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ON σ-TYPE DOUBLING AND ELECTRON SPIN IN THE SPECTRA OF DIATOMIC MOLECULES

By J. H. Van Vleck

Abstract

1. The distortion due to molecular rotation causes the width of a spin multiplet to depend on j, and tends to uncouple the spin axis from quantization relative to the axis of figure, thus bringing about a gradual passage from Hund's case (a) to (b). Another rotational effect is the "sigma-type doubling" of spectral lines due to removal of the degeneracy associated with the equality in energy of left- and right-handed axial rotations in stationary molecules. The present paper treats these two effects, especially their interrelation.

2. As a needed mathematical preliminary we calculate the *perturbing matrix elements* due to the components of angular momentum perpendicular to the figure axis, which are neglected in the usual treatment of the rotating molecule as a symmetrical top. This calculation would be similar to Kronig's and Wigner and Witmer's were it not for inclusion of the spin. This is handled by Pauli's scheme of two wave functions per electron, especially his method of transforming them from one Cartesian system to another by the Cayley-Klein parameters. The results also hold with Dirac's "quantum theory of the electron," as Dirac's quartet of wave functions transform under a rotation like two independent Pauli pairs. Although the orbital and spin angular momentum operators look superficially different, it is shown that their gyroscopic effects enter additively as commonly supposed, and that in the first approximation the effect of the spin is to make the rotational energy (except for an additive constant) that of the symmetrical top with $\sigma_l+\sigma_s$ in place of σ_l.

3. Neglect of the relatively small sigma-doubling yields identically the formulas for the *rotational distortion of spin multiplets* which Hill and Van Vleck obtained by a different, alternative method that used Hund's case (b) rather than (a) as the unperturbed system.

4. *Singlet P states* should exhibit a sigma doubling proportional to $j(j+1)$ and D states ordinarily a negligible doubling. Our technique of calculation differs slightly from that of Kronig, who obtained a similar result for singlet spectra (as did Hill and V. V. with a simple model), in that the degeneracy is removed in the final rather than in the initial approximation.

5. In *^2P states* the spin profoundly modifies the sigma doubling. In case (b) both spin components should exhibit equal doublings proportional to $j_k(j_k+1)$, but in case (a) the $P_{3/2}$ sigma doubling should be negligible, but the $P_{1/2}$ fairly large and proportional to $j+1/2$. Formulas are developed for the sigma-doublet width which apply throughout the range between (a) and (b). The pronounced doubling of the $P_{1/2}$ component in case (a) is due to a rather complicated superposition of the rotational distortion on the magnetic coupling between the components of spin and orbital angular momentum which are perpendicular to the axis of figure.

6. *^2S states.* A similar superposition explains the so-called "rho-type doubling" in ^2S states whereby levels of like j_k but unlike j differ by small amounts proportional to $j_k+1/2$. This explanation differs from the usual interpretation of this doubling as due to magnetic moment developed by orbital motions, and seems to give a slightly larger effect.

7. *^3P states.* In case (b) all three components should have equal doublings proportional to $j_k(j_k+1)$ but in (a) the P_0 and P_1 doublings should be respectively independent of j and proportional to $j(j+1)$, while the P_2 is negligible. The large

splitting of the P_0 component, whose exceptional behavior is due to its having $\sigma=0$, is due largely to magnetic action effective even in a stationary molecule, and so has a different origin than the usual sigma doubling due to rotational distortion.

8. *A summary and comparison with experimental data* taken from Mulliken's following paper are finally given. There is a striking agreement between theory and experiment on the type of variation with j in the various cases, especially the asymmetrical behavior of the various multiplet components in case (a). The theoretical orders of absolute magnitude are also confirmed, as evidenced by the reasonable values of the frequencies which must be assumed to give the observed separations.

I. INTRODUCTION[1]

STATIONARY MOLECULES. To calculate the electronic, though not of course the rotational and vibrational, levels of a diatomic molecule one can, to a first approximation suppose the nuclei at rest. This has been shown by Born and Oppenheimer.[2] Such a fictitious molecule with fixed nuclei we term stationary. Its "parallel" components of orbital and of spin angular momentum ordinarily have quantized values σ_l and σ_s. We throughout measure angular momentum in multiples of the quantum unit $h/2\pi$, and also for brevity we always speak of the "parallel" or "perpendicular" component when more explicitly we mean the component which is parallel or perpendicular to the axis of figure connecting the nuclei. (Unless otherwise stated, it is supposed that the nuclei are far enough apart so that the resultant field which they together exert on the electrons departs appreciably from central character. If this "non-centralness," as we shall call it, were not large compared to the magnetic interaction, only the sum $\sigma=\sigma_l+\sigma_s$, rather than σ_l and σ_s individually, would be quantized.) Two features of stationary molecules which are of particular importance for the present paper are the following: (1) with given σ_l different values of the quantum number σ_s generate a "spin multiplet," which arises from the so-called magnetic interaction between the spin and orbital angular momenta. (2) The energy is invariant if the signs of both σ_l and σ_s are simultaneously reversed, which merely converts a left into a right-handed rotation about the axis of figure, or vica versa. The energy levels $+\sigma_l, +\sigma_s$ and $-\sigma_l$, $-\sigma_s$ are thus a degenerate pair.

Rotating molecules. Besides introducing primarily the familiar rotational and vibrational energies, the motion of the nuclei modifies the effects (1) and (2), as first suggested by Hund.[3] The study of these modifications is the purpose of this paper. As regards (1), the energy due to magnetic interaction is no longer the same as in a stationary molecule, but depends on the amount of rotation j. This is the phenomenon of the rotational distortion of spin multiplets, which was treated in the old quantum theory by Kemble.[4] If this distortion is large, the parallel component of spin angular momentum

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[1] A preliminary account of the present paper was given in abstract 36 of the June 1928 program of the American Physical Society (Phys. Rev. **32**, 327, 1928).

[2] Born and Oppenheimer, Ann. der Physik **84**, 457 (1927).

[3] F. Hund, Zeits. f. Physik **36**, 657 (1926); **42**, 93 (1927).

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

no longer has a quantized value σ_s. Instead in the limit of negligibly weak magnetic interaction compared to rotation, which is Hund's case (b), the orbital electronic angular momentum is compounded with that due to nuclear motion to form a resultant j_k, and then j_k and s are compounded to form a resultant j. The other limiting case of relatively strong magnetic interaction, where the parallel component of s is quantized, constitutes Hund's case (a). (See diagrams, p. 253 of ref. 5). As regards (2), it is found that the degeneracy associated with the pair of states $+\sigma_l$, $+\sigma_s$ and $-\sigma_l$, $-\sigma_s$ is removed by the rotation. The attendant separation of otherwise coincident energy levels and splitting up of spectral lines constitutes in Mulliken's terminology the phenomenon of "sigma-type doubling," and is not to be confused with the much coarser spin doubling found in molecules having $s=1/2$.

Previous work. After Kemble's[4] ingenious pioneer work in the old quantum theory, Hill and Van Vleck[5] calculated formulas for the rotational distortion of spin multiplets in the new quantum mechanics, using Hund's case (b) as the unperturbed system. Their paper will be referred to as "Hill and V. V." Its last section gave an elementary treatment of sigma-type doubling in singlet spectra, using Hund's case (d) as the initial system. By (d) is meant that the non-centralness is so small compared to rotational distortion that not even the parallel component of orbital angular momentum is quantized. The present paper uses (a) rather than (b) or (d) as the original system from which perturbations are figured. In the problem of multiplet distortion this use of (a) simply furnishes an alternative and about equally good method to that of Hill and V. V., but in the treatment of sigma-doubling it permits a much more accurate representation of the details of the molecular dynamics than did the over-simplified though very convenient model used in Hill and V. V.'s last section. The theory of sigma-type doubling in singlet spectra has also been discussed in two papers by Kronig,[6] and has also been studied by Wigner and Witmer.[7] Kronig's first paper, which was previous to Hill and V. V., demonstrated the possibility of sigma-doubling and developed selection rules, previously formulated empirically by Hulthén,[8] which govern the combinations of the various types of levels. Kronig's second article calculated the magnitude of the frequency separation of the

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[5] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928). This paper used the notation σ_k, k instead of the present σ_l, l. Their choice of arbitrary phases is different from ours and would require insertion of a minus sign in our Eq. (31). With our choice the two elements of the transformation matrix T given in their Eq. (38) would be reversed in sign.

[6] R. de L. Kronig, Zeits. f. Physik, **46**, 814; **50**, 347 (1928). Unless otherwise stated, all references to Kronig's equations, etc., are to his second rather than first paper, and by Kronig symmetry or antisymmetry we mean even or oddness under his transformation (15). The writer is indebted to Professor Kronig for the opportunity of seeing his second manuscript in advance of publication.

[7] E. Wigner and E. E. Witmer, Zeits. f. Physik **51**, 859 (1928), especially footnote, p. 860. To avoid duplication with Kronig they do not publish the details of their calculation of the sigma doubling.

[8] E. Hulthén, Zeits. f. Physik **46**, 349 (1927); also R. S. Mulliken, Phys. Rev. **28**, 1202 (1926).

sigma-doubling components, and also gave a more accurate formulation and more elegant proof of the selection principles than in his first paper. The present article will not attempt to treat these selection rules, but only the doublet widths, as the combining properties of the terms are nicely covered in Kronig's papers, as well as analysed for a simple model by Hill and V. V. The previous work shows that it is indeed possible to divide the levels into two classes x and y (Kronig's "even" and "uneven" terms) such that the only possible transitions are those connecting an x and a y state, so that two x or two y states never combine in the absence of external fields. One sigma-doublet component is, of course, of the x-type and the other of the y, the component of higher energy being alternately x and y as j progressively increases by unity. We show in footnote 9 that the extension of the selection principles to include the electron spin occasions no difficulty.

Kronig's papers did not consider the electron spin, nor did the part of Hill and V. V. on sigma doubling, and an essential feature of the present article is that it treats the theory of sigma-doubling inclusive of spin. This is an important increase in generality, for some of the most striking sigma-doubling phenomena are found in other than singlet spectra, and are influenced by the spin in a very interesting way.

The following section 2 of the present paper is primarily mathematical in character and is fairly distinct in content from the remainder. It consists of the calculation of the matrix elements which are neglected in treating a molecule in Hund's case (a) as a symmetrical top, and which are responsible for both the rotational distortion and sigma-doubling phenomena. To a considerable extent this calculation parallels Kronig's though made independently. It, however, includes the spin, and gives some details, such as are involved in passing from our Eq. (10) to (29), which Kronig omits, but which do not seem trivial. Although the final result (29) of section 2 is vital to later sections, we have tried to make these fairly readable without a thorough perusal of section 2.

Quantum number notation. Our nomenclature is in the main the same as in Mulliken's well known series of papers. The recent Hund-Wigner-Witmer scheme appeared too late to be feasible. The numbers σ_l, σ_s and $\sigma(=\sigma_l+\sigma_s)$

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[9] Although Kronig did not consider the spin, the invariance of the wave equation under a "reflection" such as is embodied in his Eq. (15) and from which he derives the selection rules, still holds even when the Pauli or Dirac spin operators are included. For it is readily seen that the transformation $x=x$, $y=-y$, $z=z$, which is our system of coordinates is equivalent to the ξ, η, ζ, ϕ, part of Kronig's transformation (15) demands the reversal of the sign of the operators s_x, s_z but not s_y, just as it does the reversal of the orbital angular momentum operators $l_x=i^{-1}(y\partial\cdot\cdot/\partial z-z\partial\cdot\cdot/\partial y)$ and l_z but not l_y. Further our Eqs. (9–10) show that the orbital and spin angular momentum operators enter in identically the same fashion in the wave equation, and as we have seen that they both transform in the same way in Kronig's reflection (15) it follows that inclusion of the spin does not destroy the invariance. But with it's inclusion Kronig's number n must signify the total rather than just orbital parallel component of angular momentum, as the total is now what is involved in the symmetrical top. The observed combination of two x or two y levels cannot be attributed to the spin as conjectured by Hill and V. V., and is presumably due to perturbing external fields.

measure respectively the parallel components of orbital, spin, and total electronic angular momentum. Molecular spectral terms are classed of the S, P_i, D_i, F_i type according as $\sigma_l=0, 1, 2, 3$. The value of the subscript i is that of σ and fixes the multiplet component. j and j_k measure the total angular momentum of the entire molecule, respectively inclusive and exclusive of spin. (j_k is used only in Hund's case b.) The magnetic quantum number m quantizes the component of j in the direction of an axis z' fixed in space. s is the spin quantum number which determines the spin angular momentum and has the values 0, 1/2, 1, . . . in singlet, doublet, triplet . . . spectra. l is roughly equal to the orbital electronic angular momentum, which is constant only if the non-centralness is negligible. Unlike the recent Hund-Wigner-Witmer scheme, this l does not include the essentially nuclear contribution due to molecular rotation. v is the vibrational quantum number, and n denotes the totality of electronic quantum numbers other than the σ's. We throughout use the letter B to denote the expression $h^2/8\pi^2Mr.^2$ All symbols written in bold-face type in section 2 are operators, and in later sections are vectors.

2. Calculation of the Perturbing Matrix Elements

Stationary Molecules. We suppose the reader familiar with Pauli's[10] scheme of representing the spin in a system of f electrons by means of 2^f wave functions

$$\begin{gathered}\Phi_{\alpha_1\cdots\alpha_f},\ \Phi_{\beta_1\alpha_2\cdots\alpha_f},\ \Phi_{\alpha_1\beta_2\cdots\alpha_f},\ \cdots,\ \Phi_{\alpha_1\alpha_2,\cdot\beta_f},\\ \Phi_{\beta_1\beta_2\alpha_3\cdots\alpha_f},\ \cdots,\ \Phi_{\alpha_1\cdots\alpha_{f-2}\beta_{f-1}\beta_f},\ \cdots,\ \Phi_{\beta_1\beta_2\cdots\beta_f}.\end{gathered} \tag{1}$$

The subscripts α_k and β_k correspond to the spin axis of the kth electron being quantized respectively parallel and antiparallel to the z-axis, which we throughout suppose to coincide with the axis of figure of the molecule. If a solution could be obtained in which each individual spin axis was quantized separately relative to the z-axis, only one of the wave functions (1) would need to be different from zero, but usually the magnetic interaction between the spins and the orbital angular momentum makes this impossible, and so requires 2^f simultaneous wave functions (1), the square of the modulus of any one of which can be regarded as the probability of the corresponding orientation of the spin axes. A stationary molecule will have 2^f simultaneous wave equations of the form

$$(\boldsymbol{H}_0 - W_0)\Phi_{i_1\cdots i_f} = 0 \quad \text{with} \quad i_k=\alpha_k \quad \text{or} \quad \beta_k. \tag{2}$$

where $\boldsymbol{H}_0$ is an operator function of the coordinates $x_1, \cdots, y_1 \cdots z_1 \cdots z_f$ of the f electrons, and also of the Pauli spin operators $\mathbf{s}_{1x} \cdots$, $\mathbf{s}_{1y} \cdots$, $\mathbf{s}_{1z} \cdots \mathbf{s}_{fz}$ corresponding to the x, y, z, components of angular momentum of the various electrons. These operators have the following properties:

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[10] W. Pauli, Jr., Zeits. f. Physik **43,** 601 (1927), especially p. 620 ff. Our spin operators (3) differ by a factor 1/2 from Pauli's, as his unit of angular momentum is $h/4\pi$.

$$\begin{aligned}
&\mathbf{s}_{kx}\Phi_{\alpha_1\cdots\alpha_k\cdots}=\tfrac{1}{2}\Phi_{\alpha_1\cdots\beta_k\cdots}, && \mathbf{s}_{ky}\Phi_{\cdots\alpha_k\cdots}=-\tfrac{1}{2}i\Phi_{\cdots\beta_k\cdots},\\
& && \mathbf{s}_{kz}\Phi_{\cdots\alpha_k\cdots}=\tfrac{1}{2}\Phi_{\cdots\alpha_k\cdots}\\
&\mathbf{s}_{kx}\Phi_{\cdots\beta_k\cdots}=\tfrac{1}{2}\Phi_{\cdots\alpha_k\cdots}, && \mathbf{s}_{ky}\Phi_{\cdots\beta_k\cdots}=+\tfrac{1}{2}i\Phi_{\cdots\alpha_k\cdots},\\
& && \mathbf{s}_{kz}\Phi_{\cdots\beta_k\cdots}=-\tfrac{1}{2}\Phi_{\cdots\beta_k\cdots}\cdot
\end{aligned}\qquad(3)$$

The inter-nuclear distance r will also be involved as a parameter in $\boldsymbol{H}_0$. To include explicitly the coordinate arguments, usually omitted for brevity, we would thus write the first wave function, for instance, of (1), as $\Phi_{\alpha_1\cdots\alpha_f}(x_1,\cdots,y_1,\cdots,z_1,\cdots,z_f,\mathrm{r})$.

