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ON THE QUANTUM MECHANICS OF THE ROTATIONAL DISTORTION OF MULTIPLETS IN MOLECULAR SPECTRA

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Abstract

Most of the paper is on the effect of molecular rotation on spin multiplets, but the last section 5 considers the rather different subject of "σ-type doubling."

1. **Hund's limiting cases (a) and (b),** those commonly considered, are realized when the coupling between the electronic spin and the molecular axis of figure is very strong or very weak. Preparatory to the new analysis for the intermediate case, amplitude matrices are given both for cases (a) and (b), including phase factors in (b).

2. **The general intermediate case** can be handled (except for purely algebraic difficulties) both for frequencies and intensities by our mathematical method. The procedure is to start with case (b) and to introduce a coupling energy which is proportional to the cosine of the angle between the axis of electronic spin s and the molecular axis of figure, and which when increased adaibatically converts the system over into case (a). The formula for the energy W is the solution of an algebraic equation of order $2s+1$. Approximate solutions are given for nearly case (b) with any s and for nearly case (a) in triplet spectra ($s=1$).

3. **The doublet case** ($s=\frac{1}{2}$) is particularly satisfactory as (unlike the old quantum theory) the analysis yields a simple closed formula for the energy, viz.,

$$W=\left[(j+\tfrac{1}{2})^2-\sigma_k{}^2\pm\tfrac{1}{2}\left\{4(j+\tfrac{1}{2})^2+\lambda(\lambda-4)\sigma_k{}^2\right\}^{1/2}\right](h^2/8\pi^2I)$$

which holds throughout the interval from (a) to (b) both for regular and inverted multiplets. Here λ is an abbreviation for $8\pi^2AI/h^2$, where A is the proportionality factor in the magnetic coupling energy $As\cdot\sigma_k$. This formula yields an adiabatic correlation of energy levels in case (a) with those in case (b) which is precisely that predicted by Hund and Kemble including the anomalous behavior of the component $j=\sigma_k-1/2$ in "regular" multiplets ($A>0$). The agreement with the experimental doublet widths in the OH band 2811 is slightly better than in the old quantum theory. Intensity formulas are given which apply throughout the range from (a) to (b). Here account is taken of the fact that the moment of inertia I and coupling constant A are different in the initial and final states if there are changes in "electronic" quantum numbers.

4. **Simple special cases of the doublet intensity formulas** arise when there is (a) type coupling in the initial states and (b) in the final or vice versa. The ${}^2P\rightarrow{}^2S$ bands usually meet this condition and formulas for them are developed; the main new result is that for a given initial state the transitions ending on $j_k=j-1/2$ and $j_k=j+1/2$ are of equal intensity. As another illustration intensity formulas are given for ${}^2D_a\rightarrow{}^2P_b$.

5. **An elementary theory of σ-type doubling** is developed by using mathematics very similar to that in the preceding but introducing adiabatically a coupling proportional to the *square* rather than first power of the cosine of the angle between an angular momentum vector k and a "core" consisting of the non-gyroscopic "dumb-bell" molecular model. In a stationary molecule the sign of σ is arbitrary and if $\sigma\neq0$ there are two states of identical energies. It is shown that actually the rotation removes this degeneracy and creates a small splitting into two levels for a given value of σ^2 which Mulliken calls "σ-type doubling." Kronig's result is obtained that the doubling is smaller for large σ^2. The combination relations predicted by Hulthén and treated mathematically by Kronig are shown to apply exactly even when the perturbing effect of the angular momentum perpendicular to the figure axis in case (a) is considered, and the coupling is no longer rigorously of type (a). Interaction of σ-type degeneracy with the spin is reserved for a later paper, so section 5 applies primarily to singlets.

IN HIS important recent work, Hund[1] has introduced the concept of the spin electron into the theory of the spectra of diatomic molecules, and has concluded that the spectral terms of a given molecule can be classed in one or another of a number of groups which he calls case (a), case (b), etc. These cases correspond to special limiting molecular configurations occurring for particular asymptotic values of the molecular rotational energy relative to the energy of interaction between the spin axis and the rest of the molecule; e.g., for very tight coupling of the spin axis the motion is that of case (a), while for very weak coupling it may be that of case (b).

The purpose of the present paper is to give frequency and intensity formulae, for diatomic molecules, applicable to the transition stage intermediate between these limiting cases, which are the only ones ordinarily considered. The initial step in this direction has been taken by Kemble.[2] Using the methods of the old quantum theory, he derived energy formulas which are applicable over certain portions of the transition range from case (a) to case (b), and which give good agreement with the experimental data in the case of the OH band λ2811. The treatment of the problem by the new quantum mechanics, which we give in the present paper, has the advantage of yielding a simple frequency formula for the doublet case, as well as exact expressions for the intensities.

1. The Limiting Cases (a) and (b)

The present section will summarize information about the limiting cases (a) and (b) which is to a considerable extent not entirely new, but which is prerequisite to the mathematical treatment of the intermediate case.

Common features of (a) *and* (b). In either case the effective component of electronic angular momentum is a vector $\boldsymbol{\sigma}_k$ directed along the axis of symmetry of the molecule. Here and throughout the article, expressions printed in boldface type are vector matrices. Angular momentum is throughout measured in multiples of the quantum unit $h/2\pi$, so that by an angular momentum $\sigma_k=1$ for instance, we mean really an amount $h/2\pi$, etc. The resultant spin angular momentum of all the electrons in the molecule is given by the vector $\mathbf{s}$, the elements of $\mathbf{s}^2$ being $s(s+1)$. In case there is more than one valence electron we assume the behavior characteristic of "normal multiplets," viz., that the spins $s_\tau=\frac{1}{2}$ of the individual electrons are coupled together to form a quantized resultant $\mathbf{s}$. This assumption seems to be justified by the empirical facts of molecular spectra, as well as by the dy-

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[1] F. Hund, Zeits. f. Physik **36**, 657 (1926). Cf. also the two later papers: Zeits. f. Physik **40**, 742 (1927), and Zeits. f. Physik **42**, 93 (1927).

For a very good qualitative discussion of Hund's theory, cf. E. C. Kemble, "Molecular Spectra in Gases," Chap. VII, sec. 5, Bull. Natl. Research Council, **57**, (1926). For extensive discussions of cases (a) and (b) particularly with reference to the experimental data on band spectra, cf. R. S. Mulliken, Phys. Rev. **29**, 637 (1927); Phys. Rev. **30**, 138 (1927); Phys. Rev. **30**, 785 (1927). The notation used in this paper is the same as that of Mulliken.

[2] E. C. Kemble, Phys. Rev. **30**, 387 (1927).

namics of the situation.[3] Spectroscopists classify terms as S, P, D, F states according as $\sigma_k=0$, 1, 2, 3, and further, the spectra are singlets, doublets, triplets, according as $s=0$, $\frac{1}{2}$, 1, $\cdots$. The total angular momentum of the molecule is always given by the vector j, and its projection in the direction of spacial quantization yields the magnetic quantum number m, which has the range of values $m=-j, -(j-1), \cdots, j$.

As customary, we have neglected the component of electronic orbital angular momentum perpendicular to the axis of symmetry of the molecule. The justification for doing this is that due to the rapid precession of the orbital angular momentum k about the axis of figure, the elements of the perpendicular component are of the "high frequency type" which disappear on averaging over the "electronic frequencies" and need not be considered in calculating the important perturbative terms. Also we neglect what Mulliken calls "σ-type doubling"; i.e., a hyper-doubling of the multiplet components when $\sigma\neq 0$, although at the end of the article there is a rather detached section on σ-type doubling in the absence of internal spins (i.e singlet spectra). Such doubling arises from the Heisenberg resonance effect associated with the fact that the states $-\sigma$ and $+\sigma$ have the same energy if one neglects the interaction between the rotation and the component of electronic angular momentum perpendicular to the axis of figure. This effect, however, has only a subordinate influence on the energy, as the width of σ-type doublets is small compared to the spin multiplet structures, and so we are justified in relegating it to a neglected higher order approximation.[4]

Distinction between cases (a) *and* (b). In case (a) there is a strong interaction, essentially of a magnetic nature,[5] between $\mathbf{s}$ and $\boldsymbol{\sigma}_k$, and the former precesses rapidly about the latter; i.e., about the axis of symmetry of the molecule, to which the spin is thus tightly coupled. This involves a quantization of the projection $\boldsymbol{\sigma}_s$ of $\mathbf{s}$ in the direction of the axis of figure, and thus introduces the quantum number σ_s which takes on the values $-s$, $-(s-1), \cdots, s$. The total electronic angular momentum about the axis of symmetry consequently has the value $\sigma=\sigma_k+\sigma_s$.

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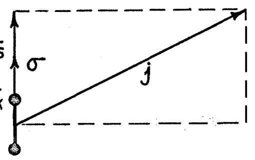
[3] The orbital angular momentum precesses too rapidly about the axis of figure for the spins to be quantized relative to an individual k_τ or even k. For explanation as to why the s_τ form a resultant s even though the interaction between σ_k and s_τ be comparable with that among the s_τ, see Heisenberg, Zeits. f. Physik, **41,** 252 (1927).

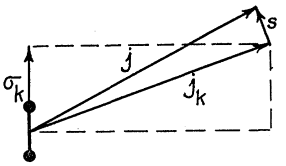
[4] Due to the resonance involved in σ-type doubling, the component of angular momentum parallel to the axis of figure is continually changing sign, so that we can no longer suppose $\sigma_k=0, 1, 2, 3, \cdots$, but we have $\sigma_k^2=0$, $1,^2$ $2,^2$ $3^2,\cdots$, for S, P, D, F, $\cdots$, terms. For the present purposes no harm is done in supposing σ_k always preserves the same sign, because the high-order resonance effects cannot appreciably influence lower order effects such as spin multiplets.

[5] According to the important recent work of Dirac, Proc. Roy. Soc., **117A,** 610 (1928); **118A,** 351 (1928) the physical concept of a "spinning" electron must not be taken too literally, for it seems to be replaceable mathematically by the condition that the Schrödinger wave equations be consistent with the restricted theory of relativity and still be linear. Curiously enough, however, for most problems it seems that the older notion of an actual spin electron will give correct results, and so the term "spin" is a convenient label for certain terms in the energy which will result even with the purely relativistic treatment.

