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ON THE ZEEMAN EFFECT IN DOUBLET BAND SPECTRA

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Abstract

A theoretical investigation is given of the Zeeman effect for doublet bands of diatomic molecules which are included in the type forms of Hund's cases (a) and (b). With case (b) as a starting point, using the perturbation theory of the new quantum mechanics, the magnetic terms are first treated as a small correction to the coupling energy between the electron spin and orbital magnetic moments.

In the next approximation the terms which lead to a Paschen-Back effect are included. The physical interpretation according to which the term system degenerates into that due to a free spin electron plus that due to a symmetrical top, is discussed briefly in its relation to the experimentally observable patterns. The formal mathematical solution is then given and briefly discussed.

Introduction

In view of some experimental work which has been carried out in this laboratory[1] on the Zeeman effect in the 5211A band of MgH, it has become of interest to extend previous theoretical work on the effect of a magnetic field on the spectra of diatomic molecules. We shall consider only molecules which can be included in the type form of Hund's case (a) or (b), or which are intermediate between these limiting cases. Hund has considered the general arrangement of the magnetic terms for the limiting cases.[2] Van Vleck has also considered the question[3] from a qualitative point of view, and on the basis of Hund's analysis and an assumed behavior for the spin electron in strong magnetic fields, has proposed a scheme which might be expected to account for some abnormally large Zeeman patterns which had previously been observed experimentally. The basic idea of the theory is that of a gradual uncoupling (Paschen-Back) effect of the electron spin from the rest of the molecule by the magnetic field, and a consequent degeneration of the term system into that

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[1] F. H. Crawford and G. M. Almy, Phys. Rev. **33**, 1084 (1929). See also the following paper in this issue.

[2] F. Hund, Zeits. f. Physik **36**, 657 (1926). For various other papers dealing with different phases of the Zeeman effect in band spectra see:

E. C. Kemble, Chapter VII, Sec. 6 of Bulletin 57 of the National Research Council, "Molecular Spectra in Gases."

E. C. Kemble, R. S. Mulliken, and F. H. Crawford, Phys. Rev. **30**, 438 (1927).

E. U. Condon, Phys. Rev. **30**, 781 (1927).

R. de L. Kronig, Phys. Rev. **31**, 195 (1928); Zeits. f. Physik **46**, 814 (1928); Ibid., **50**, 347 (1928).

W. Watson and B. Perkins, Jr., Phys. Rev. **30**, 592 (1927).

F. H. Crawford, Phys. Rev. **33**, 341 (1929).

[3] J. H. Van Vleck, Phys. Rev. **28**, 980 (1926).

due to a free spin on which is superposed the pattern due to a symmetrical top. At that time the theory was mainly suggestive, although its general correctness was undoubted, but it is the purpose of the present paper to put it on a more definite footing by applying to it the methods of the new quantum mechanics. We are thus enabled to follow quantitatively the progression from zero to strong fields. The reader is referred to the following paper in this issue for a discussion of the relation of the theoretical predictions to the experimental data in the above-mentioned band of MgH.

Notation. At present the symbolic designations for the various quantum numbers in diatomic molecules are by no means standard. In this paper we shall conform to some suggestions for a standard notation which have been recently communicated to us by Professor R. S. Mulliken. For the convenience of the reader a conversion table from the symbols used in reference 4 to those used in the present paper is appended. The reader is referred to reference 4 for a complete discussion of the meanings of these symbols.

Reference 4. $k, s, \sigma_k, \sigma_s, \sigma, j_k, j, m, m_k, m_s, S, P, D, \cdots$
Present $L, S, \Lambda, \mathrm{X}, \Omega, K, J, M, M_k, M_s, \Sigma, \Pi, \Delta, \cdots$

HAMILTONIAN FUNCTION

Let (xyz) be a fixed set of Cartesian axes in space such that the external magnetic field is symmetrical about the z-axis, the field strength being H (gauss). We shall start with Hund's case (b) as an appropriate unperturbed system. Equivalent results could undoubtedly be obtained by starting at case (a), and have been partially so obtained by the author (through stage I) but the complete analysis involving the Paschen-Back effect of the spin is analytically more complicated by such a procedure.

