B \sum_{nn'} \left\{ \frac{\nu^2 a(nn')}{(\nu(n'n)^2 - \nu^2)^2} + \frac{\nu^2 b(nn')}{\nu(n'n)^2 - \nu^2} + \frac{\nu^2 c(nn')}{T(\nu(n'n)^2 - \nu^2)} \right\} e^{-W_n/kT}, \quad (2)$$

with $B = 1/\sum_{n} e^{-W_n/kT}$. The three kinds of terms appearing in Eq. (2) will be called "a terms," "b terms," and "c terms," respectively. The a terms are the contributions of the Zeeman effect; the c terms are due to the altered distribution of molecules in the various normal states caused by the magnetic field. The b terms arise from the perturbation of the amplitude elements of the electric moment by the magnetic field. This perturbation is, of course, a consequence of the existence of matrix elements of the magnetic moment between the various states.

Definition of the term "magnetic interaction"

For brevity, when an element of the magnetic moment between two states exists, we shall speak of the magnetic interaction between the states.

Coalescence of b terms into a and c terms

The magnetic interaction between a state n' and a state n'' gives a rotation proportional to the difference quotient⁶

$$\frac{1}{\nu(n'n'')} \left\{ \frac{1}{\nu^2 - \nu(n'n)^2} - \frac{1}{\nu^2 - \nu(n''n)^2} \right\}.$$
 (3)

If $\nu(n'n'')/(\nu-\nu(n'n))$ is small the difference quotient can be expanded in powers of this ratio (since $\nu(n'n'') = \nu(n'n) - \nu(n''n)$) giving

$$\frac{2\nu(n'n)}{(\nu^2 - \nu(n'n)^2)^2} \left\{ 1 - \frac{2\nu(n'n)\nu(n'n'')}{\nu^2 - \nu(n'n)^2} + \cdots \right\}.$$

⁴ Kronig has calculated the rotation explicitly only for diatomic molecules in ¹ Σ states. In comparing Kronig's result (p. 511, reference 3) with our Eq. (1), the factor 2 in his expression must be absorbed by summing over $\Lambda = \pm 1$ rather than only over $\Lambda = 1$. Making the substitution $|a_0(l_0l_1)|^2 = 4 |P_{\xi}(l_0l_1)|^2$, and remembering that in a central field $|P_{\xi}(l_0l_1)|^2 = \frac{1}{3} |P(l_0l_1)|^2$, one readily verifies that the two expressions differ by a factor 1/3.

⁵ Throughout this paper the term *molecule* is to be understood as including *atom*.

⁶ It must be cautioned that this picture is incomplete, as not all b terms appear in the form of difference quotients (see Eq. (8)).

Neglecting terms after the first we see that the two b terms contained in Eq. (3) have reduced to a single a term. Similarly, b terms due to magnetic interactions between states with slightly different Boltzmann factors give rise to c terms when expanded in powers of hv(n'n'')/kT. Of course b terms caused by interactions between states of widely different energies cannot be simplified in this way.

The net result of the operations just described is the enrichment of a and c terms at the expense of b terms. These modified terms will be called A, B, and C terms to distinguish them from the a, b, and c terms. It should be noted that the A and C terms can not be ascribed any such simple origin as was possible for the a and c terms. Hereafter, whenever we refer to Eq. (2) we shall mean the equation modified in this way, rather than the equation as originally given.

Elimination of Boltzmann factors

The exponential factors drop out of Eq. (2) when the following conditions are satisfied:

a. The over-all spin-multiplet width is small compared to kT/h; or

a'. The separation between the two lowest spin-multiplet components is large compared to kT/h.

b. There are no electronic states with separations from the lowest state of the order of kT/h.

c. The separations between the rotational levels of the normal state are small compared to kT/h.

d. The molecule can be considered rigid (e.g., rotational distortion neglected).

e. The states of the molecule can be divided into groups.⁷ A set of states n_1, n_2, \dots, n_t , will be said to constitute a group if $\nu(n_r n_s)$ is small compared to both $\nu - \nu(n_r p)$ and $\nu(n_r m)$, n_r and n_s representing any two members of the set, p one of the normal states, and m any state, normal or excited, not belonging to the set. Thus in Fig. 1 the states g form a group.

It is evident that condition (e) restricts us to case (II) discussed in the introduction, for if $\nu - \nu(n_r p)$ is too small (i.e., if the incident light is "near resonance with any absorption line") division of states into groups will be impossible. When ν is restricted to such a range that (e) is satisfied, the allowable spread of a group will be widely different in different parts of the spectrum. For example, groups lying near ν or near the normal level may consist of states differing only in their rotational quantum numbers, while groups far from ν and the normal level may include different vibrational states, or even states arising from different electronic configurations.

When either set of conditions, (a), (b), (c), (d), (e), or (a'), (b), (c), (d), (e), is met, the rotation is given by a formula of the form

$$V = \sum_{n'} \left\{ \frac{\nu^2 A(nn')}{(\nu(n'n)^2 - \nu^2)^2} + \frac{\nu^2 B(nn')}{\nu(n'n)^2 - \nu^2} + \frac{\nu^2 C(nn')}{T(\nu(n'n)^2 - \nu^2)} \right\}, \quad (4)$$

⁷ In dividing the states into groups not all states need be considered, but only those having nonvanishing terms in Eq. (8).

with A(nn'), B(nn'), C(nn') constants independent of temperature. Both A and B terms are thus diamagnetic, the C terms paramagnetic. One must not be misled by the terminology into supposing that the signs of paramagnetic and diamagnetic terms are necessarily opposite, for this is not the case. The presence of diamagnetic B terms, having the same frequency dependence as the paramagnetic terms, has been generally overlooked in the previous theories (it was noted, however, by Van Vleck⁸), although, as will be shown later, the B terms are actually no less important than the more customary A terms.



In virtue of condition (e) and in view of the discussion of Eq. (3), we can now say that the A terms are due to magnetic interactions between states lying in the same group, while B terms are due to interactions between states in different groups.

The A terms of Eq. (4) are of a more general type than the A terms obtained by Kronig and Rosenfeld, since ours include the interactions between various states in a group. These interactions were neglected by Kronig⁹ and did not exist in the case considered by Rosenfeld. Rosenfeld's case of atoms with multiplet widths small compared to kT/h is simplified by the fact that M_L and M_s can be considered constants of the motion,¹⁰ and so the z com-

⁸ J. H. Van Vleck, reference 2, p. 370.

⁹ Kronig, to be sure, included the elements of μ_z between states of different *j*, but not between states of different electronic quantum numbers. It is to the latter sort that we refer.