In case (b) the forces exerted on $\mathbf{s}$ due to the molecular rotation are large compared to the interaction between $\mathbf{s}$ and $\boldsymbol{\sigma}_k$. Consequently the spin axis is loosely coupled to the rest of the molecule, and makes a constant angle only with the total angular momentum j, whereas in case (a) it did with the axis of figure of the molecule. Before introducing the spin one must first quantize the total angular momentum j_k exclusive of the spin but inclusive of both the orbital angular momentum and the angular momentum developed by rotation of the nuclei about the center of gravity. The total angular momentum j is then the resultant of j_k and $\mathbf{s}$. On the other hand in case (a) we quantize the spin relative to a fixed molecule before introducing the rotation about the center of gravity. The types of coupling characteristic of the two cases are shown in the following figure:



Case (a)



Case (b)

The range of values for the quantum number j in case (a) is $j=|\sigma|, \cdots, \infty$, whereas in (b) we have instead $j_k=|\sigma_k|, \cdots, \infty; j=|j_k-s|, \cdots, j_k+s$. In either case there are the selection principles $\Delta\sigma_k=0, \pm 1; \Delta j=0, \pm 1; \Delta m=0, \pm 1$ and in case (a) $\Delta\sigma_s=0$, while in (b) $\Delta j_k=0, \pm 1$. The quantum number j_k in case (b) is seen to replace the number σ_s used in (a), and the adiabatic correlation of the values of j_k and σ_s is one of the problems to be considered in the present paper.

Amplitude matrices for case (a). These elements have been given by a number of investigators,[6,7,8,9] and are essentially equivalent to the London-Hönl intensity formulas. They can be extended to include transitions in the vibrational and electronic quantum numbers by noting that the effect of these transitions is to multiply the "symmetrical top" amplitudes by a set of complex factors, $D(n, n')$,[10] where the single letter n denotes the totality of these quantum numbers. This is not to be confused with the same letter n which other writers use to denote the vibrational quantum number alone. As the experimental data on intensities in the Zeeman effect for band lines are very meager, we shall not give the complete amplitude formulas, but shall

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[6] H. Hönl and F. London, Zeits. f. Physik, **33**, 803 (1925).

[7] D. M. Dennison, Phys. Rev. **28**, 318 (1926). Eq. (2) of the present paper is essentially Dennison's Eq. (25).

[8] H. Rademacher and F. Reiche, Zeits. f. Physik, **39**, 444 (1926); **41**, 453 (1927).

[9] R. de L. Kronig and I. I. Rabi, Nature, **118**, 805 (1926); Phys. Rev. **29**, 262 (1927). Cf. also Kronig, Zeits. f. Physik **45**, 458 (1927).

[10] This occurs due to the fact that the Schrödinger "Eigenfunktion" can be split into two parts, one involving only the internal coordinates of the molecule, and one involving the precession coordinates. Cf. Born and Oppenheimer, Ann. der Physik **84**, 457 (1927). Cf. also Kronig, Zeits. f. Physik **46**, 814 (1927).

give a set of quantities which are derived from them, and which are proportional to the total intensities. These quantities, which are Hermitian,[11] are defined by:

$$\begin{aligned} |q_a(n,\sigma_k,\sigma,j\,;\; n',\sigma_k',\sigma',j')|^2 = \textstyle\sum_{m,m'} & |x(n,\sigma_k,\sigma,j,m\,;\; n',\sigma_k',\sigma',j',m')|^2 \\ & + |y(n,\sigma_k,\sigma,j,m\,;\; n',\sigma_k',\sigma',j',m')|^2 \\ & + |z(n,\sigma_k,\sigma,j,m\,;\; n',\sigma_k',\sigma',j',m')|^2, \end{aligned} \tag{1}$$

from which their explicit values are found to be:

$$\begin{aligned} |q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k\pm 1,\ \sigma\pm 1,\ j+1)|^2 &= D^2[O(j+1,\ \pm\sigma+1)/4(j+1)] \\ |q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k\pm 1,\ \sigma\pm 1,\ j)|^2 &= D^2[P(j,\ \pm\sigma)(2j+1)/4j(j+1)] \\ |q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k,\sigma,j+1)|^2 &= D^2[Q(j+1,\sigma)/(j+1)] \\ |q_a(n,\sigma_k,\sigma,j\,;\, n',\sigma_k,\sigma,j)|^2 &= D^2[Q(\sigma,0)(2j+1)/j(j+1)], \end{aligned} \tag{2}$$

where:

$$\begin{aligned} O(a,b) &= (a+b)(a+b-1), & P(a,b) &= (a+b+1)(a-b), \\ Q(a,b) &= a^2-b^2, & D &= |D(n\,;\,n')|. \end{aligned} \tag{3}$$

In the usual treatment of the "symmetrical top," $\sigma=\sigma_k$; but it is to be noted again that here $\sigma=\sigma_k+\sigma_s$, where $\sigma_s=-s,\ -(s-1),\cdots,(s-1),\ s$. As $\Delta\sigma=\Delta\sigma_k$, we have $\Delta\sigma_s=0$—a selection principle which we have already quoted.

Amplitude matrices for case (b). These may be obtained by superposition of the London-Hönl[6] and Kronig-Russell-Sommerfeld-Hönl[12,13] intensity formulas. This procedure has, in fact, already been used by Mulliken,[14] who has given most of the intensity relations appropriate to case (b). The precession of $\boldsymbol{\sigma}_k$ around j_k in case (b) is analogous to that of $\boldsymbol{\sigma}$ around j in case (a), as $\boldsymbol{\sigma}_k$, $\boldsymbol{\sigma}$ are both directed parallel to the axis of figure, and therefore perpendicular to the angular momentum due to rotation of the nuclei about the center of gravity, with which $\boldsymbol{\sigma}_k$ and $\boldsymbol{\sigma}$ are compounded to form vectorially respectively in cases (b) and (a) the resultants j_k and j. Therefore if in case (b) we average over the various j values consistent with given j_k, and thereby expurgate the fine-structure caused by different orientations of the loosely-coupled vector $\mathbf{s}$, we must then have the same dependence on the quantum numbers σ_k, j_k as that on σ, j in case (a). This dependence is, of course, that furnished by the Hönl-London amplitudes already given. On the other hand the precession of j_k and $\mathbf{s}$ about their resultant j in case (b) is entirely analogous to that of $\boldsymbol{k}$ and $\mathbf{s}$ about j in the ordinary atomic "normal multiplets," for which the intensity formulas were proposed in-

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[11] A quantity is said to be "Hermitian" if interchanging the first and second sets of indices changes the quantity into its conjugate; i.e., if $f(a;\,a')=f^*(a';\,a)$.

[12] A. Sommerfeld and H. Hönl, Sitzungsberichte der Preuss. Akad. der Wissenschaften IX, 141 (1925). R. de L. Kronig, Zeits. f. Physik **31**, 885 (1925).

[13] H. N. Russell, Nature **115**, 835 (1925).

[14] R. S. Mulliken, Phys. Rev. **30**, 138 (1927); **30**, 785 (1927).

dependently by Kronig,[11] Sommerfeld and Hönl,[12] and Russell,[13] and justified in quantum mechanics by Dirac.[15] Thus proper relative intensities for given j_k but variable j can be obtained simply by substituting j_k for k in the ordinary atomic formulas (or j_k, j, s, m for $K-\frac{1}{2}$, $J-\frac{1}{2}$, $R-\frac{1}{2}$, M in terms of the Landé notation employed by Kronig). The absolute values of the intensities are obtained by proper normalization of Kronig's constant factors of proportionality B which are independent of j, i.e., of the relative orientation of k and s. This normalization is effected by securing agreement with the Hönl-London formulas in the manner described at the beginning of the paragraph. This can be done by making the B-factors such functions of j_k and σ_k that Kronig's intensity formulas become identical with those of Hönl and London provided in the former we set $j=j_k$, $s=0$ and in the latter $\sigma=\sigma_k$. This assumes that B is independent of s, a supposition which is legitimate since the precessions arising from the spin surely cannot appreciably affect the total intensity of radiation.

The above procedure for superposing the Kronig and Hönl-London formulas is reminiscen, of what Kemble called the "hypothesis of continuity of intensities" in the old quantum theory and may be given a more rigorous proof by means of the principle of spectroscopic stability which is one of the important consequences of the new quantum mechanics. Consider an external field strong enough to overpower the internal coupling between $\mathbf{j}_k$ and $\mathbf{S}$, so that the projection of each along the field is quantized separately, and let m_k and m_s be the corresponding magnetic quantum numbers. As the spin is then completely split off from the rest of the molecule, the coordinate matrices will be identical with those for case (a) except that j_k and σ_k will replace j and σ. The principle of spectroscopic stability shows that an expression such as

$$\sum_{m_k,m_s,m_k',m_s'} |\, q(n,\sigma_k,j_k,m_k,m_s,;n',\sigma_k',j_k',m_k',m_s')\,|^2 \tag{4}$$

is invariant of the mode of quantization and hence must be equal to the expression

$$\sum_{j,m,j',m'} |\, q(n,\sigma_k,j_k,j,m;n',\sigma_k',j_k',j',m')\,|^2 \tag{5}$$

which represents the quantization for case (b) in the absence of strong external fields. Here t may be taken to be any function of the coordinate matrices, and in particular may be considered to represent the sum of the squares of the x, y, z coordinate elements in a fashion analogous to Eq. (1). Now in the case of the strong field $\Delta m_s=0$, and further the coordinate matrices are independent of m_s since the spin is not coupled to the rest of the molecule. Hence (4) becomes

$$(2s+1)(2j_k+1)\sum_{m_k'} |\, q(n,\sigma_k,j_k,m_k;n',\sigma_k',j_k',m_k')\,|^2 \tag{6}$$

inasmuch as the Burgers-Dorgelo sum rule shows that the sum over m_k' is independent of m_k, and for a given j_k there are $(2j_k+1)$ values of m_k and $(2s+1)$ of m_s. The sum-rule also shows that the sum over j' and m' in (5) has a value independent of both j and m, and hence (5) becomes

$$(2s+1)(2j_k+1)\sum_{j',m'} |\, q(n,\sigma_k,j_k,j,m;n,\sigma_k,j_k,j',m')\,|^2 \tag{7}$$

as for given j_k there are $\sum_{j=|j_k-s|,\ldots,j_k+s}(2j+1)$ or $(2j_k+1)$ $(2s+1)$ pairs of values of j and m. On equating (6) and (7) we obtain precisely the scheme for normalizing the Kronig B-factor described above.