Rotating molecules. The wave equations for an actual molecule with moving nuclei are[11]

$$\left[\boldsymbol{H}_0-\frac{h^2}{8\pi^2Mr^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\cot\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\theta^2}+\operatorname{cosec}^2\theta\frac{\partial^2}{\partial\omega^2}\right)-W\right]\psi_{i_1'\cdots i_f'}=0$$

$$(i_k'=\alpha_k' \text{ or } \beta_k')\qquad(4)$$

where θ and ω are the polar and azimuth angles specifying the position of the axis of figure relative to a fixed coordinate system x', y', z', and where M is the "reduced mass" $M_1M_2/(M_1+M_2)$ of the nuclei. On the other hand $\boldsymbol{H}_0$ is most readily expressed in terms of the x, y, z reference system which has the z axis parallel to the axis of figure, and which hence travels with the nuclei. $\boldsymbol{H}_0$ is, of course, the same function of these moving coordinates, and related operators, as in (2). It would, of course, also be possible to express $\boldsymbol{H}_0$ in the fixed reference system, but then $\boldsymbol{H}_0$ would involve θ and ω explicitly inasmuch as the axis of figure is in general obliquely located in this system, and its position is involved in the potential energy binding the electrons to the nuclei. We suppose the mutual potential energy $Z_1Z_2e^2/r$ of the nuclei incorporated in $\boldsymbol{H}_0$ and hence it does not appear explicitly in (4). Without loss of generality we may suppose the x axis to lie in the $x'y'$ plane. Then the moving and fixed axes are connected as follows

$$\begin{gathered}
x=y'\cos\omega-x'\sin\omega,\quad y=z'\sin\theta-(x'\cos\omega+y'\sin\omega)\cos\theta\\
z=z'\cos\theta+(x'\cos\omega+y'\sin\omega)\sin\theta.
\end{gathered}\qquad(5)$$

Following Born and Oppenheimer,[2] also Kronig,[6] but with the generalization to include spin, we now seek approximate solutions of the form $\psi=\Phi\chi(r,\theta,\omega)$ where $\Phi(x_1\cdots,z_f)$ is what we shall term an "internal" wave function, i.e. a solution for the stationary molecule, and χ is a function of the nuclear coordinates alone. In performing the explicit differentiation with respect to the polar coordinates in (5), Φ must be regarded as a function

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[11] The origin of all coordinate systems we suppose to be at the molecule's center of mass, which we assume is at rest. We thus neglect the molecule's translational energy, which enters in a trivial additive fashion. Also we neglect the difference between the center of mass of the molecule and of the nuclei. The inclusion of this difference would add only small terms of the order m/M times the ordinary rotational and vibrational energies, where m is the mass of an electron.

of r, θ, ω as this differentiation is to be performed under the assumption that the electronic coordinate axes are fixed in space, and by (5) the transformation from the moving axes used in (1–2) to fixed axes will cause the entrance of θ, ω.

It is particularly to be noted that in (4) we use a set of subscripts involving the α's and β's rather than α's and β's. This is to indicate that we are using an x', y', z' rather than x, y, z system of reference for the Pauli wave functions, . . . i.e. referring the quantization of the spin relative to the fixed rather than moving system. This is, of course, necessary because (4) presupposes a fixed system of reference. It is thus necessary to transform our spin solution from the α, β to the α', β' system. Without this transformation we would neglect entirely the gyroscopic effect of the spin on the molecular rotation. The desired transformation is accomplished by means of the Cayley-Klein parameters and is explained in Pauli's paper. Pauli's angles Φ, θ are the same as $-(\omega+\frac{1}{2}\pi)$, $-\theta$ in our system and his third Eulerian angle Ψ is zero, as we suppose the x axis to fall in the x' y' plane. He formulates the transformation scheme for one electron, but the extension to any number furnishes no difficulty, as there is a simple superposition of the coefficients for the individual electrons, as already given by Neumann and Wigner.[12] The generalized Pauli transformation scheme, with one minor correction which appears necessary,[13] is

$$\Phi_{i_1'\cdots i_f'}=\sum_{i_1\cdots i_f} A(i_1'\cdots i_f';i_1\cdots i_f)\Phi_{i_1\cdots i_f}(x_1,\cdots,y_1\cdots,z_1,\cdots,z_f) \tag{6}$$

where the summation extends over the two values α_k and β_k for each i_k, and

$$A(i_1\cdots i_f';i_1\cdots i_f)=A(i_1';i_1)A(i_2';i_2)\cdots A(i_f';i_f) \tag{7}$$

with

$$\begin{aligned} &A(\alpha_k';\alpha_k)=\cos\tfrac{1}{2}\theta e^{-i\Omega/2}, && A(\alpha_k';\beta_k)=-i\sin\tfrac{1}{2}\theta e^{-i\Omega/2} \\ &A(\beta_k';\alpha_k)=-i\sin\tfrac{1}{2}\theta e^{i\Omega/2}, && A(\beta_k';\beta_k)=\cos\tfrac{1}{2}\theta e^{i\Omega/2}. \end{aligned} \tag{8}$$

Ω is an abbreviation for $\omega+\frac{1}{2}\pi$. By means of (6–7–8) the differentiation of the internal wave function with respect to ω and θ may now be performed. Thus

$$\frac{\partial\Phi'}{\partial\omega}=\sum_{k=1,\cdots,f}\left(\frac{\partial x_k}{\partial\omega}\frac{\partial}{\partial x_k}+\frac{\partial y_k}{\partial\omega}\frac{\partial}{\partial y_k}+\frac{\partial z_k}{\partial\omega}\frac{\partial}{\partial z_k}\right)\Phi'-\frac{1}{2}i\Phi'\sum c_k'$$

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[12] J. V. Neumann and E. Wigner, Zeits. f. Physik **47**, 203; **49**, 73 (1928).

[13] It is necessary to interchange Pauli's S and S^{-1}. In other words the coefficients in his development (12a) of the ψ''s in the ψ's are S_{11}, S_{12}, S_{21}, $S_{22}=\alpha, \gamma, \beta, \delta$, rather than the inverse $\alpha^*, \beta^*, \gamma^*, \delta^*$. It is easily verified that without this correction the matrices which he defines at the bottom of p. 609 do not transform in the fashion (11), p. 612, from one coordinate system to another. Apparently the reason for the modification is that Ss_zS^{-1} gives the elements of s_z in the α', β' system rather than s_z' in the α, β system. The same correction is apparently needed in other literature, though not in Darwin's paper[28] on Dirac's theory, which has the same modification as ours.

where c_k' equals $+1$ or -1 according as i_k' equals α_k' or β_k', and where we have for brevity written Φ' for $\Phi_{i_1'\cdots i_f'}$. The first right-hand term results because by (5) the arguments $x_1, \cdots, z_f$ of Φ involve ω and the second term results from the dependence of the coefficients in the expansion (6) upon ω. This second term can be simply expressed by means of the Pauli spin operators, as by (2) $\frac{1}{2}\Phi'\Sigma c_k' = \sum \mathbf{s}_{zk}'\Phi'$ where $\mathbf{s}_{zk}'$ is similar to $\mathbf{s}_{zk}$ except that it refers to the primed system. If we use (5) and the relation $\mathbf{s}_{zk}' = \mathbf{s}_{zk}\cos\theta + \mathbf{s}_{yk}\sin\theta$ we find that

$$\partial\Phi'/\partial\omega = -i(\boldsymbol{P}_z\cos\theta + \boldsymbol{P}_y\sin\theta)\Phi'$$

with

$$\boldsymbol{P}_z = \sum_{k=1,\cdots,f}\left[-i(x_k\partial\cdot\cdot/\partial y_k - y_k\partial\cdot\cdot/\partial x_k) + \mathbf{s}_{z_k}\right] \tag{9}$$

and analogous definitions of $\boldsymbol{P}_x$ and $\boldsymbol{P}_y$. The operator $\boldsymbol{P}_z$ corresponds to the total combined orbital and spin electronic angular momentum about the z-axis, i.e., the axis of figure.

In like manner it is easily seen that $\partial\Phi'/\partial\theta = -\mathrm{i}\boldsymbol{P}_x\Phi'$, and consequently the complete wave equations (4) become

$$\begin{aligned}\Bigg\{H_0 - \frac{h^2}{8\pi^2 M}\frac{1}{r^2}\Bigg[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \cot\theta\left(\frac{\partial}{\partial\theta} - i\boldsymbol{P}_x\right) + \left(\frac{\partial}{\partial\theta} - i\boldsymbol{P}_x\right)^2 \\ + \operatorname{cosec}^2\theta\left(\frac{\partial}{\partial\omega} - i\sin\theta\boldsymbol{P}_y - i\cos\theta\boldsymbol{P}_z\right)^2\Bigg] - W\Bigg\}\psi_{i_1'}\ldots = 0.\end{aligned} \tag{10}$$

Here in the differentiations with respect to θ and ω, only the explicit dependence of Ψ on θ, ω is to be considered, and not the implicit effects resulting from the appearance of these angles in the transformation from the moving to the fixed system. In case $\Psi = \Phi\chi(r,\theta,\omega)$ this means that $\partial/\partial\theta$, $\partial/\partial\omega$ operate only on the factor χ, but this restriction on the form of Ψ is unnecessary.

It is possible to construct a solution of the customary form[14]

$$\psi_{i_1'}\ldots = \Phi'(x_1, \cdots, z_f, r)R(r)u(\theta,\phi) \tag{11}$$

if one neglects certain terms, viz.,

$$\frac{h^2 i}{8\pi^2 Mr^2}\left[\cot\theta(\boldsymbol{P}_x - i\boldsymbol{P}_y\boldsymbol{P}_z - i\boldsymbol{P}_z\boldsymbol{P}_y) + 2\operatorname{cosec}\theta\boldsymbol{P}_y\frac{\partial}{\partial\omega} + 2\boldsymbol{P}_x\frac{\partial}{\partial\theta}\right]\psi_{i_1'}\ldots \tag{12}$$

and the "high frequency" part of the expression

$$\frac{h^2}{8\pi^2 Mr^2}\left[(\boldsymbol{P}_x^2 + \boldsymbol{P}_y^2)\Phi' - 2r\frac{\partial\Phi'}{\partial r} - r^2\frac{\partial^2\Phi'}{\partial r^2} - \frac{2r^2}{R}\frac{\partial R'}{\partial r}\frac{\partial\Phi'}{\partial r}\right]Ru \tag{13}$$

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[14] In verifying Eqs. (12–15) it is well to remember that the P operators do not commute among themselves in multiplication, but being functions only of the internal coordinates, do commute with all functions, operator or otherwise, of the variables r, θ, ω. Because the P's do not commute, $\boldsymbol{P}_z\boldsymbol{P}_x\Phi'$ is by (20) $(\sigma\pm1)\boldsymbol{P}_x\Phi'$ rather than $\sigma\boldsymbol{P}_x\Phi'$, with an analogous formula for the y component.

i.e. the part of (13) which vanishes on averaging over the frequencies connected with the "electronic" quantum numbers n, σ. The construction of such an average consists in discarding all matrix elements not diagonal in n, σ. The matrix elements of (12) are entirely of this type, as the elements of P_x, P_y are entirely of the form $\Delta\sigma = \pm 1$ (see Eq. 20 below), while P_z has only $\Delta\sigma = 0$, and hence (12) disappears on averaging over the frequency connected with σ. Now by a well known theorem in perturbation theory, high frequency terms which average to zero contribute only to the second and higher order energies. Hence, if all the internal electronic (including spin) frequencies are really high, i.e. large compared to that of molecular rotation, one can as a first approximation neglect (12) and the fluctuating part of (13). One then finds that the factors in (11) satisfy respectively the differential equations (1) and

$$\left[\frac{h^2}{8\pi^2 M r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + W - W_0(r) - W_{\mathrm{rot}}(r) - W_{13}(r)\right]R = 0 \tag{14}$$

$$\frac{h^2}{8\pi^2 M r^2}\left[\cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2} + \operatorname{cosec}^2\theta\left(\frac{\partial}{\partial\omega} - i\sigma\cos\theta\right)^2\right]u + W_{\mathrm{rot}}u = 0 \tag{15}$$

In writing (15) we have utilized the relation $P_z\Phi' = \sigma\Phi'$, as the total combined orbital and spin angular momentum of the electrons about the axis of figure has the constant quantized value σ in a stationary molecule. The term $W_{13}(r)$ in (14) denotes the time average[15] of (13) over the internal motion of the electrons. As the coefficient of u in (13) involves neither θ nor ω, $W_{13}(r)$ is independent of the rotational quantum numbers j, m, and the effect of $W_{13}(r)$ is very approximately merely the same as changing the internal energy levels W_0 by relatively small amounts $W_{13}(r_0)$.

Eq. (14) is that governing the vibrational excitation of the molecule, which the present paper does not purport to treat. About all we shall need to know is that its solution R falls off in a rapid, exponential fashion from the maximum magnitude of R at $r = r_0$. Here r_0, the "equilibrium internuclear distance," is the value of r which minimizes $W_0(r_0)$, or more accurately in a moving molecule $W_0 + W_{\mathrm{rot}} + W_{13}$. The characteristic values of (1) and (15), also the average of (13), involve r as a parameter, so that $W_0 + W_{\mathrm{rot}} + W_{13}$ plays the rôle of a sort of potential function in (14).

Eq. (15) is that of the "symmetrical top." Reiche and Rademacher,[16] also Kronig and Rabi,[17] have shown that its characteristic values are

$$W_{\mathrm{rot}} = B[j(j+1) - \sigma^2] \qquad (B = h^2/8\pi^2 M r^2) \tag{16}$$

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[15] This time average is, of course, a diagonal element of the matrix which represents (13) for the internal motion of the electrons, The diagonal elements coming from the first and third terms of (13) do not in general vanish, but those coming from the second and fourth terms can be proved equal to zero.

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

[17] R. de L. Kronig and I. I. Rabi, Nature **118,** 805 (1926); Phys. Rev. **29,** 262 (1927).

The energy levels (16) were also derived yet earlier by Dennison[18] with matrices. If we use one of the formulas for Jacobian polynomials,[19] the characteristic functions of (15), normalized to unity, are

$$u_{dsp}(t,\omega)=\left[\frac{(d+s+p)!(1+d+s+2p)!}{p!(d+p)!(s+p)!2\pi t^{d}(1-t)^{s}}\right]^{1/2}\frac{d^{p}}{dt^{p}}\left[t^{d+p}(1-t)^{p+s}\right]e^{im\omega} \tag{17}$$

where

$$t=\tfrac{1}{2}(1-\cos\theta),\qquad s=|m+\sigma|,\qquad j=\tfrac{1}{2}(d+s)+p,\qquad d=|m-\sigma|. \tag{18}$$

The quantum numbers j, m, etc. are as explained at the end of section 1.