The perturbative terms in which we are interested are of two types; 1) the coupling energy, H_1, between S and L, and 2) the added terms due to the presence of the magnetic field, with the Hamiltonian H_2. As usual we shall assume that the energy differences associated with different values of Λ are large compared to the energy differences of adjacent rotational states, so that we may average H_1 over the precession of L about the nuclear axis. Assuming the applicability of the "cosine" law of interaction between S and L we get[5]

$$H_1 = A(\Lambda \cdot S) = A(\Lambda_x S_x + \Lambda_y S_y + \Lambda_z S_z), \tag{1}$$

where A is a constant.

In H_2 we retain only terms linear in H, and neglect the small magnetic moment due to the nuclear rotation, so that[6]

$$H_2 = (He/4\pi mc^2)(\Lambda_z + 2S_z). \tag{2}$$

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[4] Cf. E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928) for a calculation very similar to that of the present paper.

[5] All energies are expressed in cm^{-1}.

[6] In this paper we shall neglect the small "rho-type" doubling which is present in $^2\Sigma$ states. On this account we cannot get complete agreement between theory and experiment for high rotational levels as the formula will not predict the proper doublet separations even in the absence of a field for transitions beginning or ending on a $^2\Sigma$ level.

The matrix elements of H_1 have already been derived (reference 4, Eqs. (16) and (17)). To find the matrix elements of Λ_z we have only to use the unnumbered equation in the middle of p. 258 of reference 4 in conjunction with the case (b) amplitude matrices (reference 4, Eq. (9)).[7] To derive the matrix elements of S_z we use an argument based on the discussion of the case (b), amplitude elements given on p. 254 of reference 4. We first note that as S is involved only in the precessions about J and about the axis of the external field, S_z will be diagonal in all quantum numbers except J. Furthermore, as the vectors S and K play quite analogous roles in the precession about J, we need only take those amplitude elements from Eq. (9) which are diagonal in K, inter-change the quantum numbers K and S in them, and then normalize the B-factors so that $\sum_{J'M'}(S_x^2+S_y^2+S_z^2)(J,M;J',M')=S(S+1)$. Lastly we must multiply each of the elements of S_x, S_y, and S_z for which $J'=J\pm 1$ by a factor (-1) in order to take account of the fact that S and K are coupled vectorially, and so have slightly different phases.

As the final result of this analysis we find for the elements of the complete perturbing function $H_p=H_1+H_2$:

$$\begin{aligned}
H_p(K,J;K+1,J+1)&=\Lambda(\Delta\nu_n)\left\{\frac{Q(K+1;\Lambda)E(J+1;K;S)E(J+2;K;S)Q(J+1;M)}{4U(K+1)U(J+1)}\right\}^{1/2}\\
H_p(K,J;K+1,J)&=\Lambda\left(A+\frac{(\Delta\nu_n)M}{J(J+1)}\right)\left\{\frac{Q(K+1;\Lambda)E(J+1;K;S)F(J-1;K;S)}{4U(K+1)}\right\}^{1/2}\\
H_p(K,J;K+1,J-1)&=-\Lambda(\Delta\nu_n)\left\{\frac{Q(K+1;\Lambda)F(J-1;K;S)F(J-2;K,S)Q(J;M)}{4U(K+1)U(J)}\right\}^{1/2}\\
H_p(K,J;K,J+1)&=(\Delta\nu_n)\left[\frac{Q(J+1;M)}{U(J+1)}\right]^{1/2}\Big\{[E(J+1;S;K)F(J;S;K)]^{1/2}\\
&\qquad-\left(\frac{\Lambda^2}{2K(K+1)}\right)[E(J+1;K;S)F(J;K;S)]^{1/2}\Big\}\\
H_p(K,J;K,J)&=\left(\frac{(\Delta\nu_n)M}{J(J+1)}\right)\left\{G(J;S;K)+\left(\frac{\Lambda^2}{2K(K+1)}\right)G(J;K;S)\right\}-\left(\frac{A\Lambda^2}{2K(K+1)}\right)G(K;S;J),
\end{aligned}\tag{3}$$