On performing this superposition of the Kronig and the London-Hönl formulas, the following values have been found for the coefficients:

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[15] P. A. M. Dirac, Proc. Roy. Soc. **111A**, 281 (1926).

$$\begin{aligned} B(n,\sigma_k,j_k\,;\,n',\sigma_k\pm 1,j_k+1) &= iD(n\,;\,n')\left[O(j_k+2,\pm\sigma_k)/16U(j_k+1)\right]^{1/2} \\ B(n,\sigma_k,j_k\,;\,n',\sigma_k\pm 1,j_k) &= \mp iD(n\,;\,n')\left[P(j_k,\pm\sigma_k)/16V(j_k)\right]^{1/2} \\ B(n,\sigma_k,j_k\,;\,n',\sigma_k,j_k+1) &= D(n\,;\,n')\left[Q(j_k+1,\sigma_k)/4U(j_k+1)\right]^{1/2} \\ B(n,\sigma_k,j_k\,;\,n',\sigma_k,j_k) &= D(n\,;\,n')\left[Q(\sigma_k,0)/4V(j_k)\right]^{1/2}. \end{aligned} \tag{8}$$

It should be noted that these B's given above are proportional to the square roots of the Kronig factors, i.e., are $B^{1/2}$ in his notation.

The elements of the coordinate matrices (which are Hermitian[11]) may then be written as:

$$\begin{aligned} x(j_k,j,m;j_k+1,j+1,m\pm 1) &= iB(j_k;j_k+1)\left[E(j+1,j_k)E(j+2,j_k)O(j+2,\pm m)/4U(j+1)\right]^{1/2} \\ z(j_k,j,m;j_k+1,j+1,m) &= B(j_k;j_k+1)\left[E(j+1,j_k)E(j+2,j_k)Q(j+1,m)/U(j)\right]^{1/2} \\ x(j_k,j,m;j_k+1,j,m\pm 1) &= \mp iB(j_k;j_k+1)\left[E(j+1,j_k)F(j-1,j_k)P(j,\pm m)/4V(j)\right]^{1/2} \\ z(j_k,j,m;j_k+1,j,m) &= B(j_k;j_k+1)\left[E(j+1,j_k)F(j-1,j_k)Q(m,0)/V(j)\right]^{1/2} \\ x(j_k,j,m;j_k+1,j-1,m\pm 1) &= iB(j_k;j_k+1)\left[F(j-1,j_k)F(j-2,j_k)O(j,\mp m)/4U(j)\right]^{1/2} \\ z(j_k,j,m;j_k+1,j-1,m) &= -B(j_k;j_k+1)\left[F(j-1,j_k)F(j-2,j_k)Q(j,m)/U(j)\right]^{1/2} \\ x(j_k,j,m;j_k,j+1,m\pm 1) &= -iB(j_k;j_k)\left[E(j+1,j_k)F(j+1,j_k)O(j+2,\pm m)/4U(j+1)\right]^{1/2} \\ z(j_k,j,m;j_k,j+1,m) &= -B(j_k;j_k)\left[E(j+1,j_k)F(j+1,j_k)Q(j+1,m)/U(j+1)\right]^{1/2} \\ x(j_k,j,m;j_k,j,m\pm 1) &= \mp iB(j_k;j_k)\left[G^2(j,j_k)P(j,\pm m)/4V(j)\right]^{1/2} \\ z(j_k,j,m;j_k,j,m) &= B(j_k;j_k)\left[G^2(j,j_k)Q(m,0)/V(j)\right]^{1/2}, \end{aligned} \tag{9}$$

where:

$$\begin{aligned} &E(j\,;\,j_k)=(j+j_k)(j+j_k+1)-s(s+1), \quad F(j\,;\,j_k)=s(s+1)-(j-j_k)(j-j_k+1), \\ &G(j\,;\,j_k)=j(j+1)+j_k(j_k+1)-s(s+1), \qquad U(a)=a^2(2a-1)(2a+1), \\ &V(a)=a^2(a+1)^2. \end{aligned} \tag{10}$$

The definitions of the functions O, P, and Q are given in Eqs. (3).

In (9) we have omitted writing in explicitly the indices n, σ_k; n', σ_k' in the elements, but to get the complete formulas one has only to use the proper B-factors from (8). The elements of the y matrix can be obtained from those for x by noting that $x(m;\,m\pm 1)=\pm iy(m;\,m\pm 1)$. The phases given above were determined by comparison with the classical Fourier expansions of the coordinates just as Kronig found a set of phases for case (a).[16]

2. ENERGY LEVELS AND INTENSITIES IN THE GENERAL INTERMEDIATE CASE

The feature which characterizes the present calculation is that we start with case (b) and work back to case (a); i.e., we at first neglect the interaction between the spin and electronic orbital angular momenta, then set up the Hamiltonian function representing this interaction and use the technique of the new quantum mechanics to determine the "Eigenwerte" and amplitudes in the general case. An alternative method would be to start with case (a); i.e., at first neglect the interaction between the rotation and the non-secular part of the spin precessions, and then calculate the effect of the

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[16] R. de L. Kronig, Zeits. f. Physik **45**, 458 (1927).

centrifugal torques on these precessions. This method will be considered in a later paper by one of us.

Hamiltonian function. The particular form of the perturbing Hamiltonian function which we take is the ordinary "cosine" expression; i.e.,

$$H_p = A(\boldsymbol{\sigma}_k \cdot \mathbf{s}) = A(\sigma_{kx}s_x + \sigma_{ky}s_y + \sigma_{kz}s_z). \tag{11}$$

It has been shown[17] that this is the form of perturbing function to be expected for the spin electron moving in a Coulomb field, and is the form which is ordinarily used for this type of calculation.[18,19]

For the determination of the matrix elements of H_p we shall employ a calculation borrowed from the classical mechanics, but which is legitimate also in the quantum mechanics as only quantities which commute with each other are involved. The calculation given here is similar to the one used by Heisenberg and Jordan[18] in their work on the Zeeman effect in atomic spectra. A more rigorous treatment can be obtained by adapting some of the formulas of Dirac.[20]

We first note that H_p can have elements concerned only with transitions for which $\Delta j_k = 0, \pm 1$, as the relative orientations of $\mathbf{s}$ and $\boldsymbol{\sigma}_k$ are not affected by the precessions about j and about the axis of the external field. Let $\boldsymbol{q}$ be any vector fixed in the molecule, denote by q_z its z-component, and by $\bar{q}_z$ the time average of q_z. The matrix $\bar{q}_z$ is then formed by keeping only the diagonal elements of q_z. In order to find $\bar{q}_z$ we first project $\boldsymbol{q}$ along and at right angles to j, and then project these components on the direction of the external field. The components of $\boldsymbol{q}$ perpendicular to j have projections on the axis of the field which vary with the time, due to the precession about j, and hence do not contribute to $\bar{q}_z$. The motion of j about the axis of the field is one of pure precession without nutation, so that the component of $\boldsymbol{q}$ along j has a projection on the field which is independent of the time.

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[17] L. H. Thomas, Nature **117**, 514 (1926); Phil. Mag. **3**, 1 (1927). J. Frenkel, Zeits. f. Physik **37**, 243 (1926).

[18] Cf. for example, W. Heisenberg and P. Jordan, Zeits. f. Physik **37**, 263 (1926). E. C. Kemble, ref.[2]

[19] In order to take account of the interaction between $\mathbf{s}$ and the field developed by the rotation of the nuclei about the molecular center of gravity, we should have $H_p = A(\boldsymbol{\sigma}_k \cdot \mathbf{s}) + K(\boldsymbol{\varepsilon} \cdot \mathbf{s})$ where $\boldsymbol{\varepsilon}$ is the nuclear angular momentum, but as $\boldsymbol{\varepsilon} = \boldsymbol{j}_k - \boldsymbol{\sigma}_k$, we have $H_p = K(\boldsymbol{j}_k \cdot \mathbf{s}) + (A - K)(\boldsymbol{\sigma}_k \cdot \mathbf{s})$. The first term contributes only to the diagonal elements of (20), while the second term changes slightly the proportionality constant between $(\boldsymbol{\sigma}_k \cdot \mathbf{s})$ and H_p. Due to the large masses of the nuclei, however, K is very much smaller than A, so that we neglect these terms. This effect should lead to a very small separation of (b) terms which would be of importance only for S states; this has been discussed by Kemble, and by Mulliken who refers to it as "ρ-type doubling."

[20] P. A. M. Dirac, Proc. Roy. Soc. **111A**, 281 (1926). Our Eqs. (17) and (16) correspond respectively to Dirac's Eqs. (48) and (60), while our Eq. (12) is analogous to his Eq. (61) considering only the first term of the right-hand side. However, his quantity r is our $\boldsymbol{\sigma}_k^{\mathrm{perp}}$, and as the latter has elements which are functions of j_k, we would not have, in Dirac's language, the commutative property of r with $\epsilon^{i\theta}$ and $\epsilon^{-i\theta}$, a condition used in the derivation of his Eq. (60). This discrepancy can be easily remedied, using his Eqs. (39) and (50), and the final results are in complete agreement with our calculations.

The elements of $\bar{q}_z$ are made up entirely of contributions from this source. Now the component of $\boldsymbol{q}$ along $\boldsymbol{j}$ is $(\boldsymbol{q}\cdot\boldsymbol{j})/|\boldsymbol{j}|$, where $\boldsymbol{j}/|\boldsymbol{j}|$ is the unit vector in the direction of $\boldsymbol{j}$; and similarly the projection of this component on the external field is $[(\boldsymbol{q}\cdot\boldsymbol{j})/|\boldsymbol{j}|](m/|\boldsymbol{j}|)$, where $m=j_z$. Consequently

$$\bar{q}_z=(\boldsymbol{q}\cdot\boldsymbol{j})m/\,|\,\boldsymbol{j}\,|\,^2. \tag{12}$$

We now identify $\boldsymbol{q}$ with the vector matrix $\boldsymbol{\sigma}_k$. The procedure for obtaining the elements of σ_{kx}, σ_{ky}, and σ_{kz}, is very similar to that used in obtaining the amplitudes for case (b). We need concern ourselves only with elements for which $\Delta\sigma_k=0$, as $\boldsymbol{\sigma}_k$ has no components at right angles to itself, and then normalize these elements so that the component along the axis of symmetry of the molecule has the value $|\boldsymbol{\sigma}_k|=\sigma_k$, for this component is nothing but $\boldsymbol{\sigma}_k$ itself.[21] The elements of σ_{kx}, σ_{ky}, σ_{kz}, then resemble, in a very striking manner, those elements of x, y, and z respectively for which the transitions are of the type $\Delta\sigma_k=0$; the only difference being (apart from the difference in the normalizing factors just mentioned) that owing to the constancy of σ_k the elements of σ_{kx}, σ_{ky}, and σ_{kz}, are diagonal with respect to transitions in the quantum numbers represented by the letter n. Mathematically stated,

$$\sigma_{kz}(j_k,j,m\,;\,j_k',j',m)=(\sigma_k/D(n\,;\,n))z(n,\sigma_k,j_k,j,m\,;\,n,\sigma_k,j_k',j',m).$$

Consider a resolution of $\boldsymbol{\sigma}_k$ into two components, parallel and perpendicular to $\boldsymbol{j}_k$, respectively. Let us designate them as $\boldsymbol{\sigma}_k^{(\mathrm{par})}$ and $\boldsymbol{\sigma}_k^{(\mathrm{perp})}$. This resolution amounts to considering separately the elements of σ_{kz} for which $\Delta j_k=0$, and for which $\Delta j_k=\pm1$.