¹⁰ Strictly speaking, this is true only if the magnetic field is strong enough to produce the Paschen-Back effect; however the distinction is trivial in view of the invariance of the spurs appearing in Eq. (9).

ponent of the magnetic moment has no nondiagonal elements. Thus there are no interaction terms like Eq. (3), with the consequence that the A terms reduce simply to the normal Verdet constant, while the B terms vanish entirely (see Eq. (9)).¹¹ Kronig's calculation of the A terms for diatomic molecules is valid in the limiting case of an axial field so far from central in character that the components of the magnetic moment perpendicular to the figure axis have elements only between states in different groups. Here obviously the A terms are due only to the parallel component of the moment, as Kronig assumed. The B terms will not vanish in this case, and, in fact, are of the same order as the A terms, although omitted by Kronig. Our A terms agree with Kronig's and Rosenfeld's in these limiting cases, but otherwise they are not the same. For example, for nonlinear polyatomic molecules the mean value of the magnetic moment along any axis is zero;¹² hence Kronig's method would give no rotation at all, although we obtain both A and B terms.

Independence of spin

An important characteristic of Eq. (2) (and consequently of Eq. (4)) is that, when (a), (c) and (e) are satisfied, it is completely independent of spin. In any calculation of the rotation, subject of course to these conditions, the spin can be regarded as completely uncoupled from the orbital angular momentum, and, in effect, forgotten completely. This result is analogous to the well-known theorem that the magnetic susceptibility is independent of the Paschen-Back effect, and like it is a consequence of the fact that we sum our expressions over all Zeeman components. In view of this property of the rotation the attempts to explain the anomalous behavior of oxygen as due to its spin are not justifiable. Another conclusion which can immediately be drawn is that the paramagnetic terms of Eq. (4) vanish for nonlinear polyatomic molecules, and for linear polyatomic molecules and diatomic molecules in Σ states. This is because the paramagnetic terms are due to the magnetic interactions between the normal states. Since spin need not be considered, these interactions are clearly zero in the cases indicated.

The absence of a spin-paramagnetic rotation is in sharp contrast to the presence of a spin term in the magnetic susceptibility under the same supposition of narrow multiplets. The difference arises because, under the circumstances, the spin and orbital moments can be regarded as completely independent systems. They thus will contribute additively to the susceptibility; on the other hand, the spin appears in the rotation only in cross terms with the orbit, and such cross terms average to zero.

Magnitude of the rotation

It frequently happens that the rotation has not been measured much beyond the visible, while all the $\nu(n'n)$ are in the far ultraviolet. The A and B

¹¹ Considering the phases proper to a central field, it is readily seen that, in this case, Eq. (9) is identical with Rosenfeld's expression.

¹² This statement might not hold if the molecule had a very high degree of symmetry; however, whenever we consider nonlinear polyatomic molecules we shall assume that this is not the case.

terms are then practically indistinguishable, the net result of the *B* terms being to change the apparent values of the A(nn'). Thus the diamagnetic terms of Eq. (4) will have, effectively, the frequency dependence, $\nu^2/(\nu(n'n)^2 - \nu^2)^2$, of the Becquerel formula. In consequence, as will be shown more fully in §5, the rotation can often be represented fairly well by the Becquerel formula with an anomalous value of e/m.

In general our knowledge of the molecule is not sufficient to permit explicit calculation of all the terms required by Eq. (4), but simple considerations lead to the conclusion that the Verdet constant should ordinarily be less than the normal value. The experimental results in all cases confirm this. The reason is roughly as follows: The rotation is largely due to the nearest intense group of lines in the ultraviolet, which are heavily weighted compared to those further out. If all the lines lay close to this nearest group a normal Verdet constant would result, as is shown in §5. The effect of removing some of the lines further into the ultraviolet, where in fact they belong, is to diminish greatly their contribution to the rotation. If the field is not central this diminution is greater than the corresponding decrease in $\partial n/\partial \nu$, and so leads to a smaller Verdet constant.

Discussion of experiment¹³

Siertsema's measurements of the rotation in hydrogen in the visible are representable almost exactly by the normal Verdet constant. This result, remarkable in its agreement with the classical theory, will be discussed in §5. However Sirk's measurements in the ultraviolet show some evidence of the presence of a *B* term. The magnitude of the observed rotation in nitrogen is 63 percent of the normal Verdet constant, i.e., the Becquerel formula is valid if we insert a factor 0.63. As the measurements have not been carried beyond the visible no differentiation between *A* and *B* terms is possible. The case of N₂O is similar. Carbon dioxide has been observed in the ultraviolet, but not far enough to give any conclusive evidence as to the presence or absence of *B* terms (see §5).

Oxygen, on the other hand, is definitely anomalous. The measurements of Siertsema and Sirks in the visible and ultraviolet cannot be fitted by Eq. (4) using the observed absorption frequencies, and, as we have seen, this cannot be blamed on the spin. However the experimental data are open to serious objection because of the high gas pressures used: Siertsema, working in the visible, used a pressure of 100 atmospheres; Sirks, 80 atmospheres in the visible, 40 in the ultraviolet below 2800A. At these pressures a considerable amount of oxygen would be in the form of the polymer O_4 .^{13a} The equilibrium constant is somewhat uncertain; at 80 atmospheres the estimates of the

¹³ An excellent account of the experimental data on the Faraday effect has been given by C. G. Darwin and W. H. Watson, Proc. Roy. Soc. **114A**, 474 (1927). The reader is referred to this paper for references to the literature.

^{13a} The existence of this polymer was kindly called to my attention by Professor R. Ladenburg.

partial pressure of O_4 range from 1 to 10 percent of the total pressure.¹⁴ According to Wulf,¹⁴ O_4 shows continuous absorption below 2400A, as well as a number of bands extending towards longer wave-lengths. Moreover, the source of light used by Sirks and Siertsema was a quartz mercury arc, and Warburg¹⁵ has shown that at high pressures the 2537A line is efficacious in producing ozone. Ozone shows strong absorption in the infrared, and in the ultraviolet beginning at about 2800A. Sirks found, in his 230 cm column of oxygen at 80 atmospheres, that absorption began at 2805A; in fact it was for this reason that he was compelled to reduce the pressure for his shorter wave-length measurements. At 40 atmospheres the absorption had moved down to 2654A. O_2 shows no absorption in this region, but both O_4 and O_3 bands have been reported at 2810A and 2654A;¹⁶ these might readily account for Sirk's results.

In view of these facts we believe the existing measurements of the rotation entirely unreliable; solution of the problem must await more unambiguous data.

Monatomic gases should, according to Rosenfeld, have a normal Verdet , constant. This has been verified for neon, although at only one wave-length, 5460A. The same result has also been found for argon.¹⁷

In general the rotations in the large number of liquids and solids cited by Darwin are not accurately representable by the Becquerel formula, even with an anomalous value of e/m. There are two obvious reasons for this: first, the A(nn') are not proportional to the f values of the Kramers dispersion formula; second, B terms are also present.