where

$$\left.\begin{aligned}
&E(a;b;c)=(a+b)(a+b+1)-c(c+1)\ ;F(a;b;c)=c(c+1)-(a-b)(a-b+1);\\
&G(a;b;c)=a(a+1)+b(b+1)-c(c+1)\ ;Q(a;b)=a^2-b^2;
\end{aligned}\right\}\tag{4}$$

$$\left.\begin{aligned}
U(a)&=a^2(2a-1)(2a+1)\\
\Delta\nu_n&=He/4\pi mc^2.
\end{aligned}\right\}\tag{5}$$

The remaining elements can be obtained by using the Hermitian character of H_p; i.e., as all elements of H_p are real, $H_p(K,J;K',J')=H_p(K',J';K,J)$. All elements are, of course, diagonal in Λ and M.

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[7] The following corrections are to be made in Eq. (9) of reference 4. In line 2 put $U(j+1)$ instead of $U(j)$; in lines 7 and 8 put $F(j,j_k)$ instead of $F(j+1,j_k)$.

The energy function of the unperturbed system can be written as the sum of two parts; i.e., W_0+H_r, where W_0 does not involve the quantum numbers[8] K, J, M, while H_r is the diagonal matrix whose elements are

$$H_r(\Lambda, K, J, M\ ;\ \Lambda, K, J, M)=B[K(K+1)-\Lambda^2] \tag{6}$$

where

$$B=h/8\pi^2cI. \tag{7}$$

As W_0 does not contain any of the quantum numbers in which H_p has off-diagonal elements, it does not enter into any of the calculations, and will not be mentioned specifically again.

Interaction with Λ-type doubling. In the perturbing Hamiltonian as given above we have listed only terms within a given electronic multiplet (n, v, Λ), and have thus tacitly left out of account the terms which are chiefly responsible for the phenomenon of Λ-type doubling. From the theoretical work of Kronig,[9] Wigner and Witmer,[10] and of Van Vleck,[11] on the symmetry properties of the wave equation, even inclusive of spins, it follows that the approximate wave functions associated with the two Λ-levels (levels with a given $|\Lambda|$) are respectively even and odd with respect to a "reflection in the origin." As our perturbing function, inclusive of magnetic terms, is even with respect to this transformation, it contains no terms connecting these so-called + and − levels, which may thus still be treated separately. These we treat in the usual manner, assuming that the electronic states are really widely separated as compared to adjacent rotational levels, and so consider first the perturbations of the terms within each electronic state separately. Inclusion of the terms non-diagonal in Λ would give the Λ-doubling corrections.

CALCULATION OF TERM VALUES

Because of the fact that our perturbing function H_p has elements off-diagonal in two quantum numbers, K and J, the term values can be found only by approximation methods. As a preliminary step let us separate H_p into two parts which we shall call H_p' and H_p'' respectively. H_p' shall consist of all elements of H_p which are diagonal in J, thus having elements which are off-diagonal as well as diagonal in K. H_p'' shall consist of all remaining elements of H_p, and thus in particular has no elements diagonal in J. This division of the calculation into two parts simplifies the analysis, as H_p' includes all of the terms of H_p which are responsible for rotational distortion in addition to some of the small magnetic terms, and represents the Hamiltonian to be associated with a molecule in a state intermediate between (b) and (a) in which the magnetic field produces only a small perturbation, while H_p'' contains the terms which lead to the Paschen-Back effect. In stage I of the calculation we use H_p' alone, neglecting H_p'', while stage II contains the considerations relative to H_p''.

Stage I. The elements of the matrix H_p' associated with a given state (Λ, J, M) are found from (3) to be, on substituting $S=\frac{1}{2}$, $K=J\pm\frac{1}{2}$,

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[8] We neglect explicitly the dependence of the vibrational energy on the quantum numbers K, S, J, as well as the variation of B with the rotational state.