Applying Eq. (12) to $\boldsymbol{\sigma}_k^{(\mathrm{par})}$, we have

$$(\sigma_k^{(\mathrm{par})})_z(j_k,j,m\,;\,j_k,j,m)=[\,|\,\boldsymbol{\sigma}_k^{(\mathrm{par})}\,|\,|\,\boldsymbol{j}_k\,|\,^2/|\boldsymbol{j}_k|\,+(\boldsymbol{\sigma}_k^{(\mathrm{par})}\cdot\boldsymbol{s})](m/\,|\,\boldsymbol{j}\,|\,^2), \tag{13}$$

where we have introduced the relation $\boldsymbol{j}=\boldsymbol{j}_k+\boldsymbol{s}$.

From the matrix expressions for $\boldsymbol{\sigma}_k$ and $\boldsymbol{j}_k$ it can be shown that[22]

$$(\,|\,\boldsymbol{\sigma}_k^{(\mathrm{par})}\,|\,/\,|\,\boldsymbol{j}_k\,|\,)=\sigma_k^2/j_k(j_k+1). \tag{14}$$

Hence, using Eqs. (9) and (14), Eq. (13) can be written:

$$\begin{aligned}
&H_p(n,\sigma_k,j_k\,;\,n,\sigma_k,j_k) &(15)\\
&\quad=A(\sigma_k/D(n\,;\,n))(j(j+1)/m)z(n,\sigma_k,j_k,j,m\,;\,n,\sigma_k,j_k,j,m)-A\sigma_k^2\\
&=A\sigma_k(j(j+1)/m)[B(n,\sigma_k,j_k\,;n,\sigma_k,j_k)/D(n\,;\,n)][G^2(j,j_k)Q(m,0)/V(j)]^{1/2}-A\sigma_k^2.
\end{aligned}$$

Applying Eq. (12) to $\boldsymbol{\sigma}_k^{(\mathrm{perp})}$ we have from Eq. (9), as $(\boldsymbol{\sigma}_k^{(\mathrm{perp})}\cdot\,\boldsymbol{j}_k)=0$,

$$\begin{aligned}
H_p(n,\sigma_k,j_k\,;\,n,\sigma_k,j_k+1)&=A(\sigma_k/D(n\,;n))(j(j+1)/m)z(n,\sigma_k,j_k,j,m\,;n,\sigma_k,j_k+1,j,m)\\
&=A(\sigma_k/D(n\,;\,n))B(n,\sigma_k,j_k\,;n,\sigma_k,j_k+1)[E(j+1,j_k)F(j-1,j_k)]^{1/2}\\
&=(A\sigma_k/2)[\{(j_k+1)^2-\sigma_k^2\}/(j_k+1)^2(2j_k+1)(2j_k+3)]^{1/2}\\
&\quad\times[\{(j+j_k+1)(j+j_k+2)-s(s+1)\}\,\{s(s+1)-(j-j_k)(j-j_k-1)\}]^{1/2}.
\end{aligned} \tag{16}$$

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[21] As $\boldsymbol{\sigma}_k$ represents only the projection of the total electronic orbital angular momentum vector $\boldsymbol{k}$ on the axis of symmetry, its absolute value is given by σ_k and not by $[\sigma_k(\sigma_k+1)].^{1/2}$

[22] This formula can be obtained by combining the relations $|\boldsymbol{\sigma}_k^{\mathrm{par}}|\,/\,|\boldsymbol{\sigma}_k|=[\sigma_k^2/j_k(j_k+1)]^{1/2}$ and $|\boldsymbol{\sigma}_k|\,/\,|\boldsymbol{j}_k|=[\sigma_k^2/j_k(j_k+1)]^{1/2}$ the second of which follows from the expressions for $|\boldsymbol{\sigma}_k|$ and $|\boldsymbol{j}_k|$, while the first is obtained by use of the elements of $\boldsymbol{\sigma}_k$.

Similarly, by substituting from Eqs. (3), (8), and (10), Eq. (15) becomes,

$$H_p(n,\sigma_k,j_k\;;\;n,\sigma_k,j_k)=A\sigma_k^2[\{j(j+1)-j_k(j_k+1)-s(s+1)\}/2j_k(j_k+1)]. \quad (17)$$

Energy determinant. According to the perturbation theory of the new quantum mechanics, the solution of our problem in the general case is essentially equivalent to the solution of the set of linear equations[23]:

$$W(r\;;r)S(r\;;r')-\textstyle\sum_l H(l\;;r')S(r\;;l)=0, \quad (18)$$

subject to the auxiliary conditions:

$$\textstyle\sum_l S(r\;;l)S^*(r'\;;l)=\begin{cases}0 \text{ if } r'\neq r\\ 1 \text{ if } r'=r.\end{cases} \quad (19)$$

Here r, r', and l assume all values of j_k consistent with a given set of values for σ_k, j, and s; i.e., r, r', $l=|j-s|, \cdots, (j+s-1), (j+s)$.

The condition for the existence of solutions, other than zero, of Eqs. (18) is that W satisfy the determinantal equation:

$$0=\begin{vmatrix} H(j_{k1}\;;j_{k1})-W & H(j_{k1}\;;j_{k1}-1) & \cdots\cdots\cdots \\ H(j_{k1}-1\;;j_{k1}) & H(j_{k1}-1\;;j_{k1}-1)-W & \cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & H(j_{k2}\;;j_{k2})-W \end{vmatrix}. \quad (20)$$

The symbols j_{k1} and j_{k2} designate respectively the largest and smallest values of j_k compatible with a given set of values for j and s; i.e., $j_{k1}=j+s$, $j_{k2}=|j-s|$.

The Hamiltonian function (which is Hermitian[11]) appearing in the above determinant is that part of the complete Hamiltonian function which involves j_k, and thus includes, besides H_p, diagonal terms concerned with the nuclear rotational energy. Thus $H=H_r+H_p$, where H_r is the diagonal matrix,

$$H_r(n,\sigma_k,j_k\;;\;n,\sigma_k,j_k)=[j_k(j_k+1)-\sigma_k^2](h^2/8\pi^2I). \quad (21)$$

The elements of H_p are those given by Eqs. (16) and (17).

The values of W which satisfy the above determinant give the energy levels for the complete transition stage from case (b) where $IA=0$, to case (a) where $1/IA=0$. The asymptotic energy formula valid for large values of A must, of course, be that for the symmetrical top, and is hence

$$W=A\sigma_k\sigma_s+[j(j+1)-\sigma^2+\overline{s^2}_{\text{perp}}](h^2/8\pi^2I)+\cdots, \quad (22)$$

although, because of algebraic difficulties, we have not succeeded in showing that Eq. (22) follows from Eq. (20) except in special cases; e.g., doublets, and triplets. The first term arises from the interaction of $\boldsymbol{\sigma}_k$ and $\mathbf{s}$, while the second term represents the energy of molecular rotation. The term $(\overline{s^2}_{\text{perp}}h^2/8\pi^2I)$ must be included to take into account the fact that for case

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[23] Born, Heisenberg, and Jordan, Zeits. f. Physik **35**, 557 (1926).

(a) the component of s perpendicular to the axis of figure makes a contribution to the energy.[24] In general $\overline{s^2}_{\text{perp}} = s(s+1) - \sigma_s^2$.

The energy determinant given above yields an algebraic equation for W of the same order as the term multiplicity $(2s+1)$, and so is not readily solvable except for low values of s, notably $s = \frac{1}{2}$, and $s = 1$ (doublet and triplet spectra respectively). The results in these special cases will be given in later sections of this paper.

Energy formula for nearly case (b) *coupling with any multiplicity.* Although the energy determinant may not be solvable for the general case of any multiplicity, the energy can be obtained as a power series development in a suitable parameter, by use of the perturbation theory formulas.[23] This expansion will be valid only when the coupling energy H_p is small compared to the rotational energy H_r; in other words, only when Hund's case (b) is a closer approximation than his case (a). Taking $\alpha = AI$ as the parameter for the expansion, the perturbing Hamiltonian function can be written as: $H = H_r + (H_p/AI)\alpha$, and the perturbation theory formulae[23] show that

$$\begin{aligned} W = {} & H_r(j_k\,;j_k) + (1/AI)H_p(j_k\,;j_k)\alpha \\ & + (1/A^2I^2)\textstyle\sum_{j_k' \neq j_k}\left[\,|\,H_p(j_k\,;j_k')\,|^2/h\nu_0(j_k\,;j_k')\right]\alpha^2 + \cdots . \end{aligned} \tag{23}$$

where

$$h\nu_0(j_k\,;j_k') = [j_k(j_k+1) - j_k'(j_k'+1)](h^2/8\pi^2I)\;; \tag{24}$$

and where the elements of H_r and H_p are given by Eqs. (16), (17), and (21).

Intensity relations. In case the energy determinant (20) can be solved, the "Eigenwerte" are to be substituted in Eqs. (18) and the elements of S determined. If q_b is any one of the coordinate matrices for case (b) and if q is the corresponding matrix in the general case, then[23]

$$q = Sq_b\tilde{S}^*, \tag{25}$$

where $\tilde{S}^*$ is the matrix formed from S by taking the conjugate of every element and then transposing the rows and columns (indicated by $\sim$).