§2. Derivation of the General Formula for the Rotation

Let the magnetic field and the light ray be directed along the z axis. The rotation of the plane of polarization per centimeter is¹⁸

$$\theta = CB \sum_{nn'} \tau(n'n) \left[P_x(nn') P_y(n'n) \right] e^{-W_n/kT}, \tag{5}$$

where

and

$$B = N / \sum_{n} e^{-W_{n}/kT}, \ C = 4\pi^{2}\nu^{2}i/ch,$$

and $P_x(nn')$, $P_y(nn')$ are the elements of the x and y components of the electric moment in the presence of the magnetic field. Here, and throughout this paper, the square brackets have the meaning

$$[P_x(nn')P_y(n'n)] = P_x(nn')P_y(n'n) - P_y(nn')P_x(n'n);$$

$$\tau(n'n) = 1/(\nu^2 - \nu(n'n)^2).$$

¹⁴ O. R. Wulf, Proc. Nat. Acad. **14**, 356, 609, 614 (1928); Jour. Am. Chem. Soc. (II) **50**, 2596 (1928).

¹⁵ References to Warburg's work are given by Wulf, reference 14.

¹⁶ Wulf, reference 14; D. Chalonge and M. Lambrey, Comptes Rendus 184, 1165 (1927).

¹⁷ R. de Mallemann, L. Gabiano, and F. Suhner; Comptes Rendus 194, 861 (1932).

¹⁸ H. A. Kramers, Kon. Acad. Wet. Amsterdam **33**, 959 (1930). Kramer's Eq. (34) should be multiplied by 4π , as can be seen from his Eq. (32).

We expand P_x , P_y , $\nu(n'n)$, W_n , B in power series of the form $P_x = P_x^0 + \Im C P_x^{(1)} + \cdots$; then, under the supposition that $\nu - \nu(n'n)$ is large compared to the Zeeman splitting, the terms of Eq. (5) linear in \Im give

$$V = \theta / \mathcal{K} = CB^{0} \sum_{\substack{nn' \\ n'n'}} \left\{ \tau^{0}(n'n) \left(\left[P_{x}^{0}(nn') P_{y}^{(1)}(n'n) \right] + \left[P_{x}^{(1)}(nn') P_{y}^{0}(n'n) \right] \right) \\ + 2\nu^{0}(n'n)\nu^{(1)}(n'n)\tau^{0}(n'n)^{2} \left[P_{x}^{0}(nn') P_{y}^{0}(n'n) \right] \\ - \left(W_{n}^{(1)} / kT \right) \tau^{0}(n'n) \left[P_{x}^{0}(nn') P_{y}^{0}(n'n) \right] \right\} e^{-W_{n}^{0}/kT}.$$
(6)

 $P_x^{(1)}(nn')$ is expressed in terms of the unperturbed amplitudes by means of ¹⁹

$$P_{x}^{(1)}(nn') = \frac{1}{h} \sum_{n''} \left\{ \frac{H^{(1)}(nn'')P_{x}^{0}(n''n')}{\nu^{0}(nn'')} - \frac{P_{x}^{0}(nn'')H^{(1)}(n''n')}{\nu^{0}(n''n')} \right\}.$$
 (7)

The prime on the summation sign indicates that n'' = n and n'' = n' are to be omitted from the summation. Denoting the z component of the magnetic moment by μ_z , we have $H^{(1)}(nn') = -\mu_z(nn')$. Using these, and a similar expression for $P_{\mu}^{(1)}(nn')$, we obtain

$$V = - (CB^{0}/h) \sum_{nn'n''} \nu^{0}(n'n'')^{-1} [P_{x}^{0}(nn')\mu_{z}(n'n'')P_{y}^{0}(n''n)] \left\{ \tau^{0}(n'n) - \tau^{0}(n''n) \right\} e^{-W_{n}^{0}/kT} - (2CB^{0}/h) \sum_{nn'} \nu^{0}(n'n)\tau^{0}(n'n)^{2} [P_{x}^{0}(nn')\mu_{z}(n'n')P_{y}^{0}(n'n)] e^{-W_{n}^{0}/kT} + (CB^{0}/h) \sum_{nn'n''} \nu^{0}(n''n)^{-1}\tau^{0}(n'n) \left\{ [P_{x}^{0}(nn')P_{y}^{0}(n'n'')]\mu_{z}(n''n) + \mu_{z}(nn'') [P_{x}^{0}(n''n')P_{y}^{0}(n'n)] \right\} e^{-W_{n}^{0}/kT} + (2CB^{0}/h) \sum_{nn'} \nu^{0}(n'n)\tau^{0}(n'n)^{2}\mu_{z}(nn) [P_{x}^{0}(nn')P_{y}^{0}(n'n)] e^{-W_{n}^{0}/kT} + (CB^{0}/kT) \sum_{nn'} \tau^{0}(n'n)\mu_{z}(nn) [P_{x}^{0}(nn')P_{y}^{0}(n'n)] e^{-W_{n}^{0}/kT}.$$
(8)

Here we have extended our definition of the square bracket to include

$$\begin{bmatrix} P_x^{0}(nn')\mu_z(n'n'')P_y^{0}(n''n) \end{bmatrix} = P_x^{0}(nn')\mu_z(n'n'')P_y^{0}(n''n) - P_y^{0}(nn')\mu_z(n'n'')P_x^{0}(n''n).$$

In accordance with our division of states into groups, all matrix elements will now be written (dropping henceforth the superscript⁰) in the form $P_{\mathcal{F}}(nk;n'k')$, where *n* and *n'* represent the quantum numbers which are the same for all states in a group, *k* and *k'* the quantum numbers which differentiate the various states within a group.

The terms of the first sum in Eq. (8) for which n'' = n' (although, of course, $k'' \neq k'$) can be simplified by expanding the factor in curly brackets in powers of $\nu(n'k';n'k'')/(\nu^2 - \nu(n'k';nk)^2)$. To simplify the terms of the third sum for which n'' = n $(k'' \neq k)$ the method of pairing terms previously used by Van Vleck²⁰ is employed.

¹⁹ See, for example, Born and Jordan, *Elementare Quantenmechanik*, p. 198.

²⁰ J. H. Van Vleck, reference 2, p. 191; Phys. Rev. 29, 727 (1927).