The derivation of (16) without the electron spins is an old story.[2,6] Our new result is that it is valid with spins, σ now denoting the combined spin and orbital angular momentum about the axis of figure. The reason for this is, of course, that Eqs. (9–10) show that the spin and orbital electronic angular momenta modify the equations of molecular rotation in exactly similar additive fashions. This identity of the spin and orbital gyroscopic effects seems only reasonable, and has commonly been assumed in band spectra without proof. It is, however, perhaps of some interest to have verified this similarity by use of the Pauli spin wave functions, for the spin effects are transformed from the fixed to moving coordinate systems by means of a method of expansion involving the Cayley-Klein parameters, which is at least superficially different from the method of transforming the orbital effects by the simple substitution (5) in the coordinate arguments. (This apparent dissimilarity in the spin and orbital transformations could, however, be removed by using Winger's[12] group theory treatment of rotations.) It is, of course, necessary to give σ, j, m all half-integral values in molecules with an odd number of electrons. This clearly does not affect the analytic character of the t part of the solution, for by (18) s, p, d still remain integral, and so the hypergeometric series encountered in solving (15) still reduces to a Jacobian polynomial for the characteristic values (16). At first sight it appears as though the factor $e^{im\omega}$ with half-integral m in (17) would destroy the single-valuedness of ψ_{i_1}'. . . . However, Eqs. (7–8) show that the explicit expansion (6) of Φ' introduces factors of each term of the form $e^{iq\omega/2}$ where q is an odd or even integer according as is the total number f of electrons. Thus by (11) the appearance of the half-quantum numbers associated with the spin does not destroy the single-valued, analytic character of the wave function, contrary to the impression which is obtained[17] when the simple symmetrical top model is used without investigating the transformation properties of the Pauli wave functions. The persistence of characteristic functions of the form (18) shows that the Hönl-London intensity formulas, ordinarily proved rigorously only for singlets, also apply to multiplet spectra provided the motion is close enough to Hund's ideal case (a) so that the neglected terms (12–13) are unimportant. Otherwise

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

[19] Courant-Hilbert, Methoden der Mathematischen Physik, p. 75, Eq. (55′).

(as in his case b) the "unperturbed" characteristic values and functions (16–17) cease to be good approximations (cf section 3).

We must now seek to take into account the omitted terms (12). This is probably best done by calculating the matrix elements. Doubtless there are readers of the category who have a peculiar abhorence of any mention of the word "matrices," but the perturbation theory even in the purest wave language is substantially equivalent, and the matrix elements can be regarded as simply convenient designations for certain quadratures involving the wave functions which are inevitably encountered, as they are the coefficients of the development of $f\psi$ in a series of orthogonal functions. The neglected part (12) may be regarded as adding a perturbative potential ("Störungsfunktion") whose matrix elements are

$$H_1(n\sigma vj\,;n'\sigma'v'j')=\sum_{i_1'\cdots i_f'}\int\cdots\int\psi^*_{ai_1'\cdots i_f'}f\psi_{a'i_1'\cdots i_f'}dx_1\cdots dz_fr^2drdtd\omega \quad (19)$$

where a denotes the totality of subscripts $n\sigma vjm$, while $f\psi$ is an abbreviation for the entire expression (12). As previously, the sum is over the two values α_k' and β_k' for each i_k', and $\psi_{i_1'}$. has the unperturbed value (11). We throughout suppose each of the factors of (11) normalized to unity, and use the asterisk to denote the conjugate imaginary. As stated in the introduction, the single index n designates all the electronic quantum numbers other than σ, while v is the vibrational quantum number. Although we are now taking into account (12) we continue to neglect the periodic part of (13). We do this as (13) gives exclusively elements which are not only independent of the amount of rotation j, but also are diagonal[20] with respect to σ. Hence the periodic part of (13) is of no interest in the rotational distortion and sigma-doubling effects considered in the present paper.

We shall consider separately, and in order, the effect of integrating in (19) over the electronic or internal coordinates $x_1, \cdots, z_f$ the vibrational coordinate r and the rotational coordinates t, ω. The effect of the internal integration, which is to be construed as including the sum over the various spin wave functions, is to replace the P operators by the matrices $P_q(n\sigma;n'\sigma')$ ($q=x, y$, or z) giving the components of total electronic angular momentum in a stationary molecule. The z-component, as mentioned in the introduction is a diagonal matrix of the form $P_z(n\sigma;\ n\sigma)=\sigma$. The elements of P_x and P_y vanish unless $\sigma'=\sigma\pm 1$, and are of equal absolute magnitude owing to the parity of the two coordinate axes perpendicular to the figure axis. Their phase relations are such that

$$P_x(n\sigma\ ;n'\sigma\pm 1)=\mp iP_y(n\sigma\ ;n'\sigma\pm 1) \quad (20)$$

These are all well-known selection principles connected with quantization

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[20] The diagonality with respect to σ of the matrix elements corresponding to the first term of (13) follows from the phase relations (20). Such diagonality of the remaining part of (13) is an easy consequence of the fact that Φ involves the angle ϕ_1 defined in footnote 21, only through the factor $e^{i\sigma\phi_1}$.

about an axis of symmetry, and are readily established[21] from the fact that there is an ignorable coordinate connected with rotation about such an axis.

The effect of integrating over r is to replace $h^2P_y(n\sigma;\ n'\sigma')/8\pi^2Mr^2$ by

$$(BP_y)(n\sigma v\ ;\ n'\sigma' v')=\int_0^\infty R_{nv}^*[P_y(n\sigma\ ;\ n'\sigma')h^2/8\pi^2Mr^2]R_{n'v'}r^2dr \tag{21}$$

with $B=h^2/8\pi^2Mr^2$, and with an analogous formula for the x component. If the electronic quantum numbers n, σ do not change except for different orientations of the spin, then as the forces exerted by the spin moment are relatively small, the equilibrium internuclear distances will be very nearly[22] the same in the initial and final states, and R_{nv} and $R_{n'}{}_{v'}$ will belong to the same set of orthogonal functions which vanish except in the vicinity of a common maximum point $r=r_0$. This makes (21) very approximately a diagonal matrix with respect to v whose elements are

$$(BP_y)(n\sigma\ ;\ n'\sigma')=\delta(v,v')P_y(n\sigma\ ;\ n'\sigma')B_0,\quad B_0=h^2/8\pi^2Mr_0{}^2 \tag{22}$$

where $P_x(n\sigma;\ n'\sigma')$ and $P_y(n\sigma;\ n'\sigma')$ (which unlike P_z, depend on r) are to be evaluated with $r=r_0$. The expression δ equals unity if its arguments are equal and vanishes otherwise. If the orbital electronic quantum numbers are different in the initial and final states, the equilibrium moments of inertia in these states will differ, and R_{nv} and $R_{n'v'}$ will belong to different sets of orthogonal functions, so that (21) cannot in general be simplified. However, it may happen that the vibrational excitation in the state n is small. Then as first mentioned by Condon[23] in discussing Franck's theory of electron jumps in molecular spectra, the amplitudes associated with

[21] Let ρ_k, z_k, ϕ_k be the cylindrical coordinates of an electron, referred to the axis of figure of the molecule, and let $\gamma_k=\phi_k-\phi_1(k=2,\cdots,f)$. If, first we neglect the spin, then it is easily seen that the internal characteristic functions are of the form $e^{i\sigma\phi_1}f(\gamma_2,\cdots,\rho_1\cdots,z_1,\cdots)$ (cf. Kronig[6]). Without the spin **P** equals **l**, and on shifting to our cylindrical coordinates the differential operators for l_x etc. given in footnote 9, it is found that because of the exponential factor the matrix elements of l_x, l_y vanish unless $\sigma'=\sigma\pm 1$ and that the phase relations are as given by (20). If we now seek to include the spin, we must add the Pauli spin operators to the orbital differential operators to get the total angular momentum operators. The selection rules are then easily proved to remain valid in virtue of the definitions (3) and the fact that if the total angular momentum is conserved, $\Phi_{i_1}\cdots$ involves ϕ_1 through a factor $\mathrm{e}^{i\sigma_l\phi_1}$ where $\sigma_l=\sigma-\frac{1}{2}\Sigma c_k$ with c_k defined as after Eq. (8).

Most of the literature (including the orginal Heisenberg-Jordan paper) has $\pm i$ where we have $\mp i$ in (20). This would mean that in the state σ the wave function had (neglecting spin) a factor $e^{-i\sigma\phi_1}$ rather than $\mathrm{e}^{i\sigma\phi_1}$, which appears legimate only if the momentum operators are defined as $ih\partial\cdots/\partial q$ rather than $h\partial\cdots/i\partial q$ or if the matrix elements are defined as having the asterisk attached to the second rather than first wave function of (19), but these are not the usual conventions such as we use. The formulas for the matrix elements of the spin angular momentum which Pauli gives at the bottom of p. 609 show that his convention on phases is the same as ours, so that (20) applies to both orbital and spin effects (in this connection one must be careful to examine the sign of Pauli's $(\mathrm{s}_y)_{\mathrm{nm}}$ rather than his operator $\mathbf{s}_y$).

[22] Throughout the paper we neglect the slight dependence of the moment of inertia on the spin quantization σ_s, also its dependence, likewise slight, on j due to centrifugal expansion.

[23] E. U. Condon, Proc. Nat. Acad. Sci. **13,** 462 (1927).

transitions to other electronic states n will be appreciable only if they have such large vibrational excitation that $R_{n'v'}$ falls off relatively slowly away from its maximum at $r=r_0'$, and so "overlaps" the sharp peak of R_{nv} at r_0. In such a case one can without much error take the bracketed factor in (21) outside the integration, evaluating it at $r=r_0$, and then (21) simplifies into

$$(BP_y)(n\sigma v\ ;\ n'\sigma'v')=BP_y(n\sigma\ ;\ n'\sigma')a(nv\ ;\ n'v') \tag{23}$$

where the $a(nv;\ n'v')$ are the coefficients of the development of $R_{n'v'}$ in the R_{nv}, i.e., the values of the right side of (21) when the bracketed factor is deleted. Since both the R_{nv} and $R_{n'v'}$ are normalized orthogonal sets, the a's form a unitary matrix, making

$$\sum_{v'}a(nv\ ;\ n'v')a^*(nv''\ ;\ n'v')=\delta(v,v''),\quad a(nv\ ;\ n'v')=a^*(n'v'\ ;\ nv) \tag{24}$$

In view of all the foregoing, Eq. (19) now becomes

$$H_1(n\sigma vj\ ;\ n'\sigma\pm 1v'j')=(BP_y)(n\sigma v\ ;\ n'\sigma\pm 1v')\int\int g(t,\omega)dtd\omega \tag{25}$$

with

$$g(t,\omega)=u^*_{d''s''p''}\left[\frac{1}{t^{1/2}(1-t)^{1/2}}\left((\sigma\pm 1)(1-2t)+i\frac{\partial}{\partial\omega}\right)\pm 2t^{1/2}(1-t)^{1/2}\frac{\partial}{\partial t}\right]u_{d's'p'}$$

where d'', s'', p'' are the values of d, s, p associated by (18) with σ, j, m, and d', s', p' are those associated with $\sigma\pm 1$, j', m'. The integration over ω shows us immediately that $m=m'$. The integration over t is slightly more difficult, but is readily effected if one uses the following relations

$$H_1(n\sigma vj\ ;\ n'\sigma\pm 1v'j')=H_1^*(n'\sigma\pm 1v'j'\ ;\ n\sigma vj) \tag{26}$$

$$\begin{aligned}\frac{dU_{dsp}}{dt}&=\frac{1}{2}\left[\frac{s}{1-t}-\frac{d}{t}\right]U_{dsp}+\left[\frac{(d+s+p)(p+1)}{t(1-t)}\right]^{1/2}U_{d-1s-1p+1}\\&=\frac{1}{2}\left[\frac{s}{1-t}+\frac{d}{t}\right]U_{dsp}-\left[\frac{(p+s)(d+p+1)}{t(1-t)}\right]^{1/2}U_{d+1s-1p}\end{aligned} \tag{27}$$

Eq. (26) merely expresses the Hermitian property, which is to be expected with proper normalization, and halves the number of terms to be calculated. Since the matrices (BP) are surely Hermitian, (26) is obtained by partial integration of (25) without using the special properties (17) of the u's. The relations (27) are identities following from the definition (17), with the notation U for the function $(2\pi)^{1/2}\ ue^{-im\omega}$ which has no factor involving ω[24]. By means of (26–27) the integrand of (25) can be reduced, after integrating over ω, to an expression of the form $CU^*_{dsp_1}U_{dsp_2}$, where C is independent of t but not of d, s, p_1, p_2. In virtue of the orthogonality and normalization of the U's, the integral of such an expression is C when $p_1=p_2$ and

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[24] The factor $(2\pi)^{1/2}$ is included to make U normalized to unity when the normalizing integral is taken over t alone, whereas that for u is to be taken over both t and ω. We suppose the normalization relative to the element of integration dt rather than $\sin\theta d\theta=2dt$.

zero otherwise. The values of p_1, p_2 and the manipulation in the reduction, depend on the particular form assumed by the connecting relations, (17) which is influenced by the signs and relative magnitudes of m and σ. The first and second forms of (27) are respectively useful according as σ is numerically greater or smaller than m. When, however, one shifts back to the σ, j, m notation the result is in all cases (barring a trivial question of sign[25])

$$H_1(n'\sigma vj\ ;\ n'\sigma'v'j')=0 \qquad \text{unless} \qquad \sigma'=\sigma\pm 1, \qquad j'=j \tag{28}$$

$$H_1(n\sigma vj\ ;\ n'\sigma\pm 1v'j)=2(BP_y)(n\sigma v\ ;\ n'\sigma\pm 1v')\left[(j+\tfrac{1}{2}-\bar{\sigma})(j+\tfrac{1}{2}+\bar{\sigma})\right]^{1/2} \tag{29}$$

where $\bar{\sigma}$ denotes the mean $\sigma\pm 1/2$ of the initial and final values of σ. This is the final answer, and is essentially similar to Kronig's[6], except for some simplifications resulting from our use of (20), etc. The diagonality with respect to j expressed in (28) could have been suspected from kinematical considerations, as a precession of the entire molecule about the "invariable axis" of total angular momentum such as is associated with the quantum number j will not affect the magnitude of the interaction between the electronic and rotational angular momentum. The complete independence of (29) of the magnetic quantum number m is, of course, due to the arbitrariness of spacial orientation.

Dirac's "quantum theory of the electron." Ostensibly we use throughout Pauli's scheme of two wave functions per electron. According to Dirac's newer "quantum theory of the electron,"[26] there are presumably four wave functions per electron, although the extension of the Dirac theory to systems with more than one electron has yet to be given. It is, however, only reason-

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[25] If the rotational characteristic function is defined in precisely the fashion (17) a minus sign must be inserted before the right hand side of (29) in the domain $m>\bar{\sigma}$. Such a difference is of no consequence, as by examination of (25) it is seen that the sign can be made positive throughout by altering the sign in the definition of some of the characteristic functions. This is legitimate because they have each an arbitrary phase factor of modulus unity. To make the sign positive throughout, as assumed in writing (29), the characteristic functions u' which must be used are $u'=(-1)^\sigma u$ for $m\geqq\bar{\sigma}$ and $u'=(-1)^m u$ for $\bar{\sigma}\geqq m$, where u is defined as in (17). As it is easily seen from (29) that $u_{dsp}(t)=(-1)^p u_{sdp}(1-t)$, it follows that $u'(j,\sigma,m,t)=(-1)^{j+m}\,u'(j,-\sigma,m,1-t)$. In the rotational characteristic functions u'' which Kronig uses he supposes that $u''(j,\ \sigma,\ m,\ t)=(-1)^{j+m+\sigma}\ u''(j,-\sigma,\ m,\ 1-t)$. This implies that $u''=u$ for $\sigma/m\leqq 0$, $u''=(-1)^\sigma u$ for $0\leqq\sigma/m\leqq 1$, $u''=(-1)^m u$ for $\sigma/m>1$. Such a definition inserts a negative sign into the right side of (29) for $\sigma<0$ and with Kronig the right side of (29) changes sign with σ. There is thus agreement with Kronig when the phase factors are considered, and his combination relations, of course, apply when we are careful to discriminate between the symmetric and antisymmetric states. He does not, however, mention these peculiarities of sign in his definition of the characteristic functions.