Energy levels in the triplet case for coupling nearly of type (a). Here and throughout the remainder of this paper we shall use the abbreviation

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[24] Born and Oppenheimer, Annalen der Physik, **84,** 457 (1927), especially p. 479. The term $\overline{s_{\text{perp}}^2}$ is theoretically just as important and inevitable as the other additive term $-\sigma^2$, but, unlike the latter, seems usually to be omitted by the band spectroscopists. It is particularly important to include this term if one is endeavoring to calculate the part of a multiplet which is due to magnetic coupling independent of a rotation, but fortunately in the particularly common case of doublets $\overline{s_{\text{perp}}^2}$ has the same value 1/2 in both the components $\sigma_s = -1/2$ and $\sigma_s = 1/2$. Instead of $\overline{s_{\text{perp}}^2}$ we ought really to write $\overline{(k+s)_{\text{perp}}^2}$ in order to include the secular effect of both the orbital and electronic angular momentum. However, the average value of $\mathbf{s}_{\text{perp}} \cdot \mathbf{k}_{\text{perp}}$ is zero, as $\mathbf{k}$ precesses very much faster than $\mathbf{s}$, and further the mean square of the perpendicular component of $\mathbf{k}$ has the same value for all the components of a multiplet, and so for our purposes it does no harm to consider the secular effect of only the spin angular momentum perpendicular to the axis of figure. As the motion of $\mathbf{s}$ is very approximately that of pure precession without appreciable nutation it is not really necessary to affix a mean value sign above the square of the perpendicular component of $\mathbf{s}$.

$$\lambda = 8\pi^2 AI/h^2. \qquad (26)$$

The value of λ is then a measure of the tightness of the coupling; i.e., it is very small for coupling nearly of type (b), and is large for nearly type (a). For triplet terms $s=1$, $2s+1=3$, and the energy equation (20) is a cubic; i.e.,

$$\begin{aligned}(W+A\sigma_k^2\lambda^{-1})^3 &- A\lambda^{-1}(3j^2+3j+2)(W+A\sigma_k^2\lambda^{-1})^2\\ &+A^2\lambda^{-2}[-\sigma_k^2\lambda^2+4\sigma_k^2\lambda+3j^2(j+1)^2](W+A\sigma_k^2\lambda^{-1})\\ &+A^3\lambda^{-3}[\sigma_k^2\lambda^2(j^2+j+2)-4\sigma_k^2\lambda(j^2+j+1)-j^2(j+1)^2(j-1)(j+2)]=0\end{aligned}$$

It has not been found possible to solve this equation generally, but asymptotic solutions can be obtained for the limiting cases (a) and (b). For (a) we expand W as a power series in λ^{-1} and solve for the coefficients by substitution in the above formula. There are three roots corresponding to the three values of σ_s; i.e.,

$$\begin{aligned}\sigma_s=+1)\quad W&=A\sigma_k+[j(j+1)-\sigma_k^2-2\sigma_k](h^2/8\pi^2I)\\ &\qquad +2A\sigma_k^{-1}\lambda^{-2}[j(j+1)-\sigma_k(\sigma_k+1)]+\cdots.\\ \sigma_s=0)\quad W&=[j(j+1)-\sigma_k^2+2](h^2/8\pi^2I)+4A\lambda^{-2}+\cdots\\ \sigma_s=-1)\quad W&=-A\sigma_k+[j(j+1)-\sigma_k^2+2\sigma_k](h^2/8\pi^2I)\\ &\qquad -2A\sigma_k^{-1}\lambda^{-2}[j(j+1)-\sigma_k(\sigma_k-1)]+\cdots.\end{aligned}$$

These expressions agree with the asymptotic formula (22). The expansion about case (b) can be made by using (23) and (24).

3. DOUBLET CASE

Energy formula. For doublet spectra $s=\frac{1}{2}$, and the term multiplicity $2s+1=2$. In the limit of case (b) there are two values of j_k; namely, $j_1=j+\frac{1}{2}$, and $j_2=j-\frac{1}{2}$, so that the energy determinant (20) becomes:

$$\begin{vmatrix} A\lambda^{-1}[(j+\frac{1}{2})(j+\frac{3}{2})-\sigma_k^2]-A\sigma_k^2(2j+1)^{-1}-W & A\sigma_k[\{(j+\frac{1}{2})^2-\sigma_k^2\}^{1/2}(2j+1)^{-1}] \\ A\sigma_k[\{(j+\frac{1}{2})^2-\sigma_k^2\}^{1/2}(2j+1)^{-1}] & A\lambda^{-1}[(j^2-\frac{1}{4})-\sigma_k^2]+A\sigma_k^2(2j+1)^{-1}-W \end{vmatrix}=0$$

which has the solution

$$W=[(j+\tfrac{1}{2})^2-\sigma_k^2\pm\tfrac{1}{2}\{4(j+\tfrac{1}{2})^2+\lambda(\lambda-4)\sigma_k^2\}^{1/2}](h^2/8\pi^2I) \qquad (27)$$

The upper sign corresponds to the state of higher rotational energy; i.e., to $j_1=j+\frac{1}{2}$.

This remarkably compact and convenient formula was originally given in a preliminary report on this work.[25] It is very gratifying that the new quantum mechanics yields such a simple expression where the old quantum theory gave only a series approximation; especially since this formula gives the energy values both for regular multiplets ($A>0$), and for inverted multiplets ($A<0$) throughout the entire range from (a) to (b).

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[25] J. H. Van Vleck and E. L. Hill, Phys. Rev. **31**, 714 (1928). Abstract. Our previous definition of the coupling factor A differs from the present one by $4\pi^2/h^2$, as we now measure angular momentum in multiples of $h/2\pi$.

Correlation of term values between (*a*) *and* (*b*). One of the most interesting properties of our doublet formula is that it yields in an unambiguous manner exactly that correlation of term values between (a) and (b) which has been predicted by Hund[26] and by Kemble.[2] In each of the limiting cases there are two component levels; i.e.,

case (*b*)	*case* (*a*)
$j_1=j+\frac{1}{2}$	$\sigma_1=\sigma_k+\frac{1}{2}$
$j_2=j-\frac{1}{2}$	$\sigma_2=\sigma_k-\frac{1}{2}$

The assignment of the two levels of case (b) to the two branches of (27) is known; namely, the level associated with the positive radical is the j_1 state. To find the assignment for case (a) consider an adiabatic change in the parameter λ from zero to a numerically large value. Whether λ be positive or negative, the discriminant of (27) never vanishes, except for the lowest state $j=\sigma_k-\frac{1}{2}$. Thus the two branches can be considered separately, and we have only to determine how each branch behaves during the change from (b) to (a). The lowest state must be investigated separately.

Regular multiplets ($A>O$). Expanding (27) as a power series in the parameter $|\lambda^{-1}|$, we have

$$W=\pm\tfrac{1}{2}A\sigma_k+(h^2/8\pi^2I)\left[j(j+1)-(\sigma_k\pm\tfrac{1}{2})^2+\tfrac{1}{2}\pm\lambda^{-1}\sigma_k^{-1}\left\{(j+\tfrac{1}{2})^2-\sigma_k^2\right\}+\cdots\right]$$

The upper sign corresponds to the j_1 state for (b), and a comparison with the asymptotic formula (22) for (a) shows that it corresponds also to σ_1. Hence the correlation of energy levels is

$$j_1\rightarrow\sigma_1,\quad j_2\rightarrow\sigma_2. \tag{28}$$

For the lowest rotational state $j=\sigma_k-\frac{1}{2}$, the j_2 level does not exist, due to the restriction $j_k\geqq\sigma_k$, so that this state is a singlet. Eq. (27) becomes $W=(h^2/8\pi^2I)[(1-4\pi^2AI/h^2)\sigma_k]$. On comparison with (22) we see that $\sigma_s=-\frac{1}{2}$, so that for this state the behavior is anomalous (the radical changing sign) and the correlation is $j_1\rightarrow\sigma_2$, just as predicted by Hund and Kemble.

Inverted multiplets ($A<O$). In this case (27) becomes:

$$W=\mp\tfrac{1}{2}A\sigma_k+(h^2/8\pi^2I)\left[j(j+1)-(\sigma_k\mp\tfrac{1}{2})^2+\tfrac{1}{2}\mp\lambda^{-1}\sigma_k^{-1}\left\{(j+\tfrac{1}{2})^2-\sigma_k^2\right\}+\cdots\right]$$

As for regular multiplets, the upper sign is correlated with the j_1 level for (b), but comparison with (22) shows that it is correlated with the σ_2 level for (a). Thus the term correlation is just the reverse of that for regular multiplets; i.e.,

$$j_1\rightarrow\sigma_2,\quad j_2\rightarrow\sigma_1. \tag{29}$$

As the discriminant of (27) never vanishes for negative values of A, there is no anomalous behavior for any of the rotational states.

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[26] F. Hund, Zeits. f. Physik **42,** 93 (1927). Cf. especially his Fig. 8.

Doublet states for OH $\lambda 2811$. This is the band used by Kemble[2] to test his formulas, and we shall take the necessary numerical data from his paper. As (27) gives the combined effects of rotational and spin energy in a given state, the energy difference between two doublet levels due to spin effects alone cannot be separated out, but it will be sufficient for our purposes to consider only the excess energy of each level over that which it would have were it a pure case (b) state having rotational energy only. With this simplification we readily find from (27) that the doublet energy difference is

$$\Delta = (h/8\pi^2cI)\left[\left\{4(j+\tfrac{1}{2})^2+\lambda(\lambda-4)\sigma_k^2\right\}^{1/2}-(2j+1)\right] \text{ cm}^{-1}.$$

This particular band is due to a $^2S \rightarrow {^2P}$ transition; i.e., $\sigma_k=0 \rightarrow \sigma_k=1$. For the ^2S state, as $\sigma_k=0$, the levels are singlets, while in the ^2P state they are doublets. This state is also inverted, so that $A<0$. According to the data given by Kemble in his Table II, the asymptotic value of the doublet separation at the origin is 140.25 cm^{-1}. The value of the constant $(h/8\pi^2cI)$ is obtained as the arithmetic average of B_1^* and B_2^*. Putting these numerical values into the above formula, it becomes,

$$\Delta = 37.16\left[\left\{(j+\tfrac{1}{2})^2+21.79\right\}^{1/2}-(j+\tfrac{1}{2})\right] \text{ cm}^{-1}.$$

Taken as a function of j this formula gives a curve practically coincident with curve c of Fig. 4 of Kemble's paper, and hence still leaves a small discrepancy with the experimental data, which may be due to our neglect of ρ-type doubling as suggested by Kemble, and may also be partly due to the somewhat arbitrary meaning which we have assigned to Δ. On calculating the values of B_1^* and B_2^* which are the "apparent" values of the constant $(h/8\pi^2cI)$ in the two component levels, they turn out to be 16.697 cm^{-1} and 20.566 cm^{-1} respectively, as compared to the experimental values of 16.60 cm^{-1} and 20.565 cm^{-1}, whereas Kemble's formula gave 16.82 cm^{-1} and 20.86 cm^{-1}.