[9] R. de L. Kronig, Zeits. f. Physik **46**, 814 (1928); **50**, 347 (1928).

[10] E. Wigner and E. Witmer, Zeits, f. Physik **51**, 859 (1928).

[11] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

$$\begin{aligned} H_p'(J_1\,;J_1)&=B\{-\beta J[1-\Lambda^2/(J+\tfrac{1}{2})]-\lambda\Lambda^2/(2J+1)\}\\ H_p'(J_1\,;J_2)&=H_p'(J_2\,;J_1)=B\{(\lambda+\beta)\Lambda/(2J+1)\}\{(J+\tfrac{1}{2})^2-\Lambda^2\}^{1/2}\\ H_p'(J_2\,;J_2)&=B\{\beta(J+1)[1+\Lambda^2/(J+\tfrac{1}{2})]+\lambda\Lambda^2/(2J+1)\}, \end{aligned}\tag{8}$$

where

$$\begin{aligned} \beta&=(\Delta\nu_n/B)(M/J(J+1))\\ \lambda&=A/B. \end{aligned}\tag{9}$$

The unperturbed energy has the elements

$$\begin{aligned} H_r(J_1\,;J_1)&=B[(J+\tfrac{1}{2})(J+\tfrac{3}{2})-\Lambda^2]\\ H_r(J_2\,;J_2)&=B[(J^2-\tfrac{1}{4})-\Lambda^2]. \end{aligned}\tag{10}$$

The notation J_1 refers to the spin component for which $K=J+\frac{1}{2}$, and similarly J_2 refers to the component for which $K=J-\frac{1}{2}$. The energies can now be found by solving the usual determinantal equation:

$$0=\begin{vmatrix} (H_r+H_p')(J_1\,;J_1)-W & H_p'(J_1\,;J_2)\\ H_p'(J_2\,;J_1) & (H_r+H_p')(J_2\,;J_2)-W \end{vmatrix}\tag{11}$$

the roots of which are readily found to be

$$\begin{aligned} W(\Lambda,K,J,M)=B\{&(J+\tfrac{1}{2})^2-\Lambda^2+\beta(\Lambda^2+\tfrac{1}{2})\\ &\pm\tfrac{1}{2}[(2J+1)^2(1-\beta)^2+\Lambda^2(\lambda+\beta)(\lambda-4+5\beta)]^{1/2}\}, \end{aligned}\tag{12}$$

where the upper sign is to be associated with the J_1 state; i.e. with $K=J+\frac{1}{2}$. It may be remarked that if we set $\beta=0$; i.e., $H=0$, (12) reduces to the rotational distortion formula (reference 4, Eq. (27)).

If one is interested only in the dependence of (12) on the magnetic field, it is probably a sufficiently accurate procedure to expand as a power series in (β) and retain terms of first order only, thus

$$W(\Lambda,K,J,M)\cong B\{(J+\tfrac{1}{2})^2-\Lambda^2\pm\tfrac{1}{2}\gamma+\beta(\Lambda^2+\tfrac{1}{2})\pm(\beta/2\gamma)[-(2J+1)^2+\Lambda^2(3\lambda-2)]\},\tag{12'}$$

where

$$\gamma=[(2J+1)^2+\lambda(\lambda-4)\Lambda^2]^{1/2}.$$

The next term of second degree in the small quantity $(\Delta\nu_n/B)$ with a coefficient of the order of $(1/J)$, is ordinarily quite negligible. The dependence of (12′) on β could also have been determined directly from the perturbation theory for non-degenerate systems by employing the case (b) transformation function S (reference 4, Eq. (33)) and the formula

$$\Delta W(K,J,M)=\sum_{K'\,K''}S(K,J;K',J)H_2(K',J,M;K'',J,M)S(K,J,M;K'',J,M).$$

This procedure would amount to first removing the degeneracy associated with H_1 by means of the transformation S, and then considering H_2 as a small correction term.