The pair of terms

 $\begin{aligned} &(1/h)\nu(nk'';nk)^{-1}\tau(n'k';nk) \left\{ \left[P_x(nk;n'k')P_y(n'k';nk'') \right] \mu_z(nk'';nk) \right. \\ &+ \mu_z(nk;nk'') \left[P_x(nk'';n'k')P_y(n'k';nk) \right] \right\} e^{-W_{nk}/kT} \\ &+ (1/h)\nu(nk;nk'')^{-1}\tau(n'k';nk'') \left\{ \left[P_x(nk'';n'k')P_y(n'k';nk) \right] \mu_z(nk;nk'') \right\} \right\} e^{-W_{nk}/kT} \end{aligned}$

 $+ \mu_{z}(nk''; nk) [P_{x}(nk; n'k')P_{y}(n'k'; nk'')] e^{-W_{nk''}/kT}$

can be written

$$\left\{ \left[P_x(nk; n'k') P_y(n'k'; nk'') \right] \mu_z(nk''; nk) + \mu_z(nk; nk'') \left[P_x(nk''; n'k') P_y(n'k'; nk) \right] \right\}$$

$$\frac{1}{h\nu(nk'';nk)} \left\{ \frac{e^{-W_{nk}/kT}}{\nu^2 - \nu(n'k';nk)^2} - \frac{e^{-W_{nk''}/kT}}{\nu^2 - \nu(n'k';nk'')^2} \right\}$$

Putting

$$\begin{split} W_{nk''} &= W_{nk} + h\nu(nk''; nk), \\ \nu(n'k'; nk'') &= \nu(n'k'; nk) - \nu(nk''; nk) \end{split}$$

and expanding gives (the first bracket representing the first line of the above expression)

$$\begin{cases} \begin{cases} \left\{ \frac{1}{2kT} \frac{e^{-W_{nk}/kT}}{\nu^2 - \nu(n'k'; nk)^2} \left[1 + \left(1 - \frac{h\nu(nk''; nk)}{kT} \right) \right] \\ + \frac{2\nu(n'k'; nk)e^{-W_{nk}/kT}}{h(\nu^2 - \nu(n'k'; nk)^2)^2} \left[1 - \frac{h\nu(nk''; nk)}{kT} \right] \end{cases} \end{cases}$$

plus higher order terms which are very small. Apart from them, this is the same as

 $\{ [P_{x}(nk; n'k')P_{y}(n'k'; nk'']\mu_{z}(nk''; nk) + \mu_{z}(nk; nk'')[P_{x}(nk''; n'k')P_{y}(n'k'; nk)] \}$ $\{ (1/h)\nu(n'k'; nk)\tau(n'k'; nk)^{2} + (1/2kT)\tau(n'k'; nk) \} e^{-W_{nk}/kT}$ $+ \{ [P_{x}(nk''; n'k')P_{y}(n'k'; nk)]\mu_{z}(nk; nk'') + \mu_{z}(nk''; nk)[P_{x}(nk; n'k')P_{y}(n'k'; nk'')] \}$ $\{ (1/h)\nu(n'k'; nk'')\tau(n'k'; nk'')^{2} + (1/2kT)\tau(n'k'; nk'') \} e^{-W_{nk'}/kT}.$

The purpose of these manipulations is to remove all small ν 's from the denominators of Eq. (8). A primed sum is no longer required for the terms written in this form, since the diagonal terms (i.e., k'' = k) are already present in Eq. (8): namely, the fourth and fifth sums there appearing. The expansion of the first sum of Eq. (8) leads to a similar simplification, the diagonal terms being contained in the second sum.

It is now convenient to introduce the übermatrix notation used, for example, in Born and Jordan's *Elementare Quantenmechanik*. In this notation $P_x^{(nn')}$ signifies the matrix of all the elements $P_x(nk;n'k')$ having a given n and n'. Sp is an abbreviation for *spur*.

One finds, on carrying out the operations described above that Eq. (8) becomes

$$V = (CB/h) \sum_{n'} \nu(n'n) \tau(n'n)^{2} \operatorname{Sp} \left\{ (-2 \left[P_{x}^{(nn')} \mu_{z}^{(n'n')} P_{y}^{(n'n)} \right] \right] + \left[P_{x}^{(nn')} P_{y}^{(n'n)} \right] \mu_{z}^{(nn)} + \mu_{z}^{(nn)} \left[P_{x}^{(nn')} P_{y}^{(n'n)} \right] \right] e^{-W^{(n)}/kT} \right\} + (CB/h) \sum_{n'n''(n' \neq n'')} - \nu(n'n'')^{-1} \left\{ \tau(n'n) - \tau(n''n) \right\}$$

$$\operatorname{Sp} \left\{ \left[P_{x}^{(nn')} \mu_{z}^{(n'n')} P_{y}^{(n'n)} \right] e^{-W^{(n)}/kT} \right\} + \nu(n''n)^{-1} \tau(n'n) \operatorname{Sp} \left\{ \left(\left[P_{x}^{(nn')} P_{y}^{(n'n')} \right] \mu_{z}^{(n''n)} + \mu_{z}^{(nn'')} \left[P_{x}^{(n'n')} P_{y}^{(n'n)} \right] \right) e^{-W^{(n)}/kT} \right\} + (CB/2kT) \sum_{n'} \tau(n'n) \operatorname{Sp} \left\{ \left(\left[P_{x}^{(nn')} P_{y}^{(n'n)} \right] \mu_{z}^{(nn)} + \mu_{z}^{(nn)} \left[P_{x}^{(nn')} P_{y}^{(n'n)} \right] \right) e^{-W^{(n)}/kT} \right\}.$$
(9)

As all small ν 's have been removed from the denominators of Eq. (8) we have been able, in Eq. (9), to write $\nu(n'k';nk) = \nu(n'n)$. In the first sum of Eq. (9) small terms involving $\nu(nk';nk)$ have been omitted. This corresponds to neglecting the pure rotation spectrum.

§3. INDEPENDENCE OF SPIN

The spurs appearing in Eq. (9) are invariant of a transformation to a system of representation appropriate to strong fields. If the over-all spinmultiplet width is small compared to kT/h the matrix $e^{-\mathbf{w}^{(n)}/kT}$ is independent of spin. Then the "strong field" representation the spin appears only in μ_z , which breaks up into two parts, $\mu_{lz} + \mu_{sz}$, of which only the second contains the spin. On summing over m_s this term vanishes, since μ_{sz} is a diagonal matrix with elements ranging from $-2\beta s$ to $2\beta s$. Thus, when the over-all multiplet width is small and when ν is not near resonance with any line, the rotation is independent of the spin.²¹ This result, of course, is valid for all field strengths (barring saturation effects).

In §5, dealing with the magnitude of the rotation, we shall consider only narrow multiplets; μ_z may accordingly be taken as representing only that part of the magnetic moment due to the orbital angular momentum.