Intensity formulas. Putting the energy values from (27) into (18), we get

$$\begin{aligned} S(j_1\,;j_1)&=C_1[H(j_2\,;j_1)], & S(j_1\,;j_2)&=C_1[W(j_1)-H(j_1\,;j_1)] \\ S(j_2\,;j_1)&=C_2[H(j_2\,;j_1)], & S(j_2\,;j_2)&=C_2[W(j_2)-H(j_1\,;j_1)] \end{aligned} \tag{30}$$

where the constants C_1 and C_2 are to be determined by use of (19). We have here introduced specifically the notation j_1 and j_2 for the two values of j_k. We shall throughout the rest of the paper write the elements of S in this condensed notation in which we omit writing all arguments except the j_k, as S is a diagonal with respect to other quantum numbers. The C's may in general have arbitrary phase factors but it will be shown below in fine print that for our purposes they can be disregarded, so that we can take the elements of S to be real. If then we introduce the abbreviations:

$$\gamma_1 = \left\{\lambda\sigma_k^2(2j+1)^{-1}\right\} - (j+\tfrac{1}{2}) \tag{31}$$

$$2\gamma_2 = \left[(2j+1)^2+\lambda(\lambda-4)\sigma_k^2\right]^{1/2}, \tag{32}$$

and utilize the relation $\gamma_1^2-\gamma_2^2=[\sigma_k^4\lambda^2/(2j+1)^2]-(\sigma_k^2\lambda^2/4)$ we find that after the normalization (19) becomes

$$\begin{aligned} S(j_1\,;\,j_1)=S(j_2\,;\,j_2)&=[(\gamma_2-\gamma_1)/2\gamma_2]^{1/2}\\ S(j_1\,;\,j_2)=-S(j_2\,;\,j_1)&=[(\gamma_1+\gamma_2)/2\gamma_2]^{1/2} \end{aligned} \tag{33}$$

The intensity formulas for the general intermediate case can now be found by Eq. (25) and the expressions for S given in (33) and for q_b given in (9). We have verified directly in a large number of instances that in the limit $\lambda=\infty$ Eq. (25) actually converts the (b)-formulas (9) into the Hönl-London (a)-formulas. It is interesting to note that the selection rule $\Delta\sigma_s=0$ for case (a) can actually be established in this way, as we find the elements of the left side of (25) for which $\Delta\sigma_s\neq 0$ vanish in the limit $\lambda=\infty$.

As most readers are probably more familiar with the amplitudes for (a) than for (b) we shall give an alternative method, perhaps simpler than (25) for finding the general intensities, starting instead with those for case (a). This method has the further practical advantage that because of the selection rule $\Delta\sigma_s=0$ there are never more than two terms in the summations involved in expanding the matrix products, whereas with (25) there may be three or more terms in this summation. The idea is to transform from (a) to (b) and then from (b) to the general case. Thus if q_a, q_b, and q, represent any given coordinate matrix for case (a), case (b), and the intermediate case respectively, and if S_1 is the matrix $S_1=\lim_{A\to\infty}S$,[27] then $q_a=S_1q_b\tilde{S}_1$, and as also $\tilde{S}_1=S_1^{-1}$, then $q_b=\tilde{S}_1q_aS_1$. But as indicated in the preceding paragraph, $q=Sq_b\tilde{S}$, hence

$$q=Tq_a\tilde{T}, \tag{34}$$

where

$$T=S\tilde{S}_1, \qquad \tilde{T}=S_1\tilde{S}. \tag{35}$$

From (33) and (28), letting $A\to\infty$,

$$\begin{aligned} S_1(\sigma_1\,;\,\sigma_1)=S_1(\sigma_2\,;\,\sigma_2)&=[\{(j+\tfrac{1}{2})-\sigma_k\}/(2j+1)]^{1/2}\\ S_1(\sigma_1\,;\,\sigma_2)=-S_1(\sigma_2\,;\,\sigma_1)&=[\{(j+\tfrac{1}{2})+\sigma_k\}/(2j+1)]^{1/2} \end{aligned} \tag{36}$$

where we use the notation σ_1 and σ_2 instead of the double indices $(\sigma_k,\ \sigma_s)$. Putting the expressions from (33) and (36) in (35) we get for regular multiplets,[27]

$$T(\sigma_1;\sigma_1)=T(\sigma_2;\sigma_2)=K[(\gamma_2-\gamma_1)(j+\tfrac{1}{2}-\sigma_k)]^{1/2}+K[(\gamma_1+\gamma_2)(j+\tfrac{1}{2}+\sigma_k)]^{1/2} \tag{37}$$

$$T(\sigma_1;\sigma_2)=-T(\sigma_2;\sigma_1)=K[(\gamma_1+\gamma_2)(j+\tfrac{1}{2}-\sigma_k)]^{1/2}-K[(\gamma_2-\gamma_1)(j+\tfrac{1}{2}+\sigma_k)]^{1/2} \tag{38}$$

where $\qquad K=[2\gamma_2(2j+1)]^{-1/2}.$

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[27] In the remainder of this section we shall assume that $A>0$; i.e., the formulae are for regular multiplets, but they can easily be found for $A<0$ by defining $S_1=\lim_{A\to-\infty}S$. The form of the general equations (34) and (35) is, of course, unchanged.

These elements, of course, satisfy the conditions that $\lim_{A\to\infty} T = 1$ and $\lim_{A\to 0} T = \tilde{S}_1$ (e.g., in the limit $A = \infty$, $T(\sigma_1;\sigma_1) = T(\sigma_2;\sigma_2) = 1$; $T(\sigma_1;\sigma_2) = T(\sigma_2;\sigma_1) = 0$). The explicit expansion for (34) is

$$q(n,\sigma_k,\sigma,j,m\ ;\ n',\sigma_k',\sigma',j',m') = \sum_{\sigma'',\sigma'''}\big[T(n,\sigma_k,\sigma,j,m\ ;\ n,\sigma_k,\sigma'',j,m)$$

$$\times q_a(n,\sigma_k,\sigma'',j,m\ ;\ n',\sigma_k',\sigma''',j',m')T(n',\sigma_k',\sigma',j',m'\ ;\ n',\sigma_k',\sigma''',j',m')\big], \quad (39)$$

where the q_a's can be taken directly from (2), and the T's from (37-8).

The summation over σ'' embraces only the two values $\sigma'' = \sigma_k - \frac{1}{2}$, $\sigma_k + \frac{1}{2}$, and σ''' can only equal $\sigma'' + (\sigma_k' - \sigma_k)$ since $\Delta\sigma_s = 0$ in case (a). Consequently (39) *never involves a summation over more than two terms, and permits calculation of the intensity for any coupling intermediate between* (a) *and* (b) *in either the initial or final state or both.*

In the application of (39) to the calculation of intensities for particular transitions for which there are jumps in the electronic quantum numbers, it must be noted that although T is diagonal with respect to the quantum numbers represented by n, the elements of T still are functions of them through the coupling constant A and the moment of inertia I, which may be different for the upper and lower states. Consequently *in "electronic" bands the function T in front of q_a in* (39) *is of a different form (viz. has different constants I and λ) than the T after q_a.* Examples are given in section 4.

Question of phases. In using Eq. (25) to determine even only the magnitudes of the elements of q, it is essential that one know the phases as well as absolute values of the amplitudes q_b. For this reason we have in Eq. (9) given the amplitudes in case (b) inclusive of the phases. The phases of the final amplitudes q depend on how one choose the phases in the normalizing factors C_1 and C_2 involved in S (cf. Eq. 30). However, if, as is usually the case, we are interested in finding only the magnitudes of the elements of q by means of (25) the arbitrariness of phase in C_1 and C_2 is trivial. This is true because the C's are connected with only the first index in $S(j_k, j_k')$ or the last in the transposed matrix $S(j_k', j_k)$ and so the phase element coming from the C's is not involved in the variable or inner indices over which one sums in multiplying together the matrices involved in (25); thus the phase element of C merely introduces a complex factor of modulus unity into (25).

On the other hand at first sight it looks as though the phase of C might be of importance in using (34), for the phase of C is connected with the inner as well as outer indices in (34), as (35) shows that the construction of T involves transposition of S. In general one might expect that to use (34) correctly it is imperative to determine the phases in the C's in a way which is consistent with the phases in q_a; or in other words that (34) will work only with proper phases in the q_a. Now very fortunately there is the selection principle $\Delta\sigma_s = 0$ in case (a) and consequently the differences between the initial and final quantum numbers in the elements q_a will be the same in both terms of the summation in (39). Further the phase factor depends on the difference of the quantum numbers; this can, for instance, be seen from the correspondence principle, as the difference of quantum numbers determines the corresponding classical harmonic. This means that the phase factor for q_a has the same values for both terms of the summation in (39), and so need not be included if we are interested in knowing the absolute values of the elements of q. Consequently we may take S to be real and need not consider the phases in the q_a (an advantage of 34 over 25). (One might perhaps question whether with the most general complex solutions of Schroedinger's equation the phase factors in q_a are functions only of the differences of the quantum numbers, but it is easily seen that if the phases in q_a were chosen in some more complicated way then with any simple choice of the phases in T, especially real T, that Eq. (34) would in the limit $A = 0$ yield expressions for the elements of

q_b which are complex quantities neither real nor pure imaginaries, contrary to our selection of phases in the q_b in Eq. (9). In other words our choice of phases in the original unperturbed b-type system demands that the phases in q_a be functions only of the differences of quantum numbers).

4. APPLICATION OF DOUBLET INTENSITY FORMULAS TO PARTICULAR TRANSITIONS

As illustrations of the use of Eq. (39) we shall calculate the intensities for two transitions: i.e., (1) The important case of $^2P \rightarrow {}^2S$ in which ordinarily the ^2P state is case (a) and the ^2S state is case (b), and (2) a particular case of $^2D \rightarrow {}^2P$ in which ^2D is case (b) and ^2P is case (a). For both transitions we shall use unprimed letters for the quantum numbers in the upper state and primed (′) letters for those in the lower state.