It is to be noted that (29) does not involve the spacial quantum number m. This is just what we should expect, as the energy cannot depend on spacial orientation in the absence of external fields. If this independence of orientation be accepted at the oustset, it is only necessary to make the calculation for one particular value of m. As Witmer notes in connection with a somewhat different problem, (Proc. Nat. Acad. Sci. 13, 60, 1928) the special case $j=m$ is particularly easy, since here by (18) $p=0$. It is, however, a rather satisfying check to have verified that m does drop out in the general case.

[26] P. A. M. Dirac, Proc. Roy. Soc. **117A**, 610; **118A**, 351 (1928).

able to suppose that an extended theory would possess the following features: (a) the terms representing the kinetic energy of the nuclei enter in the Hamiltonian, at least very approximately, in an additive fashion with the ordinary electrostatic potential energy term,[27] (b) that the transformation cofficients in rotation can be obtained as in Eq. (7) by superposition of those of individual electrons separately, and (c) that operators corresponding to spins of individual electrons are defined as in the one-electron case. The supposition (a), of course, neglects internal spins of the nuclei, but this is presumably a very high order effect still shrouded in obscurity. If one grants these premises, the use of four rather than two wave functions per electron occasions no difficulty in our work, for in a one-electron system each quartet of Dirac wave functions is separable into two pairs such that the members of each pair transform under a rotation independently of the other pair, and in exactly the same fashion as Pauli's two wave functions.[28] Thus by (b) even if we use 4^f rather than 2^f wave functions, each one of them in the x', y', z' system is still expressible in the fashion (6) as the sum of only 2^f wave functions in the x, y, z one. The passage from (6) to (10) proceeds as before because according to Dirac the spin angular momentum operators $\mathbf{s}_{xk}$ etc. work independently on each pair of the quartet in just the Pauli fashion. After Eq. (10) there are no modifications worth mentioning except that in the formula (19) for the matrix elements we must, of course, (unlike Eq. 6) sum over all 4^f wave functions. The final formulas (16–17) (28–29) ensue, and so all the results of the present paper hold with the Dirac theory.

3. Rotational Distortion of Spin Multiplets

In a stationary molecule the motion of the spin angular momentum $\mathbf{s}$ is very approximately that of a regular precession about the axis of figure. Following Heisenberg and Jordan's work[29] on the Zeeman effect, we may then take the non-vanishing matrix components of s to be

$$\pm i s_x(\sigma_s\sigma_s\pm 1)=s_y(\sigma_s\,;\,\sigma_s\pm 1)=\tfrac{1}{2}[s(s+1)-\sigma_s(\sigma_s\pm 1)]^{1/2} \qquad s_z(\sigma_s\,;\,\sigma_s)=\sigma_s \quad (30)$$

Actually, as will be shown on p. 492, the influence of the perpendicular component of orbital angular momentum distorts the precession and hence formulas (30), but this is a higher order effect important only in the later sections on sigma-doubling. In considering the effect of the molecular rotation on the spin motion, we need use only the spin part of the angular momentum P_y in (29). Actually $P_y=s_y+l_y$ but very approximately the terms coming from the orbital part l are independent of σ_s and have $\Delta\sigma_l=\pm 1$

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[27] The writer is indebted to Dr. J. R. Oppenheimer for this suggestion regarding the additivity of the nuclear and potential energy terms.

[28] Cf. C. G. Darwin, Proc. Roy. Sec. **118A**, 656 (1928).

[29] Heisenberg and Jordan, Zeits. f. Physik **37**, 263 (1926). They applied to the spin the formulas for angular momentum first derived in the following reference. Besides the reversal of the sign of i explained in note 21, we use x,y axes differing by 90° from Heisenberg and Jordan's, so that our x,y are the same as their $y, -x$. We do this because it is convenient for the elements of the y component to be real in our work.

rather than $\Delta\sigma_s = \pm 1$. Using the independence of moment of inertia of spin expressed in (22), we may now consider the perturbation matrix (29) to be

$$H_1(\sigma_s\,;\,\sigma_s\pm 1) = B[j(j+1)-(\sigma_l+\sigma_s)(\sigma_l+\sigma_s\pm 1)]^{1/2}[s(s+1)-\sigma_s(\sigma_s\pm 1)]^{1/2} \tag{31}$$

The diagonal elements of the magnetic plus rotational energy are

$$H_0(\sigma_s\,;\,\sigma_s) = f(\sigma_s)+B[j(j+1)-(\sigma_l+\sigma_s)^2]+B[s(s+1)-\sigma_s^2] \tag{32}$$

Here $f(\sigma_s)$ is the ordinary so-called "magnetic energy" of interaction between the spins and orbital angular momentum. Of course f depends on the other electron quantum numbers n, σ_l, besides σ_s, but these are fixed within a multiplet and so not listed as arguments. If the ordinary "cosine-law" of coupling between s and the component of l parallel to the figure axis is applicable, then

$$f(\sigma_s) = A\sigma_l\sigma_s. \tag{33}$$

The second term of (32) gives the ordinary "symmetrical top" rotational energy (16). The third term of (32) is the contribution of s to the mean value W_{13} of the expression (13). As $P_x = s_x + l_x$, the first term of (13) involves s, and from (30) $s_x^2 + s_y^2$ is a diagonal matrix $s(s+1)-\sigma_s^2$, while the average of $s_x l_x$ or $s_y l_y$ is zero, at least with the independence of spin and orbital precessions presupposed by (30). We have discarded the balance of W_{13}, as it is independent of σ_s.

If the frequency of molecular rotation is small compared to the spin multiplet frequency intervals, the energy can be developed as a power series in the ratio $\lambda' = B/A$, then small, of the orders of the molecular and magnetic energies. Well-known perturbation formulas[30] show that then the energy is to terms of the order λ'^2

$$W = H_0(\sigma_s\,;\sigma_s) + \frac{|H_1(\sigma_s\,;\,\sigma_s+1)|^2}{h\nu(\sigma_s\,;\,\sigma_s+1)} + \frac{|H_1(\sigma_s\,;\,\sigma_s-1)|^2}{h\nu(\sigma_s\,;\,\sigma_s-1)}\,\cdot \tag{34}$$

The denominators $h\nu(\sigma_s;\,\sigma_s') = H_0\,(\sigma_s;\,\sigma_s) - H_0(\sigma_s'\,;\,\sigma_s')$ can by (32) be taken as $f(\sigma_s) - f(\sigma_s')$ to an adequate approximation since they enter only in second order terms. The values of the H elements in (34) can immediately be substituted from (31–32). If we then assume (33), the formulas so obtained for the three levels of the triplet case $s=1$ are those already given more explicitly on p. 261 of Hill and V. V. An interesting thing to note is that by (31) the two last terms in (34), which are the corrections for rotational distortion, involve j only through a factor $j(j+1)+C$ where C is independent of j but not of the multiplet component. This means that for any s the effect of rotational distortion is approximately, assuming the coupling always remains nearly type (a), simply to change the constants A' and B' in the conventional formula $A' + B'j(j+1)$ for molecular energy levels. As the

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[30] Born, Heisenberg, and Jordan, Zeits. f. Physik **35**, 587 ff (1926).

constants by which $j(j+1)$ is multiplied in the correction terms of (34) depend on σ_s, A' and B' will have different values in the various multiplet components. Thus the apparent moment of inertia, deduced from experimental values of the constants A' and B' without care to resolve the rotational distortion, i.e. the last two terms of (34) from the first term, may have entirely different values in the various multiplet components, even though the true moment of inertia is very nearly the same. One further point is that regardless of whether the multiplet is "regular" or "inverted" the largest apparent moment of inertia B' always goes with the spin component of largest energy f. Hence comparison of the different values of B' will not tell whether a multiplet is regular or inverted.

It is to be emphasized that (34) is a good approximation only if the rotational distortion, which increases rapidly with j, is so small that Hund's case (a) (explained in the introduction) is a good approximation. An analagous development in $\lambda = 1/\lambda'$, valid instead near Hund's case (b), is given in Eq. (23) of Hill and V. V. In the general intermediate case between (a) and (b) standard matrix transformation theory shows that the energy levels are the roots of the "secular" determinant

$$\left| H(\sigma_s\,;\,\sigma_s') - \delta(\sigma_s\,;\,\sigma_s')W \right| = 0 \qquad \sigma_s, \sigma_s' = -s, \cdots, s \tag{35}$$

which yields an algebraic Eq. [31] for W of order $2s+1$. For the doublet case $s = 1/2$ this reduces to the simple formula[32]

$$W = \tfrac{1}{2}[f(-\tfrac{1}{2}) + f(\tfrac{1}{2})] + B[(j+\tfrac{1}{2})^2 - \sigma_l^2] \pm \tfrac{1}{2}[4B^2(j+\tfrac{1}{2})^2 + \Delta E(\Delta E - 4B\sigma_l)]^{1/2} \tag{36}$$

with ΔE denoting the spin doublet width $f(1/2) - f(-1/2)$ for a stationary molecule. If we assume the "cosine" law (33), which we now see is unnecessary, (36) is identical with Hill and V. V's formula (27) obtained by an entirely different method, in which the unperturbed system had the spin loosely coupled in Hund's fashion (b) and included the rotational rather than magnetic energy in the unperturbed Hamiltonian. In the doublet case the transformation matrix T associated with the determinant (35) can immediately be determined, and the effect of rotational distortion on intensities thereby determined by the familiar matrix formula $q = Tq_0T^{-1}$. The formulas for T are similar[5] to Hill and V. V's Eqs. (37–38) and the original unperturbed case (a) amplitudes q_0 are, of course, the Hönl-London

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[31] It is doubtless possible to establish the general identity of the determinantal Eq. (35) with the corresponding Eq. (20) of Hill and V. V., instead of verifying numerically the agreement, as we do, only in the special cases $s = 1/2$, 1. Perhaps methods similar to those given by Schlapp (Proc. Roy. Soc. **119A**, 313, 1928) would be useful.

[32] Eq. (36) can be derived in a semi-theoretical manner without going through the labor of calculating the perturbing matrix (29) or (31) if we assume the diagonal elements to be given by (32), and if we grant that the off-diagonal elements are linear in B and independent of f. Then in the doublet case the magnitude of the needed perturbing element $H_1(-1/2;\ 1/2)$ is uniquely determined by the requirement that the formula for W yielded by the determinant (35) shall reduce to the well-known result $W = Bj_k(j_k+1) - B\sigma^{l2}$ in the limit $f = 0$ (Hund's case b).

ones given in Eq. (2) of Hill and V. V. The reader is referred to their paper for discussion of the superiority of (36) over the old quantum theory, and especially of intensity relations, including allowance in the latter for the fact that in electronic transitions the magnetic coupling strengths will be different in the initial and final states. As first noted by Mulliken,[33] Eq. (36) reduces rather fortuitously to the old Kramers-Pauli formula when $\Delta E = 2B\sigma_l$. The reader is referred to his paper for comparison of (36) with experiment.

4. Sigma-Type Doubling in Singlet States.

We shall first treat sigma-doubling in states which have zero resultant spin angular momentum and which hence belong to the singlet spectral system. Our procedure is superficially different from Kronig's, as we use an unperturbed solution corresponding to a constant angular momentum σ about the figure axis (i.e. a wave function involving the cyclic angle ϕ, defined in footnote 21 only through a factor $e^{i\sigma\phi_1}$) whereas Kronig uses a wave function which is a linear combination of those corresponding to angular momenta $+\sigma$ and $-\sigma$. In a one electron system this means that Kronig uses sines and cosines where we use exponentials. Kronig's method is probably the more elegant, as by dividing states into two classes which do not combine with each other in the Hamiltonian function he is able at the outset to remove the degeneracy difficulties coming from the identity of energies for $+\sigma$ and $-\sigma$ in the stationary molecule. It is, however, an alternative method, possibly of some interest, to keep as long as possible a solution corresponding to a constant angular momentum of uniform sign relative to the axis of figure. In fact the procedure is illustrative of a perturbation method when degeneracy is encountered only in higher approximations. We shall seek to develop the energy as a power series in $B = h^2/8\pi^2 Mr^2$, as is legitimate if the rotational frequencies are small compared to the internal electronic frequencies of the molecule. To a first approximation, i. e. terms of the order B, there is no difficulty with sigma-type degeneracy, as the perturbing matrix elements given by (29) have only $\Delta\sigma = \pm 1$ and so do not connect the states $+\sigma$ and $-\sigma$ if σ is an integer. We can then use the perturbation theory of non-degenerate systems, which tells us that to a first approximation the perturbing elements (29) have no effect on the energy, owing to the absence of diagonal elements, while the corresponding transformation matrix is $S = 1 + S_1$[34] with

$$S_1(n\sigma vj\,;\,n'\sigma'v'j) = H_1(n\sigma vj\,;\,n'\sigma'v'j)/h\nu(n\sigma vj\,;\,n'\sigma'v'j) \tag{37}$$

where $\sigma' = \sigma \pm 1$ and $h\nu(n\sigma vj;\, n'\sigma'v'j) = H_0(n\sigma vj) - H_0(n'\sigma'v'j)$, while H_1 is

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[33] R. S. Mulliken, Phys. Rev. **32,** 388 (1928).

[34] We write our series development as $1 + S_1 + \cdots$ rather then the more usual $1 + \lambda S_1 + \cdots$. The customary form could, of course, be obtained by multiplying the right side of (29) by λ. This, however, is unnecessary, for although B, being a matrix, cannot be used as an ordinary parameter, nevertheless the power to which its elements are raised identifies the order of approximation.

given by (29). The unperturbed energy H_0 we now and henceforth suppose *inclusive* of the vibrational and ordinary "symmetrical top" rotational energies associated with Eqs. (14–15–16), as well as of the internal energy, whereas in section 2 we used H_0 to denote just the internal energy of a stationary molecule. Use of (37) makes the transformed Hamiltonian

$$S(H_0+H_1)S^{-1}$$

a diagonal matrix only to a first approximation, i. e., if we keep the portion $H_0+S_1H_0-H_0S_1$ which is of order B or lower, and discard the remaining portion,

$$H_0S_1^2-S_1H_0S_1+S_1H_1-H_1S_1+\cdots.$$

To solve the problem to a second approximation we can regard this part as constituting a new perturbation matrix, which we may call[35] $H^{(2)}$, and which, if we do not go beyond B^2, will involve elements of the form $\Delta\sigma=0$ and $\Delta\sigma=\pm 2$. We can now, provided $\sigma>1$, again apply the perturbation theory of non-degenerate systems and find another, superposed, canonical transformation, which will make the Hamiltonian a diagonal matrix to terms of the order B^2. . . . . This process could be repeated indefinitely were it not for the complication that after applying the transformation of order $B^{2\sigma-1}$ we find that when we set up the new perturbing matrix $H^{(2\sigma)}$ of order $B^{2\sigma}$, it will contain "degenerate" elements of the form $H^{(2\sigma)}(n\sigma vj;\, n-\sigma vj)$ connecting states which up to this stage have been of identical energy. The explicit formula for these elements is a bit formidable appearing, but with the aid of conventional perturbation theory is seen to be[36, 37]

$$H^{(2\sigma)}(n\sigma v\,;\, n,\ -\sigma v)$$

$$=\sum_{n'v'n''v''\cdots n^x v^x}\frac{H_1(n\sigma v\,;n'\sigma-1v')H_1(n'\sigma-1v'\,;n''\sigma-2v'')\cdots H_1(n^x,-\sigma+1v^x\,;n,-\sigma,v)}{h^{2\sigma-1}\nu(n\sigma v\,;\,n'\sigma-1v')\nu(n\sigma v'\,;\,n''\sigma-2v'')\cdots\nu(n\sigma v\,;\,n^x,-\sigma+1,\,v^x)} \tag{38}$$

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[35] Our $H^{(2)}, \cdots$ are not the same as Born, Heisenberg and Jordan's $H_2, \cdots$, as our expressions result from applying successive transformations to a Hamiltonian originally of the form H_0+H_1, whereas they consider the more general problem in which the perturbative potential has at the outset terms of higher order $H_2, \cdots$.