Stage II. The perturbative Hamiltonian H_p'' which we have so far neglected, contains interaction terms between levels with values of J differing by one unit and values of K which may or may not differ. Up to the present we have assumed that such terms do not lie close enough together to influence one another appreciably. This, however, is by no means a sufficient approximation, for if we consider the arrangement of terms as a function of the parameter λ in the absence of an external field ($\beta=0$), we find that for $\lambda \cong 0$ and $\lambda \cong 4$, levels differing by an unit in J, but having the same value of K lie very close together. The same is true for high rotational states even in molecules where λ differs appreciably from these critical values (e.g., in the upper level for the 5211A band of MgH where $\lambda \sim 6$). This behavior of the terms is predicted by (12) and is also found experimentally.[12] We must accordingly make a second transformation in order to eliminate these terms from H_p''. That it is not a valid procedure to use the perturbation theory of non-degenerate systems follows from the fact that such a calculation would be made by a series expansion in terms of the parameter $(\Delta\nu_n/\nu(K, J; K, J'))$ where $h\nu\ (K, J, M; K, J', M) = W(K, J, M) - W(K, J', M)$. We have just seen that this quantity may become very large.

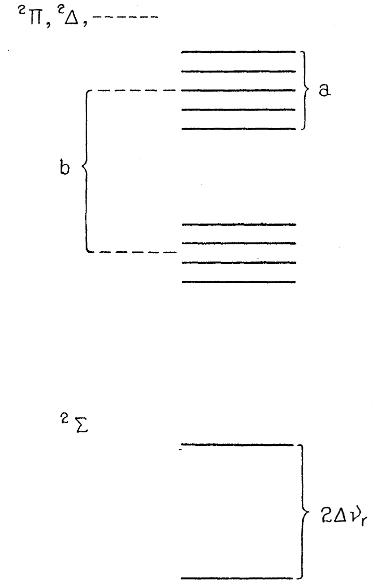

Fig. 1.

The physical interpretation of this phenomenon has already been discussed by Van Vleck,[3] but we shall repeat and amplify the argument here in order to elucidate the mathematical formalism. Levels of the type just mentioned, having the same value of K but different values of J, compose the so-called "spin-doublets" ($S=\frac{1}{2}$), and their separations are measured by the magnitude of the coupling between S and Λ. If the separations of these levels are small, so that the effective forces between S and the rest of the molecule are weak, the magnetic field may be strong enough to over-power these forces and to partially or wholly uncouple S from the rest of the molecule. In the limit in which the Zeeman separations are great compared to the spin doublet separations, S becomes completely free from the rest of the molecule, and is

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[12] Cf. especially R. S. Mulliken, Phys. Rev. **32**, 388 (1928).

quantized parallel or anti-parallel to the axis of the external field. In this limit the term system should consist of the terms due to a symmetrical top superposed on the two states for the free spin in the magnetic field. In a $^2\Sigma$ state, neglecting the presence of the small "rho-type" doubling, the part due to the top should be absent, so that each rotational level splits into a doublet with separation $(2\Delta\nu_n)$ in the field. The more general condition as existing in $^2\Pi$, $^2\Delta$, $\cdots$ states is roughly as shown in Fig. 1. From the Zeeman formulae for the symmetrical top,[13] it can be seen that "a," which is approximately the pattern width due to a symmetrical top, vanishes $\sim 1/K$, the number of levels in the group increasing as K, and the separations between the individual components decreasing as $1/K(K+1)$. The deviation of "b" from $(2\Delta\nu_n)$ is a rough measure of the interaction energy between S and Λ.