^{2}**P**→^{2}**S**. Eq. (38) shows that for the upper state $T=1$, while for the lower state $T=\tilde{S}_1$. Hence $q=1q_aS_1$, where

$$S_1(j_1'\,;j_1')=S_1(j_2'\,;j_2')=S_1(j_1'\,;j_2')=-S_1(j_2'\,;j_1')=(\tfrac{1}{2})^{1/2}.$$

The transitions involved may be conveniently divided, in the usual manner, into three groups for which $\Delta j=0,\ \pm 1$, corresponding to the Q, P, and R branches respectively. Putting these values into (39) it is found that in any given branch the transition probabilities from a given level in the upper state to each of the levels $j_k'=j'\pm\frac{1}{2}$ in the lower state are equal. The following table gives the intensities for transitions from the two upper levels for each branch:

P-branch $\quad j'=j+1\,;\ j_k'$ either $j'+\frac{1}{2}$ or $j'-\frac{1}{2}$.

$$\sigma_1 \sim D^2[(4j^2-1)/32(j+1)]\,; \qquad \sigma_2 \sim D^2[(2j+1)(2j+3)/32(j+1)]$$

Q-branch $\quad j'=j\,; \quad j_k'=j'\pm\frac{1}{2}$

$$\sigma_1 \sim D^2[(4j^2-1)(2j+3)/32j(j+1)]\,; \qquad \sigma_2 \sim D^2[(2j+1)^3/32j(j+1)]$$

R-branch $\quad j'=j-1\,; \quad j_k'=j'\pm\frac{1}{2}$

$$\sigma_1 \sim D^2[(2j+1)(2j+3)/32j]\,; \qquad \sigma_2 \sim D^2[(4j^2-1)/32j].$$

An interesting though qualitative correlation of these formulae with the experimental results can be made for the compounds HgH, ZnH, OH, and CH.[28] For HgH the ^2P level is, to a good approximation, case (a). There are twelve strong branches of which those differing only with respect to the final value of j_k' are of about equal intensities. This agrees very well with our conclusions concerning the equality in the intensities of transitions from a given σ-level in ^2P to either j_k-level in ^2S. In ZnH the ^2P level is not as near true case (a) as in HgH, and here the branches for which $\Delta j_k \neq \Delta j$ (i.e., $\Delta\sigma_s \neq 0$) are weaker than those for which $\Delta j_k=\Delta j$. In OH the weaker bands are reduced to satellite series and in CH they are practically absent. Considering this progression as one in which the ^2P state changes from (a) in HgH to practically (b) in CH, there is a general agreement in the experi-

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[28] The writers are indebted to Prof. R. S. Mulliken for the experimental material in this section. Cf. also, R. S. Mulliken, Phys. Rev. **31**, 310 (1928) and especially Sept. 1928.

mental and theoretical intensities, as (9) shows that for transitions between two case (b) states the branches for which $\Delta j_k \neq \Delta j$ should be much weakened especially for the lines at some distance from the origin.

$^2D \rightarrow {}^2P$. For the upper state, which is taken as case (b)

$$T(j_1\,;j_1) = T(j_2\,;j_2) = [(j-\tfrac{3}{2})/(2j+1)]^{1/2}$$
$$T(j_1\,;j_2) = -T(j_2\,;j_1) = -\,[(j+\tfrac{5}{2})/(2j+1)]^{1/2},$$

while for the lower state $T=1$.

As the total intensities for the transitions from a given j_k-level in the upper state to each of the σ-levels in the lower state are here not equal, we give the expressions for all twelve branches.

P-branch $j'=j+1$

$j_1 \rightarrow \sigma_1 \sim D^2[(2j-1)(2j-3)^2/32(j+1)(2j+1)]$; $j_1 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j+5)/32(j+1)]$

$j_2 \rightarrow \sigma_1 \sim D^2[(2j-1)(2j-3)(2j+5)/32(j+1)(2j+1)]$; $j_2 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j-3)/32(j+1)]$

Q-branch $j'=j$

$j_1 \rightarrow \sigma_1 \sim D^2[(2j+5)(2j-3)^2/32j(j+1)]$; $j_1 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j+3)(2j+5)/32j(j+1)]$

$j_2 \rightarrow \sigma_1 \sim D^2[(2j-3)(2j+5)^2/32j(j+1)]$; $j_2 \rightarrow \sigma_2 \sim D^2[(2j-1)(2j-3)(2j+3)/32j(j+1)]$

R-branch $j'=j-1$

$j_1 \rightarrow \sigma_1 \sim D^2[(2j-3)(2j+3)(2j+5)/32j(2j+1)]$ $j_1 \rightarrow \sigma_2 \sim D^2[(2j+3)(2j+5)/32j]$;

$j_2 \rightarrow \sigma_1 \sim D^2[(2j+3)(2j+5)^2/32j(2j+1)]$; $j_2 \rightarrow \sigma_2 \sim D^2[(2j-3)(2j+3)/32j]$.

5. ELEMENTARY THEORY OF σ-TYPE DOUBLING

A mathematical method very similar to that used in the preceding part of the paper may be used to demonstrate the existence of "σ-type doubling." Such doubling, as predicted by Hund[1] and Hulthén,[29] and as shown much more fully by Kronig,[30] arises because the molecular rotation removes the degeneracy caused by the identity of the energy for the states $-\sigma$ and $+\sigma$ in a stationary molecule. This hyper-doubling is not to be confused with the coarser spin doubling considered in sections 2–4, and the connection of the present section with the rest of the paper is in the type of mathematics rather than of doubling. The present treatment is not intended to include the interaction between spin and the σ-type degeneracy, and so applies primarily to singlet states. This interaction, which actually greatly influences the σ-doubling, will be considered in a later paper which will use case (a) as the unperturbed system and which will use a more complete perturbation theory better adapted to represent details of molecular structure than the simple "anschaulich" model used in this section. The characteristic feature of the present section is that even though we are calculating σ doubling primarily for case (a) we begin with Hund's case (d) as the unperturbed system. We, however, throughout simplify his case (d) by assuming no spin. Case (d) means that the electronic orbital angular momentum is so loosely coupled to the rest of the molecule that we no longer quantize its component in the direction of the axis of figure, just as in (b)

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[29] E. Hulthén, Zeits. f. Physik, **46**, 349 (1927).

[30] R. de L. Kronig, Ibid., **46**, 814 (1928).

the spin s is no longer bound to this axis. We start calculating from (d) for two reasons: first, it is very easy to do this after the mathematics in the preceding sections, and second, even though a later paper will start with case (a) it is illuminating to calculate perturbations from both (a) and (d) and so pass continuously from one case to the other and vice versa.

The angular momentum vectors are the important factors in rotational distortions, and to represent their secular effect we may suppose the system to consist of two parts: (I) a "core" which is essentially the dumb-bell model of a diatomic molecule without electronic angular momentum and (II) an angular momentum vector k which represents at least qualitatively the angular momentum of the valence electrons. Let us suppose initially that the force field which part I exerts on part II is very nearly central. Then we have Hund's coupling (d) and the squares of the angular momenta of parts I and II are respectively $j_r(j_r+1)$ and $k(k+1)$, while the square of their resultant is $j(j+1)$. We use the notation j_r for the angular momentum of the core stripped of all electronic angular momentum, whereas the number j_k in case (b) included both nuclear and electronic orbital moments of momentum. Now introduce a coupling proportional to the square of the cosine of the angle α between k and the axis of part I. This, of course, destroys the centralness of the field. When this coupling is very tight, the square of the component σ[31] of k in the direction of this axis will have the quantized values $0, 1^2, 2^2, 3^2, \cdots$. Each of these values correspond to a pair of states, because of the possibility that σ be either positive or negative, or, more generally that the wave functions be two independent linear combinations of those for $-\sigma$ and $+\sigma$.[32] With a stationary molecule each constituent of a pair has the same energy $A\sigma^2$, where A is a proportionality factor determining the strength of the coupling introduced above, and our problem is to show that the Coriolis and centrifugal forces due to molecular rotation causes a small splitting of the energies associated with the two members of a pair. The mathematics for doing this is virtually identical with that used in section 2, except that now k rather than s is being bound to the axis of the molecule and that now the coupling energy is taken proportional to $\cos^2\alpha$ rather than $\cos\alpha$. The latter modification is, of course, to give equality of coupling energies between parallel and antiparallel positions and hence the degeneracy of the character associated with σ-type doubling. The matrix elements of $\cos\alpha$ may be obtained from those of $\cos(\sigma_k,s)$ given except for a factor $[A^2\sigma^2 s(s+1)]^{-1/2}$ in Eqs. (16–17) by substituting k for s, j_r for j_k, and also setting $\sigma_k=0$ as the core is without electronic angular momentum. By the rules for matrix multiplication the elements of the coupling energy $Ak(k+1)\cos^2\alpha$ are then

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[31] As we are not considering the spin, we may use the notation σ in place of σ_k.

[32] The values $-\sigma$ and $+\sigma$ correspond to factors in the wave function of respectively the form $e^{-i\sigma\phi}$ and $e^{+i\sigma\phi}$, where ϕ is an ignorable coordinate associated with rotation of the electrons about the axis of figure. However, the wave functions which remove properly the degeneracy in the problem of σ-type doubling turn out to have factors of the form $\cos\sigma\phi$ and $\sin\sigma\phi$, or are thus symmetrical and antisymmetrical combinations of the wave functions for the states $-\sigma$ and $+\sigma$. The writers are indebted to Professor Kemble for first calling this to our attention.

$$
\begin{gathered}
H_p(j_r,j_r')=0,\ j_r'\neq j_r, j_r\pm 2\ ; \qquad H_p(j_r\ ;j_r)=A\left[f(j_r)+f(j_r-1)\right] \\
H_p(j_r,j_r+2)=H_p(j_r+2,j_r)=A\left[f(j_r)f(j_r+1)\right]^{1/2}
\end{gathered}
\tag{40}
$$

with the abbreviation

$$f(j_r)=(j_r+k+j+2)(j_r+k-j+1)(j_r-k+j+1)(-j_r+k+j)/16(j_r+\tfrac{1}{2})(j_r+\tfrac{3}{2}).$$

The expressions H_p and f are functions of n, k, j as well as j_r, but for brevity we do not list n, j, k among the arguments as H is diagonal with respect to these quantum numbers. Precisely the same procedure as was used in deriving Eq. (20) shows that the energy levels W are the roots of the determinant

$$\left|\ H(j_r,j_r')-W\delta(j_r,j_r')\ \right|=0 \tag{41}$$

where the off-diagonal elements are identical with the expressions given in (40), while $H(j_r,j_r)$ equals $H_p(j_r,j_r)+Bj(j+1)$, as we must include the rotational energy of the core as well as the perturbing coupling energy. Here and elsewhere B is an abbreviation for the expression $h^2/8\pi^2I$ (not to be confused with the factor B used in section 1). The indices j_r and j_r' in (41) range from $j+k$ down to $j-k$ if $j>k$ or to $k-j$ if $j<k$. δ is the conventional symbol for an expression which equals unity when its arguments are equal and vanishes otherwise.