§4. ROTATION IN RIGID MOLECULES

We will make the approximation of supposing the molecule rigid, that is, we suppose the "internal" wave functions, which are expressed in terms of a coordinate system rotating with the molecule, independent of j. Then the summation over j, m, j', m', j'', m'' implied in Eq. (9) can be readily performed by a method given by Niessen.²² Let x', y', z' be the rotating system of coordinates. On applying Niessen's method to Eq. (9) we find²³

$$V = (C N/3hg) \sum_{x'y'z'} \sum_{n'} \nu(n'n)\tau(n'n)^{2} \operatorname{Sp} \left\{ -2 \left[P_{x'}^{(nn')} \mu_{z'}^{(n'n')} P_{y'}^{(n'n)} \right] \right. \\ \left. + \left[P_{x'}^{(nn')} P_{y'}^{(n'n)} \right] \mu_{z'}^{(nn)} + \mu_{z'}^{(nn)} \left[P_{x'}^{(nn')} P_{y'}^{(n'n)} \right] \right\} \\ \left. + (CN/3hg) \sum_{x'y'z'} \sum_{n'n''}^{(n'n'')} - \nu(n'n'')^{-1} \left\{ \tau(n'n) - \tau(n''n) \right\} \right. \\ \left. \operatorname{Sp} \left[P_{x'}^{(nn')} \mu_{z'}^{(n'n')} P_{y'}^{(n'n')} \right] + \nu(n''n)^{-1} \tau(n'n) \\ \left. \operatorname{Sp} \left\{ \left[P_{x'}^{(nn')} P_{y'}^{(n'n'')} \right] \mu_{z'}^{(n'n')} + \mu_{z'}^{(nn'')} \left[P_{x'}^{(n'n')} P_{y'}^{(n'n)} \right] \right\} \right. \right.$$

$$\left. + (CN/6kTg) \sum_{x'y'z'} \sum_{n'}^{(nn')} \tau(n'n) \operatorname{Sp} \left\{ \left[P_{x'}^{(nn')} P_{y'}^{(n'n)} \right] \mu_{z'}^{(nn)} \right] \right\} \right.$$

$$\left. + \mu_{z'}^{(nn)} \left[P_{x'}^{(nn')} P_{y'}^{(n'n)} \right] \right\} .$$

$$\left. \right\}$$

$$\left. \right\}$$

$$\left. \left. \right\}$$

The symbol $\sum_{x'y'z'}$ indicates a summation of the three terms obtained by a cyclic interchange of x', y', z'. g is the statistical weight of the normal state

²¹ This result has been given, for central fields, by Rosenfeld, reference 1, and in the old quantum theory, also for central fields, by Darwin, Proc. Roy. Soc. **112A**, 814 (1926).

²² K. F. Niessen, Phys. Rev. **34**, 253 (1929). Niessen's derivation is valid only for diatomic molecules, but the proof can be given for the general case.

²⁸ It should be noted that Eq. (10) holds when either condition (a) or (a') is satisfied.

of the stationary molecule. The elements of matrices such as $P_{x'}{}^{(nn')}$ are, of course, independent of j, m, j', m'.

Making a simple rearrangement of the terms in the second sum of Eq. (10), we find the explicit expression for the A(nn'), B(nn'), C(nn') of Eq. (4):

$$C(nn') = (CN/6kg\nu^2) \sum_{x'y'z'} \text{Sp} \left\{ \left[P_{x'}^{(nn')} P_{y'}^{(n'n)} \right] \mu_{z'}^{(nn)} + \mu_{z'}^{(nn)} \left[P_{x'}^{(nn')} P_{y'}^{(n'n)} \right] \right\}.$$

§5. MAGNITUDE OF THE ROTATION

For nonlinear polyatomic molecules the matrix $\mu^{(nn)}$ will be zero, there being no "precession frequencies" which are not large compared to kT/h. Thus the C(nn') will vanish. Diatomic molecules and linear polyatomic molecules in Σ states will also have no elements in $\mu^{(nn)}$ different from zero, so the C(nn') again vanish. In these cases there will be no paramagnetic rotation.

The work of Rosenfeld and Kronig give limiting values for the A(nn'). We have shown in §1 that in a central field the A(nn') have just the values which give the normal Verdet constant, and in the other limiting case (for diatomic molecules) of an extreme axial field the A(nn') are reduced to onethird the previous value (the three terms of the $\sum_{x'y'z'}$ sum reducing to a single term), unless both n and n' are Σ states, in which case A(nn') vanishes entirely.²⁴ The A(nn') of polyatomic molecules similarly vanish for sufficiently asymmetrical fields.

The whole question of the magnitude of the rotation is greatly clarified by consideration of a few simple examples. The molecular wave function (in the x', y', z' system) will be supposed the product of the hydrogenic wave functions of the individual electrons. This makes Λ a constant of the motion.

Let the normal state be $(ns\sigma)^2\Sigma$, as in the hydrogen molecule. Take for excited states $ns\sigma n'p\pi\Pi$ and $ns\sigma n'p\sigma\Sigma$, and let ν_1 , ν_2 , ν_3 be respectively the $ns\sigma n'p\sigma\Sigma - (ns\sigma)^2\Sigma$, $ns\sigma n'p\pi\Pi - (ns\sigma)^2\Sigma$, $ns\sigma n'p\sigma\Sigma - ns\sigma n'p\pi\Pi$ separations. This situation is illustrated in Fig. 2 (a). No assumption will be made as to the relative magnitudes of ν_1 and ν_2 , other than that condition (e) is satisfied; they must accordingly be considered as belonging to two different groups. This procedure, of course, is valid even when $\nu_1 - \nu_2$ (i.e., ν_3) is small. Using the well-known hydrogenic moment matrices we readily find from Eq. (10),²⁵

²⁴ We are thinking here of the practically important case, in which the normal state is a Σ state. In general the one-third remaining after passage to the axial field limit will be divided among the states of different Λ into which the central field group breaks up.

$$V = \frac{4\pi e N \nu^2}{3 h m c^2} \left\{ \frac{P^2}{\nu_3 (\nu_2^2 - \nu^2)} - \frac{P^2}{\nu_3 (\nu_1^2 - \nu^2)} + \frac{\nu_2 P^2}{(\nu_2^2 - \nu^2)^2} \right\},$$
 (11)

where $P^2 = 2 |P_{x'}(n'p\pi, ns\sigma)|^2$ in the notation of footnote (25).

The normal Verdet constant is

$$V_n = \frac{4\pi e N \nu^2}{3hmc^2} \left\{ \frac{\nu_1 P^2}{(\nu_1^2 - \nu^2)^2} + \frac{2\nu_2 P^2}{(\nu_2^2 - \nu^2)^2} \right\}.$$
 (12)

The asymptotic properties discussed above are easily verified. If ν_3 is made small compared to $\nu_1 - \nu$, Eqs. (11) and (12) both reduce to

$$V = V_n = 4\pi e N \nu^2 \nu_2 P^2 / hmc^2 (\nu_2^2 - \nu^2)^2;$$

thus V is just the normal Verdet constant. If ν_3 is very large, so that the first two terms of Eq. (11) and the first term of Eq. (12) are negligible, the rotation, as given by Eq. (11), is reduced to one-third the above value, which is Kronig's result. In this case $V = \frac{1}{2}V_n$ (the index of refraction being reduced to 2/3 its central field value, while the rotation is reduced to 1/3).