In the limit of a field sufficiently strong to practically break down the coupling between S and Λ, one can introduce the value of the component of S along the axis of the external field as a quantum number; i.e., $M_s=\pm\frac{1}{2}$. The transitions which give rise to the spectral lines can be divided into four types: 1) $M_s'=\frac{1}{2}\rightarrow M_s''=\frac{1}{2}$; 2) $M_s'=-\frac{1}{2}\rightarrow M_s''=-\frac{1}{2}$; 3) $M_s'=\frac{1}{2}\rightarrow M_s''=-\frac{1}{2}$; 4) $M_s'=-\frac{1}{2}\rightarrow M_s''=\frac{1}{2}$. Transitions of types 1) and 2) give rise to two superposed (unresolved) patterns clustering about the average position of the no-field doublets on the photographic plate. Transitions of types 3) and 4) give rise to two "wings" spaced approximately symmetrically with respect to the central pattern, and with a separation that approaches $(4\Delta\nu_n)$ as the magnetic field is increased, or as one proceeds out in the band to successively higher rotational states. It may be remarked that the decrease in intensity of the outer "wings" with increasing magnetic field (or molecular rotation) is directly attributable to the selection rule $\Delta M_s=0$ which may be expected to obtain accurately in the limit. The reader is referred to the following paper in this issue for a discussion of these relations in the band MgH λ5211.

In putting these considerations into mathematical dress, we must first find the transformation function T appropriate to the determinantal Eq. (11). According to standard perturbation theory we have only to solve the set of linear equations obtained from the single matrix equation

$$T(H_r+H_p')=WT, \tag{13}$$

the elements of T to be normalized to satisfy the condition

$$TT^{-1}=1. \tag{14}$$

The following solution may readily be shown to satisfy (13) and (14)

$$\begin{aligned} T(J_1, M\,; J_1, M) &= T(J_2, M\,; J_2, M) = \left\{ [\tau(J, M)+\omega(J, M)]/2\tau(J, M) \right\}^{1/2} \\ T(J_1, M\,; J_2, M) &= -T(J_2, M\,; J_1, M) = \left\{ [\tau(J, M)-\omega(J, M)]/2\tau(J, M) \right\}^{1/2}, \end{aligned} \tag{15}$$

where

$$\begin{aligned} \tau(J, M) &= \left\{ (2J+1)^2(1-\beta)^2+\Lambda^2(\lambda+\beta)(\lambda-4+5\beta) \right\}^{1/2} \\ \omega(J, M) &= \left\{ (2J+1)(1-\beta)-\Lambda^2(\lambda+\beta)/(J+\tfrac{1}{2}) \right\}. \end{aligned} \tag{16}$$

[13] Cf. e. g., D. M. Dennison, Phys. Rev. **28**, 318 (1926); E. U. Condon, Phys. Rev. **30**, 781 (1927).

The perturbing function in the new system of quantization is given by the matrix

$$TH_p''T^{-1} \tag{17}$$

for which the element $(K, J, M; K', J', M)$ is given by

$$\sum_{K'',K'''} T(K,J,M;\ K'',J,M)H_p''(K'',J,M\ ;K''',J',M)T(K',J',M;\ K''',J',M) \tag{18}$$

as

$$T^{-1}(K''',J',M\ ;K',J',M) = T(K',J',M\ ;K''',J',M).$$

In the application of (18) it is sufficient to neglect the dependence of the elements of T on the magnetic quantum number M to the same degree of accuracy that one has in using (12′) in preference to (12). With this simplification T becomes identical with the transformation function S derived in the rotational distortion problem (reference 4, Eq. (33)).

An examination of (18) shows that the new perturbing function contains only terms connecting states for which $J' = J \pm 1$, as H_p'' has no terms diagonal in J, by definition. The elements connecting states for which $K' \neq K$ we discard as such levels do not ordinarily lie close to each other. The remaining elements, connecting states for which $J = K \pm \frac{1}{2}$, are readily found from (18) using the matrix elements of H_p'' from (3), the result being