[36] In writing (38) and following expressions we assume the given number σ to be positive. This involves no loss of generality, as one end or other of the range $\sigma, \cdots, -\sigma$ under consideration must be positive.

[37] The product in the numerator of an expression such as (38) can be calculated neglecting entirely the sigma-type degeneracy for the "inner levels" $\sigma-1, \cdots, -\sigma+1$. In other words we can use in the numerator the values of the matrix elements which would be obtained without making for each of the inner levels transformations analogous to (42), even though the degeneracy phenomenon is encountered for the inner levels at earlier stages of approximation than for the outer ones. The reason for these statements is that the sigma doubling does not usually appreciably affect the frequencies in the denominator, and a sum of the form $\sum_k a(nk)b(km)$ over a set of degenerate levels k is invariant under a transformation T wholly within the set provided n, m do not belong to the set. (To prove the latter proposition we need only note that $a(nk)=(Ta_0T^{-1})(nk)$ reduces to $(a_0T^{-1})(nk)$ and $b(km)$ to $(Tb_0)(km)$ if m, n are not in the set k undergoing transformation. The desired invariance is then a consequence of $T^{-1}T=1$.)

where the superscript ^{x} is an abbreviation for $2\sigma-1$ primes. Here and henceforth we suppress the index j which is involved in all the elements but which remains constant as they are diagonal in j.

At this stage we must use the perturbation theory for degenerate systems. We need consider only the interaction between a pair of states $n\sigma v$ and $n-\sigma v$, as the interaction of this pair with states outside this pair gives only non-degenerate elements and a contribution to the energy of the order $B^{2\sigma+1}$. Thus the term $W^{(2\sigma)}$ of order $B^{(2\sigma)}$ in the energy is a root of the determinant

$$\begin{vmatrix} H^{(2\sigma)}(n\sigma v\ ;\ n\sigma v)-W^{(2\sigma)} & H^{(2\sigma)}(n\sigma v\ ;\ n-\sigma v) \\ H^{(2\sigma)}(n-\sigma v\ ;\ n\sigma v) & H^{(2\sigma)}(n-\sigma v\ ;\ n-\sigma v)-W^{(2\sigma)} \end{vmatrix}=0 \tag{39}$$

Now

$$H^{(2\sigma)}(n\sigma v\ ;\ n\sigma v)=H^{(2\sigma)}(n-\sigma v\ ;\ n-\sigma v), \tag{40}$$

as up the present stage there has been no discrimination between positive and negative values of σ, since simultaneous alteration of the sign of both the initial and final values of σ in (29) does not change the matrix elements (29) except possibly for phase factors involved in the P's. These phase factors do not affect the energy as this depends only on the absolute value of the matrix elements. Thus the two roots of (39) differ from each other by an amount

$$h\Delta\nu=2\left[H^{(2\sigma)}(n\sigma v\ ;\ n-\sigma v)H^{(2\sigma)}(n-\sigma v\ ;\ n\sigma v)\right]^{1/2}=2\left|H^{(2\sigma)}(n\sigma v\ ;\ n-\sigma v)\right| \tag{41}$$

Eq. (41) shows that the interaction between positive and negative values of σ causes a cleavage of pairs of energy levels which would otherwise coincide. This is the phenomenon of "sigma-type doubling." The width of a doublet is given by (41) to terms of lowest non-vanishing order in B, and the doubling is thus an effect of order $B^{2\sigma}$, as previously found by Kronig.[6] Hence the doubling should be much narrower for D or F than for P terms. In fact only in P terms is it ordinarily discernible. Obviously S states should show no doubling, as with $\sigma=0$ there can be no question of resonance between positive and negative values of σ.

The transformation connected with the determinant (39) "scrambles together" the angular momentum values $+\sigma$ and $-\sigma$, so that it is incorrect to identify one component of a sigma-type doublet with an angular momentum $+\sigma$ about the axis of figure, and the other component with an angular momentum $-\sigma$. Instead in either component this angular momentum continually changes sign, and has the average value zero, but its square is always approximately σ^2. The mathematical basis for these statements is that owing to (40) the transformation matrix[30] associated with (39) has the elements

$$\begin{aligned} S^{(2\sigma)}(n\sigma v\ ;\ n\sigma v)&=S^{(2\sigma)}(n-\sigma v\ ;\ n-\sigma v)=S^{(2\sigma)}(n\sigma v\ ;\ n-\sigma v) \\ &=-S^{(2\sigma)}(n-\sigma v\ ;\ n\sigma v)=(1/2)^{1/2} \end{aligned} \tag{42}$$

The transformation given by (42) is superposed on the transformation $S=1+S_1+S_2+\cdots$ introduced in the first $2\sigma-1$ orders of approximation made prior to the encountering of the degeneracy. However S_1, S_2, $\cdots S_{2\sigma-1}$ become infinitesimal when B does, whereas the elements (42) retain finite values. The new wave functions $\Psi^0_{n\sigma v}=\sum_{n'\sigma'v'} S(n'\sigma'v';\, n\sigma v)\Psi^0_{n'\sigma'v'}$ are thus approximately $(\Psi^0_{n\sigma v}\pm\Psi^0_{n-\sigma v})/2^{1/2}$, i.e. linear combinations of the wave functions corresponding originally to left and right-handed rotations about the axis of figure. These sum and difference combinations are precisely those used by Kronig as the starting point of his perturbation calculation.

^1P states. An explicit formula for the diagonal elements of H in (39) would be exceedingly cumbersome with arbitrary values of σ, far more so than the expression (39) already derived for the off-diagonal elements. The primary interest is in the doublet widths rather than the absolute value of the energy, and (41) shows that fortunately this width does not involve the calculation of such diagonal elements. In ^1P states, however, σ equals unity, and the sigma doubling effect appears in the second approximation in B. Here it is easy to calculate the absolute as well as relative energies, for the well-known expression[30] for W_2 in non-degenerate systems[38] shows that now the diagonal elements of (39) become

$$H^{(2)}(n1v\,;\,n1v)=H^{(2)}(n,-1v\,;\,n,-1v)$$
$$=\sum_{n'\sigma'v'}\left\{\left|H_1(n1v\,;\,n'\sigma'v')\right|^2/h\nu(n1v\,;\,n'\sigma'v')\right\} \qquad (43)$$

where $\sigma'=0,2$. Using (28), (38) and (42), we see that the roots of the determinant (39) are now

$$W^{(2\sigma)}=-2C+(C+C_1)j(j+1)\quad,\qquad -2C+(C+C_2)j(j+1) \qquad (44)$$

with

$$C=4\sum_{n'v'}\frac{|(BP_y)(n1v\,;\,n'2v')|^2}{h\nu(n1v\,;\,n'2v')},\qquad C_1=8\sum_{n'v',\mathrm{even}\,S}\frac{(BP_y)(n1v\,;\,n'0v')^2}{h\nu(n1v\,;\,n'0v')} \qquad (45)$$

where the summation over the S states $n'0$ is to be extended over only those of the even type. The expression for C_2 is similar except that the summation is over the odd S states. We classify an S state as "even" or "odd" according as its internal wave function Φ_{nov} is invariant or changes sign when one makes the transformation $x_i=x_i$, $y_i=-y_i$, $z_i=z_i$ $(i=1,\cdots f)$. This division of S levels into two types is suggested by Kronig's papers.[6] He shows that all S wave functions have either the even or odd property, as otherwise there would be two independent wave functions belonging to a single S state. Before making the tranformation (42), we can without loss

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[38] Because of the degeneracy encountered in the second approximation, the expression W_2 calculated on the assumption of a non-degenerate system is not the actual second order energy, but does equal the diagonal elements of H in (39).

of generality suppose that $\Psi_{n\sigma}(x,\ y,\ z)=\Psi_{n,-\sigma}(x,-y,z)$ as in the beginning we supposed that the states $+\sigma$ and $-\sigma$ differed only in the sense of rotation about the axis of figure. The operator $l_y=i^{-1}\sum(z_i\,\partial\cdot\cdot/\partial x_i-x_i\partial\cdot\cdot/\partial z_i)$ is invariant with respect to the transformation under consideration. Furthermore in singlet spectra $P=l$, and hence (19) shows that $P_y\ (n'0;\ n,\ -1)$ has the same or the opposite sign from $P_y(n'0;\ n1)$ according as the state $n'0$ is even or odd. This, taken with the Hermitian property (28) of the matrices, shows that each term in the sum (38) is real, and that (44–45) do indeed follow from (38, 39, 43). In certain simple systems it may happen that S states are all of the even type, making $C_2=0$, though this is not true in the general case. In a molecule with one electron, for instance, the S wave functions are all even, as they are of the form $\Psi_{no}(\rho,\ z)$, where ρ, z are cylindrical coordinates (cf. footnote 21).

The important thing to note about Eq. (44) is that it shows that the width of a ^1P sigma-type doublet is $(C_1-C_2)j(j+1)$, and therefore approximately propotional to $j.^2$ Also when (44) is added to the original energy values associated with (14–16) to obtain the complete energy, we see that the inclusion of the terms in B does not impair the ability to represent the dependence of the energy on j in a rigid molecule by an expression of the form $A'+B'j(j+1)$, but the constant B', and hence the "apparent moment of inertia" computed therefrom, will have different values in the two doublet components.

If the vibrational excitation is small in the state n, though not necessarily in the state n', the formulas (45) may be simplified by the use of (23–4). Then[39]

$$\sum_{n'\sigma'v'} \left|\ (BP_y)(n\sigma v\ ;\ n'\sigma'v')\ \right|^2=B^2\sum_{n'\sigma'}\left|\ P_y(n\sigma\ ;\ n'\sigma')\ \right|^2$$

and the summation over v' in (44) can be eliminated, as ordinarily the dependence of ν on v' can be neglected in comparison with its dependence on n'. Still further simplification of (45) can be effected if we assume that the orbital angular momentum has a constant magnitude and precesses uniformly about the axis of figure, and that further the moment of inertia is independent of σ. These assumptions we will henceforth for brevity refer

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[39] It is to be clearly understood that without the simplification resulting from (23–24) the matrix (BP_y) is not identical with the product of the ordinary band spectrum constant $B=h^2/8\pi^2I$ and the angular momentum matrix P_y, but is rather the product of the two matrices $B=h^2/8\pi^2Mr^2$ and P_y. The expression for (BP_y) is given by (21) and of course involves the initial and final states symmetrically. Similarly in the matrix Al, used in later sections, beginning with Eq. (54), A is not a constant but rather a matrix proportional approximately to $1/r^3$, as the magnetic coupling energy is proportional to this power of r in atoms. Simplification by means of (23–24) is necessary before A can be identified with the ordinary constant of proportionality in the multiplet width. In section 3, however, A could be considered as a constant in (33) etc. as we did not there consider the interaction of the given P spin doublet with any other electronic states; this amounts to taking diagonal terms in the matrix A. The expressions A_S, B_P, etc. to be used in section 5 starting with Eq. (58) denote the diagonal elements of A or B for an S or P state.

to as the *hypothesis of pure precession.* They are not good approximations except when the valence electron (or electrons) is in such a large orbit that it exerts little bonding power in holding the nuclei together. However, the hypothesis of pure precession is convenient and justifiable at least in estimating the order of magnitude of the C's. When it is made the components of l are diagonal in n, and given by expressions identical with (30) except that l, σ_l replace s, σ_s. We then find.[40]

$$C = B^2(l^2+l-2)/h\nu(1,2), \qquad C_1 = 2B^2 l(l+1)/h\nu(1,0), \qquad C_2 = 0 \tag{46}$$

If we further suppose $l=1$, and that in a stationary molecule $W(\sigma) = A\sigma^2$ (i.e. that the coupling of l to the axis of figure is proportional to the square of the cosine between l and this axis) we have a model so simplified that it is the same as that used in Hill and V. V.'s[5] section on sigma-doubling, which employed a different method using Hund's case (d) (loose coupling of l relative to the rest of the molecule) rather than case (a) as the unperturbed system. Eqs. (44–45) are then identical with their corresponding formula (third line of their Eq. 43). Incidently, with these final simplifications a closed formula (2nd and 3rd lines of Hill's and V. V.'s Eq. 42) can be obtained with either method, including all powers in B, instead of using successive approximations as we do and stopping with B^2.

D states. Here by (29), (38) and (40), the dependence of the doublet separation on j is of the form

$$h\Delta\nu = d(j-1)j(j+1)(j+2) \tag{47}$$

as already mentioned by Kronig.[6] The constant d is of the order B^4 and with the hypothesis of pure precession

$$d = 2B^4(l-1)l(l+1)(l+2)/h^2\nu(2,1)^2 h\nu(2,0)$$

5. SIGMA DOUBLING IN ^2P STATES

In section 3 we considered the rotational distortion of spin multiplets, but omitted the superposed sigma-type doubling, as we disregarded the perpendicular component of orbital angular momentum. In section 4 we treated sigma-doubling without spin, which is legitimate only in singlet spectra. We must now handle the more complicated problem of the mutual interaction of the spin and sigma doubling effects. Here the latter effect does not appreciably influence the former, but the former may completely change the latter. This is true because sigma-type doublets usually have small widths compared to the separations in spin multiplets and in rotational energy sequences, and so cannot greatly modify these separations. On the other hand, the angular momentum due to spin can profoundly alter sigma doubling, so that often the latter is entirely different in ^2P states from what

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[40] As the present section relates to singlet spectra, there is now no distinction between the vectors $\mathbf{P}$ and $\mathbf{l}$. Without the hypothesis of pure precession, however, the vector $\mathbf{l}$ does not have a constant scalar magnitude $[l(l+1)]^{1/2}$.

it is in the ${}^1P$. In general the behavior is quite distinct depending on whether we have Hund's case (b) or (a).

Case (*b*). In Hund's ideal case (b) the only effect of the spin is to cause a precession of j_k, which is the total angular momentum exclusive of spin, about the inclusive total j, but this precession is so slow as to be negligible if the spin forces are very weak. Hence with perfect case (b) the effective angular momentum is that exclusive of spin, and the interaction between orbital angular momentum and molecular rotation is identical with that in a singlet molecule of total angular momentum j_k. The sigma doubling is then the same for all components of a spin multiplet, and identical in magnitude with that calculated for singlet states except that j_k everywhere replaces j. These results hold for any multiplicity. In particular we see, using (44), that in case (b) P states, the various spin components having the same value of j_k should exhibit equal sigma doublings proportional to $j_k(j_k+1)$.