If γ is defined by $\gamma = V/V_n$, we have seen that $\gamma = 1$ for a central field, and $\gamma = 0.5$ for an extreme axial field.²⁶ In intermediate cases γ will lie between these values. For example if we take $\nu_1 = 2\nu_2$, $\nu = \nu_2/6$ we find $\gamma = 0.817$. Taking $\nu = \nu_2/4$ gives $\gamma = 0.813$. If ν_2 corresponds to a line at 1000A these two values of ν correspond to 6000A and 4000A respectively. This simple calculation strikingly illustrates the point made in §1 that A and B terms are, in such a frequency range, practically indistinguishable. Further, it shows very clearly why a Becquerel formula with an anomalous value of e/m is approximately valid for many substances. If we put $\nu = \nu_2/2.5$, corresponding to $\lambda = 2500A$, we obtain $\gamma = 0.79$. Thus even measurements this far in the ultraviolet would be of little value in distinguishing between Eq. (11) and the modified Becquerel formula.

Magnetic interactions between some of the excited states may be due to the "core," or part of the molecule exclusive of the excited electron, for when we remove an electron from a closed shell the residuum may have a magnetic moment. Of course states which have different core-configurations are greatly different in energy, and so the magnetic interactions of the core may easily connect widely separated levels. On the other hand, a normal Verdet constant requires narrow, rather than wide, separations. The essential difference

²⁵ For example, denoting the normal state by ψ_1 , the II state by ψ_2 , and the wave functions of the individual electrons by $(n|x_i)$ we have

$$\psi_{1} = (ns\sigma | x_{1})(ns\sigma | x_{2}), \quad \psi_{2} = (ns\sigma | x_{1})(n'\rho\pi | x_{2}), \\ P_{x}(12) = -ef/\psi_{1}^{*}(x_{1} + x_{2})\psi_{2}d\tau_{1}d\tau_{2} = -ef(ns\sigma | x_{2})^{*}x_{2}(n'\rho\pi | x_{2})d\tau_{2} \\ = P_{x_{1}}(ns\sigma; n'\rho\pi).$$

The elements such as $P_{x_2}(ns\sigma; n'p\pi)$ are given in all the standard texts, e.g., H. Weyl, The Theory of Groups and Quantum Mechanics, p. 200.

²⁶ If the Σ state is taken as the lower of the excited states γ would range from 1 to 0 (we are supposing $\nu < \nu_1, \nu_2$). For polyatomic molecules also, γ would be expected to range from 1 to 0. These figures are exclusive of negative terms, which will be discussed later.

between the rotations in atoms and molecules lies in the spread, in molecules, of levels which coincide in atoms; and the more complicated the core the larger this spread is likely to be. One would therefore expect the rough rule that molecules with complicated cores have lower values of γ than simpler molecules. The data confirm this, the γ values for H₂, N₂, CO₂, N₂O being respectively 1.00, 0.63, 0.56, 0.34.

The central field behaviour of hydrogen in the visible is now readily explained, for the core consists of a single electron in a σ state, and thus plays no part in determining the rotation. As one would anticipate, the potential energy curves²⁷ show that the excited $1s\sigma 2p\sigma\Sigma$ and $1s\sigma 2p\pi\Pi$ states lie quite close to each other as compared to their separation from the normal state. Since there is little possibility of exciting the core electron to obtain other states which could contribute to the rotation, the rotation is evidently due almost entirely to the two excited states mentioned above; and, as we have seen, these closely spaced levels should give a normal Verdet constant.

As an example of the case in which the core does have a magnetic moment we shall take for the normal state $(np\pi)^4(np\sigma)^2\Sigma$, the nitrogen configuration, and for excited states $(np\pi)^3(np\sigma)^2n's\sigma\Pi$ and $(np\pi)^4 np\sigma n's\sigma\Sigma$. Magnetic interactions between these states will evidently be due to the core of the Π state. Proceeding exactly as in the previous example we again find the rotation to be given by Eq. (11). In a central field the energies of our two excited states will coincide, and a normal Verdet constant will result: in such a field no distinction need be made between the magnetic moment of the core and the magnetic moment of a valence electron. In the axial field of a diatomic molecule the energies of the excited states will be widely different, since these states have different core configurations; γ will thus be considerably less than unity. This result, as contrasted with the result obtained for the hydrogen molecule, illustrates the effect of a complex core in diminishing the Verdet constant.

When we deal with homonuclear diatomic molecules another factor may enter which we have not yet considered. For such molecules P(nn') has elements only between the normal state and states of opposite symmetry with respect to reflection of the electrons in the origin. States n'' of the same symmetry as the normal state will have no effect on the refraction, but Eq. (10) shows that they will affect the magnitude of the rotation if the elements $\mu_z(nn'')$ are not negligible, although no terms containing $\tau(n''n)$ will appear.

A situation in which μ_z has elements between the normal states and an excited group of states can be obtained by inverting the energy levels of our first example, so that the $(ns\sigma)^2\Sigma$ state lies above the $ns\sigma n'p\pi\Pi$ and $ns\sigma n'p\sigma\Sigma$ states, as is shown in Fig. 2(b). Eq. (11) then holds only if ν_3 is small compared to kT/h, so that there is no difference in the concentrations of the molecules in the $ns\sigma n'p\pi\Pi$ and $ns\sigma n'p\sigma\Sigma$ states.²⁸ The second term of Eq. (11) is then due to molecules in the latter state, the first and third to those in the former.

²⁷ R. S. Mulliken, Rev. Mod. Phys. 4, 1 (1932).

 28 A weight factor 1/3 should be included in Eq. (11) in this case. There will also be a paramagnetic term; however it is of no interest for our purposes.

However if the II state is the higher of the two, that is if ν_3 is positive and large compared to kT/h, the first and third terms vanish and we are left with a negative *B* term. A negative *B* term is also obtained if the Σ state is the higher.

In our examples the effect of magnetic interactions between two excited levels is to give, when $\nu < \nu_1$, ν_2 or $\nu > \nu_1$, ν_2 , two *B* terms which, although they are of opposite sign, give a net rotation which is positive; when $\nu_2 < \nu < \nu_1$, two negative *B* terms. The effect of interaction between the normal state and an excited state of frequency ν_3 is to give a negative *B* term when $\nu < \nu_1$, a positive term when $\nu > \nu_1$. Negative *B* terms may account for the negative rotation of TiCl₄.