$$\begin{aligned}\delta B/2 = (\Delta\nu_n)&\left\{\frac{(K+\frac{1}{2})^2 - M^2}{(K+\frac{1}{2})^2}\right\}^{1/2}\\ \times\Bigg[&\left\{\frac{\tau(K+\frac{1}{2})+\omega(K+\frac{1}{2})}{2\tau(K+\frac{1}{2})}\right\}^{1/2}\left\{\frac{\tau(K-\frac{1}{2})+\omega(K-\frac{1}{2})}{2\tau(K-\frac{1}{2})}\right\}^{1/2}\left\{1-\frac{\Lambda^2}{2K(K+1)}\right\}\\ &+\left\{\frac{\tau(K+\frac{1}{2})+\omega(K+\frac{1}{2})}{2\tau(K+\frac{1}{2})}\right\}^{1/2}\left\{\frac{\tau(K-\frac{1}{2})-\omega(K-\frac{1}{2})}{2\tau(K-\frac{1}{2})}\right\}^{1/2}\left\{\frac{(K^2-\Lambda^2)\Lambda^2}{4K^2}\right\}^{1/2}\\ &-\left\{\frac{\tau(K+\frac{1}{2})-\omega(K+\frac{1}{2})}{2\tau(K+\frac{1}{2})}\right\}^{1/2}\left\{\frac{\tau(K-\frac{1}{2})+\omega(K-\frac{1}{2})}{2\tau(K-\frac{1}{2})}\right\}^{1/2}\left\{\frac{[(K+1)^2-\Lambda^2]\Lambda^2}{4(K+1)^2}\right\}^{1/2}\Bigg].\end{aligned} \tag{19}$$

The energies of the two states in question before the introduction of the perturbation (19) are found from (12) to be:

$$\left.\begin{aligned} W(K_1,M\ ;K_1,M) &= f(K+\tfrac{1}{2},M) - \tfrac{1}{2}\tau(K+\tfrac{1}{2},M) = B\epsilon_1\\ W(K_2,M\ ;K_2,M) &= f(K-\tfrac{1}{2},M) + \tfrac{1}{2}\tau(K-\tfrac{1}{2},M) = B\epsilon_2\end{aligned}\right\} \tag{20}$$

where

$$f(K-\tfrac{1}{2},M) = B\{K^2-\Lambda^2+(\Delta\nu_n/B)[M(\Lambda^2+\tfrac{1}{2})/(K^2-\tfrac{1}{4})]\}, \tag{21}$$

and where K_1 and K_2 refer to the components for which $J = K \pm \frac{1}{2}$ respectively. If $|M| \leqq K - \frac{1}{2}$ the energy values can be found from a second determinantal equation of exactly the same form as (11) using (19) and (20) instead of (8) and (10), the roots being

$$(B/2)[(\epsilon_1+\epsilon_2) \pm \{(\epsilon_1-\epsilon_2)^2+\delta^2\}^{1/2}]. \tag{22}$$

The allocation of the two roots (22) to the two levels concerned is at first sight ambiguous, inasmuch as the first term in the square root can also be written as $(\epsilon_2-\epsilon_1)^2$. This means that it is not sufficient to establish the correlation in the usual manner by the asymptotic relation of (22) with (20) when δ is formally set equal to zero. As a second condition we shall use a rule derived from perturbation theory[14] which states roughly that the first effect of a perturbation between two energy levels is to push them apart. Applying this to (22) we conclude that if $\epsilon_1>\epsilon_2$ the upper sign is to be assigned to the state (K_1,M) and the lower sign to the state (K_2,M); while if $\epsilon_2>\epsilon_1$ the reverse correlation should be used. To make the equation formally correct in the latter case for the asymptotic point $\delta=0$, one should write $(\epsilon_2-\epsilon_1)^2$ instead of $(\epsilon_1-\epsilon_2)^2$. This consideration is, in a sense, equivalent to determining the energy and its derivative (with respect to δ) for each of the two states.

Formula (22) can be thrown into a form resembling the more usual expression used in atomic spectra[15] if we use (12′) instead of (12) to determine ϵ_1 and ϵ_2, and collect powers of $(\Delta\nu_n)$; i.e.,

$$\epsilon_1+\epsilon_2=\xi+\kappa(\Delta\nu_n)\ ;\qquad \epsilon_1-\epsilon_2=\nu_0+\alpha(\Delta\nu_n)\ ;\qquad \delta=\eta(\Delta\nu_n)$$

where $B\nu_0$ is the (algebraic) frequency separation[16] of the no-field doublet levels in cm^{-1} while ξ, κ, and η, are complicated functions of the quantum numbers, which can be determined from (12′), (19), (20), and (21). Substituting these values in (22) we get

$$(B/2)\left[\xi+\kappa(\Delta\nu_n)\pm\left\{\nu_0^2+2\nu_0\alpha(\Delta\nu_n)+(\alpha^2+\eta^2)(\Delta\nu_n)^2\right\}^{1/2}\right]. \tag{22'}$$

SPECIAL CASES

There are some particular cases included under the general formula (22) to which it seems well to give special consideration, partly because of their simplicity, and partly also because of certain ambiguities which might be encountered in the preceding formal treatment.