Complications in case (*a*). As the phenomena in Hund's case (a) are more complex, we shall in the balance of this section confine our attention to ${}^2P$ levels, as they are the simplest multiplets and probably the commonest. In view of the perturbation theory given in section 4 it doubtless at first thought appears as though the ${}^2P_{1/2}$ component($\sigma_s=-1/2$, $\sigma=\sigma_l+\sigma_s=1/2$) should exhibit a sigma doubling width of the first order in B, and the ${}^2P_{3/2}$ component ($\sigma_s=1/2$, $\sigma=3/2$) one of the third order, as one transition of the type $\Delta\sigma=\pm 1$ involved in the perturbing matrix elements (29) suffices to connect the states $\sigma=1/2$ and $\sigma=-1/2$ whereas the superposition of three such transitions is needed to connect $+3/2$ and $-3/2$. This, however, overlooks the fact that with the spin the criterion for terms with sigma-type degeneracy is not just $\sigma=-\sigma'$ but is instead is the more strigent condition $\sigma_s=-\sigma_s'$ $\sigma_l=-\sigma_l'$. If we neglect all interaction between the components of s and l perpendicular to the axis of figure, the spin and orbital angular momenta will precess about this axis at different, uncoordinated rates, so that the matrix elements of l_y will be all of the form $\Delta\sigma_l=\pm 1$, $\Delta\sigma_s=0$, whereas those of s_y will all have $\Delta\sigma_l=0$, $\Delta\sigma_s=\pm 1$. As $P_y=s_y+l_y$ the perturbing matrix elements of (29) become entirely of the forms

$$\Delta\sigma_l=\pm 1,\ \Delta\sigma_s=0 \text{ and } \Delta\sigma_l=0,\ \Delta\sigma_s=\pm 1 \tag{48}$$

Three transitions of this character are needed to connect $\sigma_s=-1/2$, $\sigma_l=+1$ with $\sigma_s=+1/2$, $\sigma_l=-1$ and so without interaction between the perpendicular component of s and that of l we would obtain a doubling for the ${}^2P_{1/2}$ component of only the third order in B, the same as for ${}^2P_{3/2}$. This is contrary to the experimental fact that the ${}^2P_{1/2}$ state often shows a much larger sigma doubling than the ${}^2P_{3/2}$. The reason for this observed dissymmetry is that actually there is always interaction between the components of s and l which are perpendicular to the figure axis. This can be seen in the following way:

Digression on Hund's case (*c*). Suppose the interaction between s and l were so large as to overpower the "non-centralness" defined in the introduction, but that the effect of non-centralness is still large compared to the rotational distortion. We then have a situation which Hund[3] dubs case (c). The parallel components of s and l will cease to be separate quantum numbers, but the sum of these components will still have a constant quantized value σ, and the vector resultant of s and l will have a quantized magnitude i analogous to the usual inner quantum number. We use the notation i in place of Hund's j, as we reserve j for the total molecular angular momentum. If i executes a pure precession about the axis of figure, the elements (29) become of the type $\Delta i = 0$, $\Delta\sigma = \pm 1$ the complication of the separate parallel quantizations σ_l and σ_s now disappearing. Sigma-type doubling is encountered when $i = i'$, $\sigma = -\sigma'$. Consequently the state $\sigma = 1/2$ should exhibit a sigma doubling width of the first order in B, and proportional $j+1/2$, but the state $\sigma = 3/2$ one of the third order, and proportional to $(j-1/2)(j+1/2)(j+3/2)$, as can be seen by using Eqs. (29), (38), (41). Explicit formulas for the factors of proportionally could immediately be written down, but we shall not give them, as such strong interaction between s and l as to give case (c) is a rare, if not purely academic occurrence, and as formulas for illustrative special cases of (c) have already been given by Hill and V. V. in their Eq. (43). They used another method of calculation already described, and computed the doublet widths on the assumption of a binding force proportional to $\cos^2(i, \sigma)$, with $i = 1/2$, $3/2$ (k in their notation), the values to be expected as the resultant of $s = 1/2$ and $l = 1$. The important thing to note is that the component $\sigma = 1/2$ exhibits an enormous sigma doubling of the same order of magnitude as the rotational energy intervals themselves.

Actual case (*a*). Ordinarily Hund's case (a) represents the true state of affairs much more accurately than his case (c), but any interaction between the perpendicular component of s and that of l may be regarded as at least the beginning of a transition from case (a) to (c). Hence we can understand qualitatively why the $P_{1/2}$ state should exhibit a larger doubling than the $P_{3/2}$. Quantitatively this is due to the fact that owing to the interaction between the perpendicular component of s and that of l the matrix P_y will indeed have elements, though small, of the form $\Delta\sigma_s = +1$, $\Delta\sigma_l = -2$ which connect $\sigma_s = -1/2$, $\sigma_l = 1$ and $\sigma_s = 1/2$, $\sigma_l = -1$ in one transition $\Delta\sigma = -1$. The magnitude of these elements is calculated in a following paragraph and proves to be proportional to the product of B and the magnetic interaction energy, making the sigma doubling of the $P_{1/2}$ state not exceedingly large even though of the first order in B. By (29) and (41) the formula for the width of this doublet is

$$P_{1/2}) \qquad h\Delta\nu = a(j+1/2) \qquad \text{with} \qquad a = 4\left|(BP_y)(P_{1/2}\,;P_{-1/2})\right| \tag{49}$$

The corresponding width for the $P_{3/2}$ state may be calculated neglecting entirely the interaction between s and l, as here unlike in $P_{1/2}$, this interaction does not make the doubling of lower order in B. This width is by (29), (38), and (41)

$$P_{3/2}) \qquad h\Delta\nu = b(j-1/2)(j+1/2)(j+3/2) \tag{50}$$

If we make the hypothesis of pure precession (p. 489) for s, but not necessarily for l, the value of the constant b is by (30)

$$b=16B\sum_{S}\left[(-1)^{S}\left|(BP_y)(P\,;S)\right|^{2}/h\nu(P\,;S)h\nu(P_{3/2}\,;P_{1/2})\right] \tag{51}$$

In writing (49), (51), and all future equations, we for brevity index the matrix elements with respect to the spectroscopic nomenclature of the initial and final states, instead of the quantum number, as indicated in the following scheme

$$\begin{array}{ccccc} & & S_{1/2} & & \\ & & n,\sigma_l,\sigma_s,v=n',0,\tfrac{1}{2},v'\,; & & \\ S_{-1/2} & P_{3/2} & P_{1/2} & P_{-1/2} & P_{-3/2} \\ n',0,-\tfrac{1}{2},v', & n',1,\tfrac{1}{2},v', & n',1,-\tfrac{1}{2},v', & n',-1,\tfrac{1}{2},v', & n',-1,-\tfrac{1}{2},v' \end{array} \tag{52}$$

Otherwise it would be necessary to list four initial and four final indices, since we must now specify σ_s in addition to the quantum numbers n, σ, v used as indices in section 4. The distinction between positive and negative subscripts, we may caution, has no direct meaning in terms of observed spectroscopic levels, but is only associated with the quantization at the outset of the calculation. Actually the sigma doubling finally scrambles together the positive and negative values, the really vital type of classification being with respect to Kronig's[6] symmetry and antisymmetry. The summation over S is to be understood to extend over both all vibrational quantum numbers v' and all electronic quantum numbers n' giving rise to S states. The omission of subscripts from the arguments as in (51) means that the spin does not appreciably influence the amplitude or frequency under consideration. In writing (51) we have neglected terms with two PS frequencies in the denominator and have utilized the fact that

$$(Bl_y)(P_+\,;S)(Bl_y)(S\,;P_-)=(-1)^{S}\left|(Bl_y)(P\,;S)\right|^{2} \tag{53}$$

where the exponent S of -1 is to be taken as an odd or even integer according as the S state is odd or even in the sense explained just below Eq. (45).

Calculation of (BP_y) $(P_{1/2};\,P_{-1/2})$. This calculation is needed to estimate the order of magnitude of the constant a in (49) and may be made by perturbation theory assuming that the "magnetic" interaction energy between s and l is small compared to the effect of non-centralness. Let us further suppose that this interaction obeys the cosine law. The interaction between the components of s and l which are parallel to the figure axis merely contributes a constant term (33) in the energy which has already been utilized in section 3, and which gives the bulk of the energetic effect of the coupling between s and l. The contribution of the perpendicular components vanishes as a first approximation on averaging over the electronic frequencies, and so is a higher effect which may be considered as introducing a perturbation matrix[39]

$$H_{\text{per}}=A\left[\mathbf{s}\cdot\boldsymbol{l}-s_zl_z\right]=A\left[s_xl_x+s_yl_y\right] \tag{54}$$

This is, of course, not to be confused with the other perturbation matrix (29) giving the effect of rotation. As there is hitherto no coupling except through the parallel components, we can apply the phase relations (20) to s and l separately instead of to P and furthermore take the elements of l_x or l_y to be entirely of the first form (48) and those of s_x, s_y to be entirely of the second form. Hence by (20) and (48) the elements of (54) are all of the form $\Delta\sigma=0$, as we should expect. The transformation matrix corresponding to (52) is $1+S_1+\cdots\cdots$ with

$$S_1(P_{\pm 1/2}\,;S_{\pm 1/2})=2(As_yl_y)(P_{\pm 1/2}\,;S_{\pm 1/2})/h\nu(P\,;S) \tag{55}$$

The transformed matrices for BP which are corrected for the perturbing effect of (54) are given by $SB^0\mathrm{P}_y{}^0S^{-1}=B^0P_y{}^0+S_1B^0P_y{}^0-B^0P_y{}^0S_1{}^0+\cdots\cdots$, and no longer retain the form (48). Instead we find

$$(BP_y)(P_{1/2}\,;P_{-1/2})=\text{r.p. of }2\sum\left[(-1)^S(Al_y)(P\,;S)(Bl_y)(S\,;P)/h\nu(P\,;S)\right] \tag{56}$$

where we do not bother to attach zero superscripts to the right hand elements. We have used the Hermitian property (26), and (53) which applies to A as well as B, and use r. p. to denote the real part in case the amplitudes are complex. If the vibrational excitation of the given P state and the effect of vibration on the energy are small, the vibrational quantum number implicitly involved in the sum in (56) (cf. Eq. 52) can be eliminated by using considerations analogous to those involved in (23–24). In writing (56) we have employed simplifications which result from applying the hypothesis of pure precession to the motion of s, permitting us to use (30) with $s=1/2$. We are usually well justified in applying this hypothesis to s but not to l. If, nevertheless, we do apply it to l, we have a rough simple formula which is very convenient for estimating orders of magnitudes, etc., as then the right side of (56) reduces to a single term and the constant a in (49) thus becomes

$$a=2AB[l(l+1)]/h\nu(P\,;S). \tag{57}$$

At this point we must note that in discarding the periodic part of (13), in particular the first term of (13) in our work in section 2, we have (since $P_y=l_y+s_y$) omitted a term of precisely the same form as (54) except that A is replaced by $2B$. This neglected term ought really to be included, and has the effect of replacing A in (54–56) by $A+2B$. This modification could be neglected in the preceding study of case (a), where B/A is small by hypothesis, but is vital for the forthcoming work where we consider the entire range from (a) to (b), as otherwise the formulas do not have the proper limiting values for case (b).[41]

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[41] This contribution from (13) introduces an interaction between the components of s and l which are perpendicular to the figure axis even without the supposition of magnetic forces, and shows that even without such forces the ${}^2P_{1/2}$ component should show a sigma doubling without going to the third approximation in B as stated on p. 490. This is a purely academic point, as by definition there is always a strong magnetic interaction in case (a). In writing

General case intermediate between (*a*) *and* (*b*). In treating this more complicated intermediate case, where the magnetic and rotational energies are comparable, we shall first consider the interaction between the P levels under discussion and only one particular electronic S state. The results of the interaction with the others can later be obtained by summing over all values of the electronic quantum numbers which yield S states. This procedure neglects entirely the influence of the D states, but they have only a negligible influence on the rotational distortion and sigma doubling phenomena of the P levels. With this restriction to one electronic S state, which of course has two spin components we must consider the mutual perturbation of the six levels (52). Assuming as a starting point ideal case (a) quantization as in section 3, we find that the matrix elements in the Hamiltonian connected with these six levels are as follows

$$\begin{aligned}
&H(S_{1/2}\,;\,S_{1/2})=H(S_{-1/2}\,;\,S_{-1/2})=B_S[j(j+1)+\tfrac{1}{4}]+E=\alpha\\
&H(P_{1/2}\,;\,P_{1/2})=H(P_{-1/2}\,;\,P_{-1/2})=B_P[j(j+1)+\tfrac{1}{4}]-\tfrac{1}{2}A_P=\beta\\
&H(P_{3/2}\,;\,P_{3/2})=H(P_{-3/2}\,;\,P_{-3/2})=B_P[j(j+1)-7/4]+\tfrac{1}{2}A_P=\gamma\\
&H(S_{1/2}\,;\,S_{-1/2})=H(S_{-1/2}\,;\,S_{1/2})=B_S(j+\tfrac{1}{2})=(-1)^S\delta\\
&H(P_{3/2}\,;\,P_{1/2})=H(P_{-3/2}\,;\,P_{-1/2})=B_P[(j-\tfrac{1}{2})(j+\tfrac{3}{2})]^{1/2}=\epsilon\\
&H(P_{1/2}\,;\,S_{-1/2})=(-1)^S H(P_{-1/2}\,;\,S_{1/2})=2(Bl_y)(P\,;\,S)(j+\tfrac{1}{2})=(-1)^S\zeta\\
&H(P_{3/2}\,;\,S_{1/2})=(-1)^S H(P_{-3/2}\,;\,S_{-1/2})=2(Bl_y)(P\,;\,S)[(j-\tfrac{1}{2})(j+\tfrac{3}{2})]^{1/2}=\eta\\
&H(P_{1/2}\,;\,S_{1/2})=(-1)^S H(P_{-1/2}\,;\,S_{-1/2})=(Al_y+2Bl_y)(P\,;\,S)=\theta.
\end{aligned}\tag{58}$$

Here, as elsewhere, the exponent ^{S} of -1 is to be taken as an even or odd integer, according as the S state under consideration is "even" or "odd" in the sense explained on p. 487. For convenience of later reference the various matrix elements have been designed by Greek letters, with the sign conventions which subsequently prove most convenient. The P state is taken as the origin for measuring internal electronic (or more precisely internal electronic plus vibrational) energy, so that this part of the energy will have a value $E=h\nu(P;\,S)$ different from zero, either positive or negative, often the latter, in the S state. With this observation the values given in (58) for the diagonal elements α, β, γ follow from (32–33). The values of the purely spin elements δ, ϵ follow from (29–30) or (31), and of the purely orbital elements ζ, η from (29). We suppose the magnetic interaction between the components of s and l perpendicular to the figure axis not incorporated in the unperturbed or diagonal part of the energy, as this has permitted us to calculate the other matrix elements as though the motion of s and l were completely independent, rather than perturbed by the transformation (55), a considerable simplification. Instead this interaction, when supplemented

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(58), etc., we have not included explicitly the part $B(l_x^2+l_y^2)$ coming also from the first term in (13), as this merely has the effect of altering slightly the "electronic" energy levels, and is incorporated by altering slightly the energy difference E of the S and P states.

by the correction explained in the preceding paragraph, gives rise to the matrix element θ. The specific value given for θ follows from (54) with this modification, and the assumption that the motion of s satisfies the hypothesis (30) of pure precession, but that the motion of l conforms only to the type form (20).