It is of some interest to calculate the rotation under the assumption that all excited levels lie in the same group. Suppose the electric moments have elements only between the normal states, n, k, and a group of states, n', k', having the same n'. Under this hypothesis the second sum of Eq. (10) vanishes, and the teilmatrices appearing in the remaining terms can be replaced by the complete matrices (the spur, of course, is still taken only over the normal states). The third sum of Eq. (10), and the second and third terms of the first sum, are zero in virtue of the commutability of the coordinates. On summing over all electrons we have

$$P_{x}\mu_{z}P_{y} - P_{y}\mu_{z}P_{x} = -(e^{3}/2mc)\sum_{ijk}x_{i}(x_{j}p_{yj} - y_{j}p_{xj})y_{k} - y_{k}(x_{j}p_{yj} - y_{j}p_{xj})x_{i}$$
$$= -(e^{3}/2mc)\sum_{ijk}x_{i}x_{j}(p_{yj}y_{k} - y_{k}p_{yj}) + y_{k}y_{j}(p_{xj}x_{i} - x_{i}p_{xj})$$
$$= -(e^{3}h/4\pi mci)\sum_{ij}(x_{i}x_{j} + y_{i}y_{j}) = -(eh/4\pi mci)(P_{x}^{2} + P_{y}^{2}).$$

Adding the terms obtained by cyclic interchange of x, y, z, we find

$$V = \frac{4\pi e N \nu^2}{3 h m c^2} \frac{\nu(n'n)}{(\nu^2 - \nu(n'n)^2)^2} \frac{1}{g} \sum_{kk'} |P(nk; n'k')|^2,$$

which is just the normal Verdet constant.

§6. ROTATION NEAR AN ABSORPTION LINE

Going back to Eq. (6) we see that when ν is close to one of the $\nu(n'n)$ the rotation is

$$V = 2CB \sum_{m,m'} \frac{\nu(n'n)\nu^{(1)}(n'm';nm) \left[P_x(nm;n'm') P_y(n'm';nm) \right]}{(\nu^2 - \nu(n'n)^2)^2} e^{-W_n/kT}, \quad (13)$$

for, since this term contains $1/(\nu^2 - \nu(n'n)^2)^2$ rather than $1/(\nu^2 - \nu(n'n)^2)$, it is very much larger than all the others. The rotation thus depends only on the Zeeman effect, the perturbation of the amplitudes being negligible.

Rotation in iodine

The iodine lines observed by Wood²⁹ come from a ${}^{3}\Pi_{0}-{}^{1}\Sigma$ transition, and so exhibit no Zeeman effect if we use the "rigid molecule" approximation. Actually, the Zeeman effect, and consequently the optical rotation, is due to rotational distortion, that is, to the effect of molecular rotation in uncoupling the spin from the nuclear axis of figure. The suggestion that rotational distortion is responsible for the behaviour of iodine was originally made by Kemble,³⁰ but an adequate mechanism was lacking, as at the time the transition was mistakenly classified as ${}^{1}\Sigma - {}^{1}\Sigma$. Kemble supposed that the orbital moment, rather than the spin moment, was uncoupled by the molecular rotation, but it now seems much more probable that spin uncoupling is the preponderant effect.

We shall use the rotating system of axes, x', y', z', previously employed by Van Vleck;³¹ the z component of the spin in fixed axes is given in terms of this rotating system by

$s_z = s_{y'} \sin \theta + s_{z'} \cos \theta,$

 θ denoting the angle between the axis of figure of the molecule and the fixed axis z. The term involving $s_{z'}$ gives the spin part of the ordinary rigid molecule Zeeman effect. In our case this just cancels the effect of the orbital angular momentum, since $\Omega = 0$ in the ${}^{3}\Pi_{0}$ state; we shall not be further interested in this term. The matrix $s_{y'}$ sin θ can be written

 $(s_{y'}\sin\theta)(\sigma_s jm;\sigma_s' j'm') = 2s_{y'}(\sigma_s \sigma_s')L(\sigma_s jm;\sigma_s' j'm').$

The elements $L(\sigma_s jm; \sigma_s' j'm')$ are defined and evaluated in a paper by Rademacher and Reiche.³² As the multiplet separations of the ${}^{3}\Pi_{0}$ state of iodine are very wide, only the first order perturbation of s_z by the molecular rotation is required. This is given by a formula similar to Eq. (7), from which we find for the diagonal elements of $s_z^{(1)}$, when $\Omega = 0$, $\sigma_l = 1$,

$$s_{z}^{(1)}(-1jm; -1jm) = 2H^{(1)}(-10)L(0jm; -1jm)s_{y'}(0-1)/h\nu(-10) + 2L(-1jm; 0jm)s_{y'}(-10)H^{(1)}(0-1)/h\nu(-10) = 4H^{(1)}(-10)L(0jm; -1jm)s_{y'}(0-1)/h\nu(-10).$$

since all the quantities involved are real.

It is convenient to write $s_{z}^{(1)}$ ($\sigma_{s}jm$; $\sigma_{s}'j'm'$), $L(\sigma_{s}jm$; $\sigma_{s}'j'm'$), and $\nu(\sigma_{s}\sigma_{s}')$ in terms of Ω rather than σ_{s} . The elements appearing above are, in this notation, $s_{z}^{(1)}$ (0jm; 0jm), L(1jm; 0jm) and $\nu(01)$. We then have³³

$$s_{u'}(\sigma_s; \sigma_s \pm 1) = \frac{1}{2} [S(S+1) - \sigma_s(\sigma_s \pm 1)]^{1/2};$$

$$H^{(1)}(\sigma_s; \sigma_s \pm 1) = b [j(j+1) - \Omega(\Omega \pm 1)]^{1/2} [S(S+1) - \sigma_s(\sigma_s \pm 1)]^{1/2}; b = h^2/8\pi^2 M r^2;$$

$$L(1jm; 0jm) = -m/2 [j(j+1)]^{1/2};$$

and from these

$$S_z^{(1)}(0jm; 0jm) = -2bm/h\nu(01).$$

²⁹ R. W. Wood and G. Ribaud, Phil. Mag. 27, 1009 (1914).

³⁰ E. C. Kemble, Bull. Nat. Res. Council 57: Molecular Spectra in Gases, Chap. VII.

³¹ J. H. Van Vleck, Phys. Rev. **33**, 467 (1929). The primed and unprimed systems of his Eq. (5) will be interchanged, to accord with our previous notation. We shall follow this paper in our choice of phases for $H^{(1)}$ and $s_{\nu'}$, and in notation: σ_i will denote the component of angular momentum along the figure axis, σ_s the component of spin along the figure axis, $\Omega = \sigma_l + \sigma_s$

³² H. Rademacher and F. Reiche, Zeits. f. Physik **41**, 453 (1927). See Eq. (13) and the table on p. 475.