$^2\Sigma$ *States* $(\Lambda=0)$. From (12) we readily find that

$$\epsilon_1=K(K+1)+(\Delta\nu_n/B)(M/K+\tfrac{1}{2})\ ;\qquad \epsilon_2=K(K+1)-(\Delta\nu_n/B)(M/K+\tfrac{1}{2})\ ;$$

while

$$\delta=2(\Delta\nu_n/B)\left\{\frac{(K+\frac{1}{2})^2-M^2}{(K+\frac{1}{2})^2}\right\}^{1/2}$$

as from (16), $\tau(J,M)=\omega(J,M)$. With these values of its arguments (22) reduces to the very simple form

$$BK(K+1)\pm\Delta\nu_n \tag{23}$$

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[14] F. Hund, Zeits. f. Physik **40,** 742 (1927); also for example the last section of E. C Kemble and C. Zener, Phys. Rev. **33,** 512 (1929).

[15] E. g., W. Heisenberg and P. Jordan, Zeits. f. Physik **37,** 263 (1926).

[16] See the preceding paragraph for consideration of the difficulties connected with the sign of ν_0.

quite in agreement with our previous conclusion that if we neglect rho-type doubling, a magnetic field of any strength should be large enough to uncouple completely the spin from the rest of the molecule and quantize it with respect to the external field. The two signs in (23) are of course to be associated with $M_s = \pm\frac{1}{2}$ respectively.

$K=\Lambda$, $J=\Lambda-\frac{1}{2}$. This is the lowest level in $^2\pi$, $^2\Delta$, $\cdots$, electronic states, and is of considerable interest as it presents an anomalous behaviour in the correlation of levels between (a) and (b)[4,12]. Here the off-diagonal elements, (as well as the term in the lower right-hand corner) of (11) vanish, leaving as the only solution

$$B[\Lambda(1-\lambda/2)]+(\Delta\nu_n)M(\Lambda-1)/(\Lambda+\tfrac{1}{2}). \tag{24}$$

To this degree of approximation, this level for a $^2\Pi$ state ($\Lambda=1$) is magnetically dead as the term in $(\Delta\nu_n)$ vanishes. In carrying through the analysis of the perturbations between the levels $K=\Lambda$, $J=\Lambda-\frac{1}{2}$, $|M|\leqq\Lambda-\frac{1}{2}$, and the levels $K=\Lambda$, $J=\Lambda+\frac{1}{2}$, $|M|\leqq\Lambda+\frac{1}{2}$, everything goes through just as before except that now ϵ_2 is given by (24), and δ may be simplified by using the condition $\tau(\Lambda-\frac{1}{2}, M)=\omega(\Lambda-\frac{1}{2}, M)$. (22) now predicts a small magnetic effect for the level $K=1$, $J=\frac{1}{2}$, in a $^2\Pi$ electronic state, but it is of practical importance only in case the separation of the doublet levels in the absence of a magnetic field is very small even at the origin.

Levels for which $M=\pm(K+\frac{1}{2})$. These two levels (for a given value of K) exist only in the magnetic components associated with the K_1 state. As by (19) the perturbing terms vanish, a situation exactly similar to that discussed in the preceding "special case" obtains, the energy being given directly by (20); i.e.,

$$W(K_1,\overline{M})=f(K+\tfrac{1}{2},\overline{M})-\tfrac{1}{2}\tau(K+\tfrac{1}{2},\overline{M})$$
$$\overline{M}=\pm(K+\tfrac{1}{2}).$$

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