The determinant (41) yields an algebraic equation for W which can be solved exactly in the cases $k=\frac{1}{2}$, 1, $\frac{3}{2}$. This equation is respectively cubic and biquadratic for $k=1$ and $k=\frac{3}{2}$, but factors at once.[33] Half integral values such as $\frac{1}{2}$, $\frac{3}{2}$ for k are, of course, impossible if k represents real orbital angular momentum but nevertheless are of interest in showing the contraction of σ-type doubling with increasing σ. Also k could be half integral if it denoted the resultant of the orbital and spin angular momenta, provided they were so firmly coupled as to always form a quantized resultant (i.e., if Hund's interaction 3 is large compared to his 2 and 4; see p. 660 of ref. 1). This proviso is, however, an idealization seldom if ever met, as ordinarily in molecules the correction for the non-centralness of the field is much larger than the width of spin multiplets. The closed solutions for the cases $k=\frac{1}{2}$, 1, $\frac{3}{2}$ are as follows:

$$
\begin{aligned}
&k=\frac{1}{2}, \quad W=\frac{1}{4}A+B\left(j+\frac{1}{2}\right)\left(j+\frac{1}{2}\pm 1\right) \\
&k=1 \quad \begin{cases} W=A+Bj(j+1) \\ W=\dfrac{1}{2}A+B(j^2+j+1)\pm\left[\dfrac{1}{4}A^2-AB+4\left(j+\dfrac{1}{2}\right)^2B^2\right]^{1/2} \end{cases} \\
&k=\frac{3}{2} \quad \begin{cases} W=\dfrac{5}{4}A+B\left(j^2+\dfrac{3}{4}\right)\pm\left[A^2+(2j-3)AB+4j^2B^2\right]^{1/2} \\ W=\dfrac{5}{4}A+B\left(j^2+2j+\dfrac{7}{4}\right)\pm\left[A^2-(2j+5)AB+4\left(j+1\right)^2B^2\right]^{1/2} \end{cases}
\end{aligned}
\tag{42}
$$

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[33] It is readily seen that for $k=3/2$ the first and third columns of the determinant in (41) must be proportional, also the second and fourth. Eq. (41) factors into two parts for any k, as by (40) the determinant in (41) involves no transitions between odd and even values of j_r.

For $A=0$ these formulas of course reduce to $Bj_r(j_r+1)$. Their significance for large A becomes more apparent if we develop the radicals as power series in the ratio[34] $1/\lambda=B/A$, which we may suppose small when the coupling is large and hence nearly type (a); and if in addition we group together the roots which correspond to the same values of k and σ. This is a different grouping than that on the basis of factorization given above. We then find

$$\begin{array}{ll}
\left.k=\frac{1}{2},\ \sigma=\frac{1}{2}\right) & W=\frac{1}{4}A+B\left(j+\frac{1}{2}\right)\left(j+\frac{1}{2}\pm 1\right). \qquad (43)\\
\left.k=1,\quad \sigma=0\ \right) & W=0+B[j(j+1)+2]-4\lambda^{-1}Bj(j+1)+\cdots\\
\left.k=1,\quad \sigma=1\ \right) & W=A+Bj(j+1)+\lambda^{-1}B(2\pm 2)j(j+1)+\cdots\\
\left.k=\frac{3}{2},\ \sigma=\frac{1}{2}\right) & W=\frac{1}{4}A+B\left[j(j+1)+\frac{13}{4}\pm(2j+1)\right]+\cdots\\
\left.k=\frac{3}{2},\ \sigma=\frac{3}{2}\right) & W=\frac{9}{4}A+B\left[j(j+1)-\frac{3}{4}\right]+\frac{1}{2}\lambda^{-1}B\left(3j^2+3j-\frac{9}{4}\right)\\
 & \qquad +\frac{3}{2}\lambda^{-2}B\left[2\left(j-\frac{1}{2}\right)\left(j+\frac{3}{2}\right)\pm\left(j-\frac{1}{2}\right)\left(j+\frac{1}{2}\right)\left(j+\frac{3}{2}\right)\right]
\end{array}$$

Here and elsewhere we for brevity write σ for $|\sigma|$; it is impossible to specify the sign of σ as the Heisenberg resonance blends the states $-\sigma$ and $+\sigma$ (cf. note 32). The first term in the above formulas is, of course, the coupling energy $A\sigma^2$ for a stationary molecule, where σ is half integral rather than integral if k is also. The second term which is of the order B is in each case, except $\sigma=\frac{1}{2}$, equal to $B[j(j+1)-\sigma^2+(k^2+k-\sigma^2)]$, the familiar Kratzer-Kramers-Pauli expression as modified by Born and Oppenheimer[24] to include the secular effect of the component of electronic angular momentum which is perpendicular to the axis of figure in case (a), and whose square has the value $k_{\mathrm{perp}}{}^2=k(k+1)-\sigma^2$ (cf. note 24). The remaining, higher order terms are ordinarily neglected, and are perturbations arising from the periodic part of this perpendicular component. A "σ-type doublet" is formed by energy levels corresponding to the plus and minus signs in (43) for given k and σ. The doublet width is, of course, proportional to the difference between the energy expressions evaluated with the plus and minus signs, and in each case the series development has been carried far enough to bring out this difference. The rotational distortion thus does indeed cause a splitting of the general type predicted by Hund. It is to be noted that the doublet width is in each cause of the order $B(1/\lambda)^{2\sigma-1}=A(1/\lambda)^{2\sigma}$, a result already mentioned in a footnote of Kronig's paper.[30] The variation of the doublet width with j is seen to be approximately as $j^{2\sigma}$ for large j; this, however, is without the spin, which modifies the situation considerably except in singlets. In the

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[34] As we now have coupling proportional to the square rather than first power of the cosine, the constants A and λ have slightly different meanings than in sections 2–4 but we do not change the notation because their mathematical roles in series developments, etc.,are virtually the same as before.

particular case $\sigma=\frac{1}{2}$, the doubling is of the same order B as the ordinary Kratzer rotational energy intervals, and so here the (a) type coupling always gives way to (d). In the case $\sigma=1$, the correction term of order $\lambda^{-1}B$, which gives the doubling, is proportional to $j(j+1)$, and so has the same effect as altering slightly the moment of inertia.

Correlation of values of j_r and σ. Although, barring $\sigma=\frac{1}{2}$, the levels coincide in pairs in the limit $\lambda=\infty$, members of such pairs pass adiabatically as the ratio $\lambda=A/B$ is gradually decreased, over into levels of distinctly different energy in the limit $A=0$. Using the same procedure as in the correlation given in Eqs. (28, 29) the adiabatic correlation is found by examination of the roots (41) to depend on the sign of A and to be as follows

$$A>0\begin{cases} k=1) & j_r=j-1\rightarrow\sigma=0\,; \qquad j_r=j,\, j+1\rightarrow\sigma=1 \\ & \text{except that when } j=0,\ j_r=1\rightarrow\sigma=0 \\ k=\dfrac{3}{2}\Big) & j_r=j-\dfrac{1}{2},\ j-\dfrac{3}{2}\rightarrow\sigma=\dfrac{1}{2}\,; \qquad j_r=j+\dfrac{1}{2},\ j+\dfrac{3}{2}\rightarrow\sigma=\dfrac{3}{2} \end{cases}$$

$$\text{except that when } j=\frac{1}{2},\ j_r=1,\ 2\rightarrow\sigma=\frac{1}{2}$$

$$A<0\begin{cases} k=1) & j_r=j+1\rightarrow\sigma=0\,; \qquad j_r=j,\, j-1\rightarrow\sigma=1 \\ k=\dfrac{3}{2}\Big) & j_r=j+\dfrac{1}{2},\ j+\dfrac{3}{2}\rightarrow\sigma=\dfrac{1}{2}\,; \qquad j_r=j-\dfrac{1}{2},\ j-\dfrac{3}{2}\rightarrow\sigma=\dfrac{3}{2} \end{cases}$$

Combination relations. The correlation relations permit us to use formally the quantum number j_r instead of σ even in the limiting case (a). Let us call an energy level of type x or type y according as j_r+k is even or odd. Then in the limit $A=0$ (case d), the only possible transitions are those which join an x level and a y level; i.e., two x (or y) levels do not combine. This follows since in (d) the motion of the "core" (part I) and the motion of the valence electrons (part II) connected with the vector k are independent except that together j_r and k form the resultant j. Hence in (d) a fixed electrical moment mounted along the axis of the core will obey the selection rules $\Delta j_r=\pm 1$, $\Delta k=0$; the transition $\Delta j_r=0$ being absent since the core is non-gyroscopic, and jumps in k being absent because with no coupling the core does not experience any of the frequencies connected with the vector k. Similarly in (d) an electrical moment associated with the motion of the valence electron will obey the rules $\Delta k=\pm 1$, $\Delta j_r=0$; the former because the field which the core exerts on the valence angular momentum is assumed perfectly central in case (d), and the latter because of the absence of coupling with the axis of the core. Hence, regardless of whether we ascribe the electrical moment to the core or to the valence electrons, the elements of the moment q_d in case (d) are always of the form $\Delta(j_r+k)=\pm 1$, and hence give only combinations between an x and a y level. Now when coupling is introduced, the moment in case (a), or in any case intermediate between (a) and (d), is the matrix $q = Sq_dS^*$, where S is the transformation matrix whose elements are obtained by solving the system of linear equations connected with the determinant (41) (cf. Eq. (18)). Now the elements of S are all either of the form $x \rightarrow x$ or $y \rightarrow y$. This follows since the system of linear equations for determining S is separable into two independent systems involving only even or only odd values of j_r, inasmuch as the elements of the Hamiltonian function H are by (40) all of the form $H(j_r, j_r)$ and $H(j_r, j_r \pm 2)$. Combining the information which we have obtained about q_d and about S, and using the rules for matrix multiplication, we see that the only elements in q even in the general case are those which involve a transition from an x to a y level, or vice versa. Now the two members of a σ-type doublet are respectively x and y states, and further the x state is alternately the upper or lower level as j is successively increased by unity. This is verified directly up to $k = \frac{3}{2}$ by the correlation given above, and examination of the general behavior of the roots leaves little doubt but that this holds also for larger k values. We thus have the combination rules predicted empirically by Mulliken[35] and especially Hulthén[29] and explained by Kronig[30] from the symmetry properties of the Schroedinger wave function. We will not attempt to illustrate how these combination relations apply to transitions between particular types of spectral terms, as this is nicely covered by the diagrams in Hulthén's or Kronig's paper. Although Kronig neglected the perturbing effect of the component of electronic angular momentum perpendicular to the axis of figure in case (a), the present work shows that the combination relations hold even without this omission, and throughout the range from (a) to (d). Professor Kramers informs us that a similar result on the generality of the combination rules has been obtained by a different method in unpublished work of Wigner. We must emphasize that in deriving these relations we have made no effort to adequately take account of the spin, which will be considered in a later paper,[36] and conceivably the spin influence explains why combinations between two x or two y levels are apparently sometimes found experimentally.

Department of Physics,
University of Minnesota,
June 1, 1928.

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[35] R. S. Mulliken, Phys. Rev. **28**, 1202 (1926).

[36] Abstract on p. 327 of this issue.