The secular determinant analogous to (35) for the matrix elements (58) connecting the six levels (52) could immediately be set up, and would at first appearance yield a sixth order algebraic equation for W. This equation, however, factors into two cubics because of the possibility of separating energy levels into the symmetric and antisymmetric types introduced by Kronig.[6] This separation is accomplished by introducing the following transformation matrix S

$$S(X_q\,;\,X_q)=(-1)^X S(X_q\,;\,X_{-q})=(-1)^X S(X_{-q}\,;\,X_{-q})$$
$$=-S(X_{-q}\,;\,X_q)=(1/2)^{1/2}$$

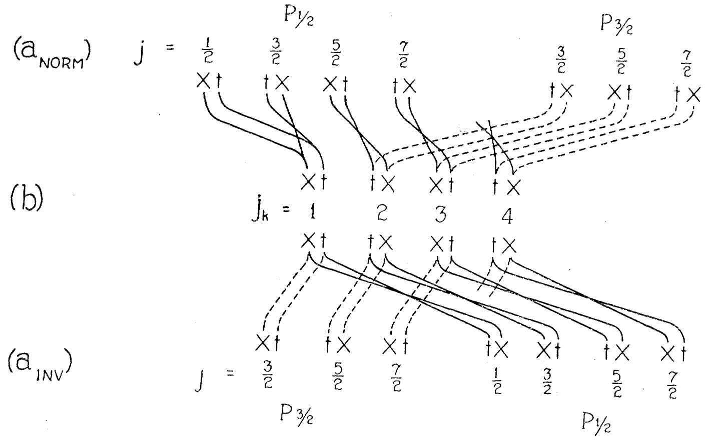
where $X=P$ or S, and where $q=-1/2$ or $1/2$, and also $-3/2$ or $3/2$ if $X=P$. The exponent X of -1 is an even integer if X represents any P state or an "even" S state, and is an odd integer if X represents an "odd" S state. As explained in connection with the somewhat similar transformation (42) this transformation is tantamount to using wave functions of Kronig's symmetric and antisymmetric types rather than those with exponential factors representing angular momentum of constant sign about the axis of figure. After the transformation the secular determinant factors into two third order determinants one of which is

$$\begin{vmatrix} \kappa-W & \mu & \eta \\ \mu^* & \beta-W & \epsilon \\ \eta^* & \epsilon^* & \gamma-W \end{vmatrix}=0 \tag{59}$$

with $\kappa=\alpha+\delta$, $\mu=\theta+\zeta$. The other is identical except that it has $\kappa=\alpha-\delta$, $\mu=\theta-\zeta$. As a check on the work, it may be verified that when the magnetic interaction is zero, making $A=0$ in (58) these two cubics each factor into a quadratic and linear equation as follows:

$$\{[E+B_S j_{k_1}(j_{k_1}+1)-W][B_P j_{k_1}(j_{k_1}+1)-B_P-W]$$
$$-8\,|\,(Bl_y)(P\,;\,S)\,|^2 j_{k_1}(j_{k_1}+1)\}\times\{B_P j_{k_2}(j_{k_2}+1)-B_P-W\}=0 \tag{60}$$

with $j_{k_1}=j\pm 1/2(-1)^S$, $j_{k_2}=j\mp 1/2(-1)^S$. The equations for W furnished by (60) are exactly those which would have been obtained by neglecting spin, as we should expect for the limiting case (b). Such equations for W neglecting spin have not previously been given explicitly, but are obtained by considerations closely related to those in our derivation of (44), the difference being that the interaction with one S state is treated in an exact secular fashion rather than that with all states by methods of successive approximations. The behavior (60) furnishes the clue to the adiabatic correlation of energy levels in cases (a) and (b), which is indicated schematically in the following diagram:



The symbols $\times$ and † represent states having the two different types of Kronig[6] symmetry. These diagrams may be regarded as supplementing the previous derivation of the correlation given by Hill and V. V.[5] which did not include the sigma doubling phenomenon but to which the reader is referred for discussion and references exclusive of it. If the interaction with the spin is supposed to completely disappear in case (b) the two components of the spin multiplet coalesce in energy, as indicated by the coming together of the heavy and dashed lines corresponding to $P_{1/2}$ and $P_{3/2}$ levels respectively. It is to be noted that in the $P_{1/2}$ levels the two sigma doublet components representing different symmetries "cross over" in going from (a) to (b) except the anomalous component $j=1/2$ in regular multiplets. This means that for any particular $j>1/2$ there is an appropriate value of the ratio of rotational to magnetic energy which makes the $P_{1/2}$ sigma doubling vanish. The so-called "non-crossing" rule does not apply to these components, as they do not "combine" in the energy or secular determinant although they do spectroscopically. As shown by Kronig, the only spectral lines which are "allowed" are those which connect levels $\times$ and † with opposite types of symmetry.[42] This rule is clearly to be distinguished from the fact that in the Hamiltonian or secular determinant the only non-vanishing matrix elements are those connecting states of similar symmetry. The reason for this difference is that the energy terms are symmetrical, the electrical moment antisymmetrical as regards Kronig's transformation (15).

Ordinarily the difference in energy between the S and P state is large compared to the width of the spin doublet. If this is true, as we assume throughout, and if we are interested only in the roots corresponding to P levels, we can to a good approximation set $\kappa - W$ equal to a constant $-h\nu$

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[42] Our symbols are essentially similar to those of Wigner and Witmer, and are not the same as the system used in Kronig's first paper and a preceding one by Hulthén.

(P, S) in the determinant (59), which then yields a quadratic equation for W. If we neglect terms above the first order in $1/h\nu(P; S)$, which incidentally is required to make the approximation legitimate, the solution for W is then

$$\begin{aligned} 2W = \beta+\gamma \pm B_P X + \{1/h\nu(P\,;S)\}\{\mu\mu^* + \eta\eta^* \\ \pm B_P^{-1}X^{-1}[(\beta-\gamma)(\mu\mu^*-\eta\eta^*)+2\mu\epsilon\eta^*+2\mu^*\epsilon^*\eta]\} \end{aligned} \tag{61}$$

with

$$X^2 = [(\beta-\gamma)^2+4\epsilon\epsilon^*]/B_P^2 = [\lambda(\lambda-4)+4(j+\tfrac{1}{2})^2], \quad \lambda = A_P/B_P \tag{62}$$

The first three right hand terms give Hill and V. V.'s formula, our (36), for the rotational distortion of a spin doublet. The remaining terms are corrections for the influence of the S state, whose most interesting effect is the introduction of sigma-type doubling. The two values of the sign before the radical X give rise to the two components of a spin multiplet, while a sigma-type doublet is generated by giving μ the two values $\theta+\zeta$ and $\theta-\zeta$ in (61). A more explicit formula for the sigma doublet width can be obtained by substituting detailed formulas (58) for the various Greek letters. At the same time we shall sum over all the electronic S states, so that we include the interaction with all rather than one of them. We thus find

$$\begin{aligned} h\Delta\nu = \text{r.p. of } 4(j+\tfrac{1}{2})\sum_S[(-1)^S/h\nu(P\,;S)] \\ \cdot[(2Bl_y+Al_y)(P\,;S)(Bl_y)(S\,;P)(1\pm 2X^{-1}\mp\lambda X^{-1}) \\ \pm 4X^{-1}(j+\tfrac{3}{2})(j-\tfrac{1}{2})\,|\,(Bl_y)(P\,;S)\,|^2] \end{aligned} \tag{63}$$

where X is as in (62) and the convention on the exponent S is as previously. The upper sign gives the $P_{1/2}$ state and the lower the $P_{3/2}$ or vice versa. It is readily verified that (63) reduces to (44–45) in the limiting case (b) and to (49–50) supplemented by (56) and (51) in the limiting case (a). Instead of first introducing a cubic secular determinant and then later summing over all the S states, Eq. (63) could also have been obtained by first applying Hill and V. V.'s transformation T to take into account the rotational distortion of the spin in which only the parallel component of s is considered, and then applying perturbation theory as in section 3 to take into account the sigma doubling phenomena, where the perpendicular components are vital. It is, however, probably more vivid to first reduce the problem to a simple algebraic equation rather than to apply the rather abstract perturbation theory at the outset.

6. RHO-TYPE DOUBLING IN ^{2}S STATES

In ^2S states the magnetic interaction is, of course, so weak that Hund's case (b) is a good approximation. The usual procedure is to neglect entirely the interaction between the spin and the rest of the molecule in such states, as a stationary molecule in an S level has no orbital angular momentum parallel to the axis of figure. The energy is then a function of j_k but not of j, and there are two states of coincident energy corresponding to the possibilities $j=j_k\pm 1/2$. Actually these two S states of similar j_k but unlike j do not coincide but form a closely spaced "ρ-type doublet" in Mulliken's terminology.[43] The reason for this nomenclature is that the S rotational energy levels can be represented empirically by a formula of the type $B_S(j\pm\rho)^2$ where ρ is not exactly 1/2, making the doublet width

$$h\Delta\nu = B_S[(j_k-\tfrac{1}{2}+\rho)^2-(j_k+\tfrac{1}{2}-\rho)^2]=2j_kB_S(2\rho-1) \qquad (64)$$

A rho-type doublet is not to be confused with the sigma-type doublets found in ^2P states, as in the latter both components have the same j values rather than values differing by one unit.

A theoretical explanation of the rho-type doubling may be found in the fact that even in S states the mean square of the orbital angular momentum does not vanish[44] but instead there is a precessing component $(l_x^2+l_y^2)^{1/2}$ perpendicular to the axis of figure. This will exert a force on the spin angular momentum, but does not influence the energy in the first approximation, as the average value of the cosine of the angle between l_x or l_y and s is zero with ideal case (b) coupling. When, however, higher approximations involving the superposition of rotational distortion and this interaction are considered, the energy of the ^2S state depends on j as well as j_k. This can be seen from the determinant (59). In the preceding section we calculated the two roots of this determinant which represent P states, and we must now compute the remaining root which is an S term and which lies close to κ. The value $W=\kappa=E+B_Sj_k(j_k+1)$ is, in fact, the usual approximate formula for ^2S levels, and is obtained by neglecting the interaction between the S and P states which is embodied by the matrix elements μ, η in (59). As we may suppose κ numerically large compared to the other Greek letters and as $\kappa-W$ is numerically small compared to $\beta-W$ and $\gamma-W$, a more accurate expression for this root may be obtained by expanding the determinant and keeping only the terms which have factors $\beta-W$ or $\gamma-W$. These two factors may be replaced by their approximate values $\beta-\kappa$ and $\gamma-\kappa$, making (59) a linear equation for W. We thus find

$$W-\kappa=[\mu\mu^*/(\kappa-\beta)]+[\eta\eta^*/(\kappa-\gamma)]$$

a result also obvious from perturbation theory, as the right-hand side is essentially Born, Heisenberg, and Jordan's expression[30] for W_2. When we substitute the explicit expressions for the various Greek letters given in (58) and in the text following (59), we find that the two W's having the same j_k are

$$W=B_S'j_k(j_k+1)+E+A_S+\tfrac{1}{4}a'\pm\tfrac{1}{2}h\Delta\nu,\quad h\Delta\nu=a'(j_k+\tfrac{1}{2}) \qquad (65)$$

with
$$a'=\text{r.p. of } 8\sum_P[(Al_y)(S\,;P)(Bl_y)(P\,;S)/h\nu(S\,;P)] \qquad (66)$$

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[43] R. S. Mulliken, Phys. Rev. **28,** 481 (1926).

[44] Cf. J. H. Van Vleck, Phys. Rev. **31** 600 (1928).

$$B_S' = B_S + 8\sum_P [\,|\,(Bl_y)(\mathrm{S}\,;\mathrm{P})\,|\,^2/h\nu(\mathrm{S}\,;\mathrm{P})], \quad A_S = \sum_P [\,|\,(Al_y)(\mathrm{S}\,;\mathrm{P})\,|^2/h\nu(\mathrm{S}\,;\mathrm{P})].$$

The two cases represented by the choice of sign correspond to $j = j_k \mp 1/2$, $\kappa = \alpha \pm (-1)^S \delta$, $\mu = \theta \pm (-1)^S \zeta$. The summation over all the electronic ${}^2P$ states is included to remove the restriction, made in deriving (59), that the given ${}^2S$ states interacts with only one ${}^2P$ spin doublet. As we should expect, the doubling phenonenon disappears and the energy becomes a function only of j_k when the magnetic interaction is disregarded by setting $A = 0$.

The variation of the rho-doublet width with j_k given by (65) is precisely that found by Mulliken except for the small difference that (65) has $j_k + 1/2$ in place of j_k, a modification which is supported by more precise experimental data[45] available subsequent to Mulliken's[43] early work. The order of magnitude of the constant a' is the same as that of the constant a in the formulas (49,56) for the width of a case (a) sigma doublet. In fact the constants are identical except for sign if a ${}^2S$ state and a ${}^2P$ spin doublet be imagined to interact only with each other and not with other electronic P or S states, and if in addition B/A is negligible. With the hypothesis of pure precession, a' is the negative of the expression (57).

This explanation of rho-type doubling, which was suggested in part by a conversation by Professor Kemble, is not quite the conventional one given by Hund[3] and others.[45] The ordinary interpretion assumes that in S states the molecule develops some angular momentum due to the orbital motion of the nuclei in their rotation about the center of gravity. This angular momentum, which will have the direction of j_k, will interact with the spin angular momentum s, and the energy of this interaction may be taken to be of the form

$$a'' j_k \cdot \mathrm{s} = \tfrac{1}{2} a'' [j(j+1) - j_k(j_k+1) - s(s+1)] \tag{67}$$

where a'' is of the order m/M times the factor of proportionality A in the ordinary spin P doublets, m/M being the ratio of the electronic mass to the "reduced mass" of the nuclei. On the right-hand side of (67) we have given the value of the vector product furnished by the cosine law of quantum mechanics. The difference between the values of (67) for $j = j_k + 1/2$ and $j = j_k - 1/2$ is

$$h\Delta\nu = a''(j_k + \tfrac{1}{2}). \tag{68}$$

The conventional explanation (67) thus gives precisely the same dependence of the rho-doubling width on j_k as our previous formulas (65–66). Actually the two effects are additive, so that the true value of the constant of proportionality in (65) or (68) should be $a' + a''$. To compare the relative importance of the two contributions, we first note that (66) and (68) give constants of proportionality respectively of the order $8B/\mathrm{h}\nu(\mathrm{S}, \mathrm{P})$ and m/M times the width of an ordinary spin doublet. Now m/M is of the order $10^{-3}/4Z$, where Z is the atomic number of the lighter of the two nuclei, while $\mathrm{B}/\mathrm{h}\nu$

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[45] Hulthén, Zeitz. f. Physik **50**, 319 (1928).

(S, P) seems ordinarily to be about 10^{-4} (see section 8 for numerical data on ν). Consequently a' is certainly larger in magnitude than the factor a'' usually given, provided Z is large. Ostensibly because of the factor 8×10^{-4} as against $10^{-3}/4$, a' should predominate slightly over a'' even in light molecules, such as the hydrides $Z=1$, but of course much credence should not be placed on a predominance merely in virtue of such numerical factors until an accurate calculation can be made of the amount of magnetic moment developed by the nuclear orbital motions or until the sum in (66) can be evaluated accurately through knowledge of the ν's and the precise form of the orbital angular momentum matrix l.