³³ Van Vleck, reference 31, Eqs. (30) and (31). From Rademacher and Reiche's table we find $L(1jm; 0jm) = |m|/2[j(j+1)]^{1/2}$. The minus sign must be taken when m > 0 to match Van Vleck's phases for $H^{(1)}$ (see Van Vleck's footnote (25)).

Using the fact that L(1jm; 0jm) = L(-1jm; 0jm), it is readily verified that the same result is obtained when $\sigma_l = -1$.

Thus for our ${}^3\!\Pi_0\!-{}^1\Sigma$ transition

$$\nu^{(1)}(j'm';jm) = -4\beta bm'/h^2\nu(01),$$

 β being the Bohr magneton number.

The elements of the electric moment appearing in Eq. (13) are the familiar amplitudes of the symmetric top, given, for example, by Kronig.³⁴ The terms different from zero are

$$\begin{split} & \left[P_x(j,m;j+1,m\pm 1)P_y(j+1,m\pm 1;j,m)\right] = \mp \frac{iP^2}{2} \frac{(j\pm m+2)(j\pm m+1)}{(2j+1)(2j+3)}, \\ & \left[P_x(j,m;j-1,m\pm 1)P_y(j-1,m\pm 1;j,m)\right] = \mp \frac{iP^2}{2} \frac{(j\mp m+2)(j\mp m+1)}{(2j+1)(2j+3)}, \end{split}$$

where $P^2 = |P_{y'}({}^1\Sigma, {}^3\Pi_0)|^2$.

The rotation is found by substituting these expressions in Eq. (13) and summing over all values of m, the result being multiplied by two, since the two upper states, $\sigma_l = \pm 1$, contribute equally to the rotation. In this way we obtain

$$V = -\frac{8\pi e b \nu_1 P^2 \nu^2 B e^{-W_j/kT}}{hmc^2 \nu_2 (\nu^2 - \nu_1^2)^2} \sum_{m=-j}^{j} \frac{(m+1)(j+m+2)(j+m+1)}{(2j+1)(2j+3)} -\frac{(m-1)(j-m+2)(j-m+1)}{(2j+1)(2j+3)},$$

with $\nu_1 = \nu({}^{3}\Pi_0, {}^{1}\Sigma)$, $\nu_2 = \nu({}^{3}\Pi_0, {}^{3}\Pi_1)$ (i.e., $\nu(01)$ in our previous notation), for the *R* branch, and an analogous expression for the *P* branch. Performing the summations,

$$V = \mp \frac{16\pi e b \nu_1 P^2 \nu^2 B e^{-W_j \pm 1/kT} j(j+1)}{3 h m c^2 \nu_2 (\nu^2 - \nu_1^2)^2} \cdot$$

j here is the *j* of the ${}^{3}\Pi_{0}$ level; the minus sign is to be taken for the *R* branch, the plus for the *P*. Our theory thus agrees with Wood's observations in giving positive (normal) rotations for the lines of the *P* branch, and negative (abnormal) rotations for the *R* branch.

Magnetic rotation spectra of the alkalis

The calculation of the rotations in the alkali vapours is similar. The lines observed by Wood and Loomis³⁵ are ${}^{1}\Pi - {}^{1}\Sigma$ transitions. Here the Zeeman effect is given by the well-known formula $W^{(1)}(\Lambda jm) = \beta \Lambda^2 m/j(j+1)$. We have

³⁴ Kronig, reference 3. The phases we use are

$$P_{y'}(\Omega, j, m; \Omega', j', m \pm 1) = \pm i P_{x'}(\Omega, j, m; \Omega', j', m \pm 1).$$

³⁵ F. W. Loomis, Phys. Rev. **31**, 323 (1928); Loomis and Nusbaum, ibid. **38**, 1447 (1931); **39**, 89 (1932).

$$\begin{split} \nu^{(1)}(1j'm';\,0jm) &= \beta m'/hj'(j'+1), \\ \left[P_x(j,m;j-1,m\mp 1)P_y(j-1,m\mp 1;jm)\right] &= \pm \frac{iP^2}{2} \frac{(j-1)(j\pm m)(j\pm m-1)}{j(2j-1)(2j+1)}, \\ \left[P_x(j,m;j+1,m\mp 1)P_y(j+1,m\mp 1;jm)\right] &= \pm \frac{iP^2}{2} \frac{(j+2)(j\mp m+2)(j\mp m+1)}{(j+1)(2j+1)(2j+3)}, \\ \left[P_x(j,m;j,m\mp 1)P_y(j,m\mp 1;jm)\right] &= \pm \frac{iP^2}{2} \frac{(j\mp m+1)(j\pm m)}{j(j+1)}, \\ P^2 &= \mid P_{x'}({}^{1}\Sigma,{}^{1}\Pi)\mid^2. \end{split}$$

The rotations are, in terms of the j of the normal state,

$$V = \frac{4\pi e\nu_1 P^2 \nu^2 B e^{-W_j/kT} f(j)}{3hmc^2 (\nu^2 - \nu_1^2)^2},$$

$$f(j) = (j+2)/(j+1) \quad R \text{ branch},$$

$$f(j) = -(j-1)/j \quad P \text{ branch},$$

$$f(j) = (2j+1)/j(j+1) \quad Q \text{ branch},$$

$$\nu_1 = \nu({}^{1}\Pi, {}^{1}\Sigma).$$

The signs of the rotations of the R and P branches are just opposite those found for iodine. These signs are confirmed by Wood's observations of the rotation in Na₂.

It may seem a little surprising that, aside from the Boltzmann factor $e^{-W_i/kT}$, the rotations of the P and R branches are nearly independent of j when j is large. However it must be remembered that although the over-all width of the Zeeman pattern decreases as 1/j, the number of components increases linearly with j. The angle of rotation is small, only a few degrees, hence the intensities, which are proportional to $\sin^2 \theta$, vary with j approximately as ${f(j)e^{-W_j/kT}}^2$.³⁶ As the intensities in the absorption spectrum vary as $(2j+1)e^{-W_j/kT}$, the intensities of lines of large j in the P and R branches of the magnetic rotation spectrum are weighted adversely, as compared to the absorption spectrum, by a factor $e^{-W_j/kT}/(2j+1)$, and so are, comparatively, greatly reduced. It is perhaps worthy of remark that the intensity of the rotation spectrum is proportional to the square of the density, rather than the first power. The intensities of the Q branch decrease much more rapidly than those of the R and P branches, which accounts for the fact that the Q branch is not observed in the rotation spectrum. For small j the R branch is considerably more intense than the P. This, together with the piling up of the Rlines at the heads of the bands, explains why sometimes the R branch alone is observed. The present theory is thus adequate to account for the principle characteristics of the magnetic rotation spectrum.

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 3^{36} It should be noted that, since the separations between lines increase with *j*, the density of lines on a photographic plate will decrease even more rapidly than the intensities.