Even the part of the rho-type doubling represented by (66) is due in a certain limited sense to magnetization by rotation, the cause ordinarily given, as the rotational distortion makes the component of electronic orbital angular momentum which is perpendicular to the axis of figure precess at a non-uniform rate, so that it precesses at different speeds in the configurations which are approximately parallel or antiparallel to j. A mean electronic angular momentum in the direction of j_k is thus developed, and the interaction between this and s will depend on the angle between j_k and s in the fashion (67), thus giving[46] the rho-type doubling (65–66). An analagous physical interpretation can be given the sigma-doubling (49) in case (a) ${}^2P^{1/2}$ states; the rotational distortion causes the perpendicular components of s and l to precess non-uniformly, so that they both slow or speed up when nearly parallel to j (Whether there is slowing or speeding up depends on the sign of the important frequencies $\nu(\mathrm{P};\mathrm{S})$.) This non-uniformity makes the mean cosine and interaction energy between these components no longer zero and removal of the degeneracy with respect to the sign of σ gives the sigma type doubling. In our treatment of ${}^2P$ states in section 5, we ought really to have included also the interaction between the electronic angular momentum, orbital and especially spin, with the magnetic moment in the

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[46] This physical picture, suggested me by Kemble, of rho-type doubling as due to development of a magnetic moment by rotational distortion may appear superficially rather different from the purely mathematical way in which we extracted the formulas (65–66) from the determinant (59). That the results are the same can be seen as follows: On the basis of this physical picture the energy of magnetic interaction responsible for the rho-doubling is the expression

$$(A\boldsymbol{l}\cdot j_k)(j_k\cdot s)/(j_k^2+j_k) \tag{I}$$

The first vector product of this expression vanishes on the average if we neglect the rotational distortion and consists of the non-diagonal elements

$$(A\boldsymbol{l}\cdot j_k)(\mathrm{S};\ \mathrm{P}_{+1})=(-1)^S(Al\cdot j_k)(\mathrm{S};\ \mathrm{P}_{-1})=(Al_y)(\mathrm{S};\ \mathrm{P})(j_k^2+j_k)^{1/2} \tag{II}$$

We include A inside the parenthesis because, unlike the factor a'' in (67), it must be treated as a matrix rather than as an ordinary numerical factor. (cf. note 39) Formula (II) can be derived by using the same type of kinematical argument as that on pp. 257–258 of Hill and V. V. but taking the electronic angular momentum as now perpendicular rather than parallel to the axis of figure. The rotational distortion has the effect of introducing the transformation matrix (37). When this is applied to (II), the diagonal elements of the expression (II) no longer vanish. When (29) and (I–II) are treated as simultaneous perturbing functions they are found to lead to the same sigma doubling as given in (65–66).

direction of j_k or j developed by the nuclear orbital motions, but this interaction which is essentially the same as that involved in the conventional explanation of rho-type doubling, is usually masked by the other terms except possibly when considering spin doubling when very, very, close to Hund's case (b). Hence we have not complicated the formulas by its inclusion.

Fine structure of ^3S states. This has been treated by Kramers[47] and will not be considered. He shows that the most important term is one which results from the interaction of the two individual electron spins that compound vectorially to give $s=1$. This term is usually absent in ^2S states because they ordinarily contain only one uncompensated electron.[48] We have therefore disregarded it in discussing them. In triplet molecules, however, it introduces a coupling proportional to the square of the cosine of the angle between s and the axis of figure. Superposed on this term in ^3S states, there are the two effects responsible for the rho-doubling considered above. Kramers does not consider these effects explicitly but notes that inclusion of a term of the type form which they give does not improve the agreement with experiment in oxygen.

7. Sigma Doubling in ^3P states

Let us now revert to sigma-doubling and study case (a) ^3P states. Case (b) is, of course, trivial, as the sigma-doubling phenomena are there the same as in ^1P states except that j_k replaces j. In case (a) the $^3P_2$ component clearly exhibits a negligible sigma-doubling, as the resonance terms enter only in the fourth approximation. The $^3P_1$ state should exhibit approximately the same doubling proportional to $j(j+1)$ as a ^1P state, the reason being that in a $^3P_1$ level the spin makes no contribution to σ. The $^3P_0$ component is particularly interesting, as it splits into two sub-components even in a stationary molecule. The resulting doubling is therefore approximately independent of j, and is quite different from the ordinary sigma doubling induced by the rotational distortion. The reason for this anomalous behavior of the $^3P_1$ state is that the magnetic interaction between s and l introduces terms in the Hamiltonian of the form $\Delta\sigma=0$, and can therefore bring about a "resonance" between $+\sigma_l$, $+\sigma_s$ and $-\sigma_l$, $-\sigma_s$ if $\sigma_l+\sigma_s=\sigma=0$. On the other hand the rotational distortion terms (29) of the type $\Delta\sigma=\pm 1$ are needed to introduce this resonance if $\sigma_l+\sigma_s\neq 0$. That the magnetic interaction actually does split the $^3P_0$ level even in a stationary molecule can be seen qualitatively by using the same sort of argument as on p. 491. In the nomenclature there used, any magnetic interaction can be regarded as at least a slight tendency from Hund's case (a) to his case (c), and with given l and $s=1$ there are states with three values of i in case (c), viz., $i=l-1$, l, $l+1$ which have $\sigma=0$. When we pass over to Hund's case (a) by

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[47] H. A. Kramers, Zeits. f. Physik, in press.

[48] In doublet spectra possessing inverted P states we ought perhaps to consider an effect analagous to that studied by Kramers, as such inverted spectra are characteristic of three rather than one uncompensated electron. (cf. R. S. Mulliken, Phys. Rev. **32**, 186, 1928.)

making the magnetic interaction gradually disappear, these three states go adiabatically into one $^3S_0$ and two $^3P_0$ levels, showing that a non-vanishing magnetic coupling gives two $^3P_0$ levels of different energies. The reason that these two energies are nearly the same in case (a) is that the magnetic interaction is overpowered by the non-centralness. The two $^3P_0$ levels are really part of a spin multiplet, and are respectively symmetric and antisymmetric as regards Kronig's transformation (15) generalized[9] to include the spin. In the nomenclature of Wigner and Witmer,[7] they would be classified as a 0, 0′ pair.

The magnitude of the $^3P_0$ doubling may be calculated quantitatively by using perturbation methods similar to those employed in preceding sections. We take a perturbation function of the form (54) and calculate the transformation matrix S_1, but with now $s=1$ instead of $s=1/2$ as in (55). Application of this transformation has the effect of introducing as on p. 485 a new perturbing Hamiltonian function of the second and higher orders which contains elements of the form

$$H^{(2)}(+1\,,\,-1\,;\,-1,+1)=2\sum_{S}(-1)\ \left[\,|\,Al_y(P\,;\,S)\,|^2/h\nu(P\,;\,S)\right] \tag{69}$$

where the indices are σ_l and σ_s. By analogy with (39–40–41) (the difference being that the perturbations are magnetic instead of rotational), the doublet width is just twice the expression (69). In obtaining (69) we have applied the hypothesis (30) of pure precession only to s. If we apply it also to l, so as to simplify the sum in (69) then

$$h\Delta\nu=A^2l(l+1)/h\nu(P\,;\,S)\ \cdot \tag{70}$$

8. SUMMARY AND COMPARISON WITH EXPERIMENT

The conclusions regarding the widths of sigma type doublets in various limiting cases are summarized in the following table:[49]

^1P	$\Delta\nu=(C_1-C_2)j(j+1)$	AlH
^2P case (b)	$\Delta\nu_{1/2}=\Delta\nu_{3/2}=(C_1-C_2)j_k(j_k+1)$	CH, OH
^2P case (a)	$\Delta\nu_{1/2}=a(j+\frac{1}{2}),\quad \Delta\nu_{3/2}=b(j^2-\frac{1}{4})(j+\frac{3}{2})\sim 0$	HgH, CdH, ZnH, BO, NO.
^3P case (b)	$\Delta\nu_0=\Delta\nu_1=\Delta\nu_2=(C_1-C_2)j_k(j_k+1)$	C_2, He_2[50]
^3P case (a)	$\Delta\nu_0=f,\quad \Delta\nu_1=(C_1-C_2)j(j+1),\quad \Delta\nu_2\sim 0$	N_2
^1D or ^2D	$\Delta\nu\sim 0$	CH
^2S (rho-type doubling).	$\Delta\nu=a'(j_k+\frac{1}{2})$	

Here $\Delta\nu_{1/2}$ means the sigma doubling width of the $P_{1/2}$ spin component, etc. The orders of magnitudes of the constants of proportionality may be estimated on the crude assumption that the motion of l is one of pure precession (cf. p. 489) and that $l=1$. Then

$$C_1-C_2=4B^2/\nu,\quad a=-a'=4AB/\nu,\quad b=8B^3/\nu A\,,\quad f=2A^2/\nu \tag{71}$$

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[49] The table and Eq. (71) are derived primarily from our Eqs. (44), (46), (47), (49), (50), (57), (65), (66), and (70) and related discussion in the text.

[50] We take only the 2^3P state of He_2, as in other states the orbital angular momentum is too loosely coupled to the axis of figure, i.e. the non-centralness is too small, to permit application of the theory as we have given it. See section (e) of Mulliken's paper.

where A denotes the width of the spin doublet (or half that of the spin triplet) in wave numbers, ν is the wave number of the $P \rightarrow S$ transition, and $B = h/8\pi^2 Ic$. This is a change for reasons of numerical convenience from our previous convention in which A, B referred to measurements in ergs and ν to the frequency scale. The explicit formula (47) for the width of a ^1D sigma doublet has not been repeated, as this width is negligible; with for instance $B=5$, $\nu=10^4$, $l=2$, (47) gives $\Delta\nu \sim 10^{-8}(j^2-1)\ (j^2+2j)$ cm^{-1}. The sigma doubling for ^2D states has not been calculated in our paper, but is also clearly too small to detect, as it is easily seen to be of the third or higher order in B. In case (a) the sigma doubling of the $^2P_{3/2}$ component is likewise negligible unless j is exceedingly large;[51] $B=5$, $A=100$; $\nu=10^4$, for instance, makes the constant of porportionality b of the order 10^{-3} cm^{-1}.

A full enumeration of empirical results on sigma type doubling is given in the following paper by Mulliken, to which the reader is referred for numerical experimental results. The right hand column in our table gives the various types of molecules listed therein whose observed doubling corresponds to the predicted. In general the qualitative agreement is very satisfactory. The ^2P states are particularly interesting, as here both the theoretical predictions and experimental data are most copious. Molecules known to conform quite accurately to case (b) coupling are found experimentally to have an approximately equal doubling for both spin components, whereas those known to conform to case (a) exhibit a highly asymmetrical behavior of the two spin components, the doubling of the $P_{3/2}$ level being too small to resolve, whereas that of the $P_{1/2}$ is large and varies linearly with j. These are just the theoretical predictions. Hulthén's[45] experimental work on HgH even confirms the additive constant 1/2 in the theoretical factor $j+1/2$ for case (a) $^2P_{1/2}$ states.

To check the predicted order of magnitude for the constant a, and especially its mode of variation with A and B, one may take the observed values of A and B given by Mulliken in still another paper[52] and then determine the values of ν which make (71) yield the values of a found by Mulliken. The ν values so found are

$$\nu \times 10^{-4} = 2.8,\ 3.3\ (\mathrm{HgH});\ 3.3\ (\mathrm{CdH});\ 3.2\ (\mathrm{ZnH});\ 2.7\ (\mathrm{BO});\ 8.4\ (\mathrm{NO})^{53}\ \mathrm{cm}^{-1}.$$

This approximate constancy of the calculated ν from molecule to molecule must be regarded as quite remarkable, for the corresponding variation of the constant of proportionality a measuring the amount of sigma doubling is by a factor over 100. This variation of a is due mostly to the different spin doublet widths A ,which likewise vary by a factor over 100, whereas B

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[51] Hulthén[45] in his Fig. 5 seems to show that there is a perceptible doubling of the $^2P_{3/2}$ level for large values of j (20 or so) as we might expect. This is not to be confused with the perturbation phenomena he finds at $j=10$. The departures from linearity which he finds for large j in the $^2P_{1/2}$ component may be the beginning of the ultimate "crossing over" for this component predicted by our figure in section 5.

[52] R. S. Mulliken, Phys. Rev. **32**, 388 (1928), especially table 2.

[53] We make this calculation only for the normal state of NO as it is still uncertain whether the experimental value of a for the upper state is .005 or .025.

varies by a factor 6 in going from BO to HgH. The HgH molecule has the widest spin multiplet, and this is reflected in its holding the record for large sigma doubling. The two values of ν given for HgH are for different vibrational states $n=0$ and $n=1$ respectively, with account taken of the different moments of inertia found by Hulthén.[45]

The orders of magnitude 3×10^4 to 10^5 obtained for ν are indeed reasonable, as they correspond to an ultra-violet region in which molecular bands are quite common; the intense HgH $^2P-^2S$ bands, for instance, have $\nu=3\times10^4$ cm^{-1}. It must be emphasized that there is no reason why ν should be constant in going from one molecule to another except as regards rough orders of magnitude (perhaps the nearest decimal), for different molecules have different spectroscopic frequencies, and in the rigorous theoretical formulas the crude hypothesis of pure precession ought to be replaced by a complicated summation over all S states. For the latter reason, and also because l may actually be different from the value 1 assumed for simplicity, no agreement should be expected between the above calculated ν and an actual spectroscopic one, except on the order of magnitude. The agreement found above is closer than we should have any right to expect—especially remarkable is the approximate constancy of ν from element to element, which must mean that the $^2P\rightarrow{}^2S$ transitions that are involved are "peripheral" rather than "central" molecular properties, connected with outer rather than inner electrons. Another point, not shown by the above formulas for $\Delta\nu$, in which the theory and experiment are in accord, is that the center of a case (a) sigma doublet, i.e. mean of the two levels, is unaffected by the sigma doublet correction so that it can be represented without introducing a linear term in j. (Cf. note 8 of Mulliken's paper.)

A similar procedure may be applied to ^1P or case (b) ^2P and ^3P levels, and the values of ν determined which with known B will by (71) yield the observed C_1—C_2. The results are as follows

$\nu\times10^{-4}=0.2$ (AlH ^1P); 2.2 (CH ^2P); 3.4 (OH ^2P); .89 (He$_2$ ^3P): 2.7 (C$_2$ ^3P) cm^{-1}

The orders of magnitude are again sufficiently reasonable.[54]

The experimental data for case (a) ^3P states are rather qualitative, but give one of the most interesting confirmations of the theory. In N_2 the data quoted by Mulliken really seem to show that here the $^3P_2$ doubling is negligible, and the $^3P_0$ doubling practically independent of j, a particularly important point since the theory in section 7 indicated that the $^3P_0$ doubling should be primarily due to a magnetic action independent of the rotation j. The data indicate a detectable and smaller doubling for the $^3P_1$ state but are too qualitative to test the theoretical proportionality to $j(j+1)$, although the data for C_2 and He_2 do actually confirm the factor $j_k(j_k+1)$ in case (b). Again, we may note that for small values of j the rotational distortion is so small that C_2 comes closer to Hund's case (a) than case (b), although we have listed it (b) in the table, and it is found that the doubling for the $^3P_0$ com-

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[54] CH has a ^2S level 25,700 cm^{-1} above the normal ^2P state, but the close agreement of the calculated value 22,000 with this may be only fortuitous.

ponent extrapolates for $j=0$ to the finite value .4, whereas for the $^3P_1$ and $^3P_2$ components it probably extrapolates to zero. Here also the predicted effect is thus confirmed. The data on ^3P states in case (a) are not sufficiently accurate to permit the calculation of ν values as in the other cases. The reason is that the multiplet widths are not known, and that further it has not yet been possible to resolve the contributions of the initial and final states to the observed spectral bands. (For this reason the ν value for C_2 in case (b) given in the preceding paragraph is not reliable). We must thus be content with examining whether the observed values .24 (N_2) and .4 (C_2) for the constant f are at all reasonable. If for example we set $A=100$, $\nu=2\times10^4$, Eq. (71) gives $f=1$, a value sufficiently close.

Some of the molecules (CO, H_2, CaH, MgH) in Mulliken's table have not been included in our right hand column. In CO the doubling is too small to resolve and in CaH, MgH the variation with j seems to be rather irregular, while the data for H_2 are too qualitative to be useful. The irregular variation in MgH or CaH may be due to a coupling intermediate between the limiting cases (a) and (b), where a simple behavior can no longer be expected, or more likely that for some of the j values there is a close resonance between an S and a P state, so that the frequency ν in the denominator is nearly zero instead of large as we suppose throughout.[55] In fact band spectrum analysis shows that in CaH there is a ^2S state very near the ^2P, and under these circumstances we should expect a large, irregular doubling. This is reflected in the ^2S state actually exhibiting an unusually large rho-doubling, as we should expect with the explanation of rho-doubling given in section 6 as a rotational distortion effect, but not with the older explanation as magnetization by nuclear rotation. Such a close resonance between an S and a P state gives rise to the phenomena of "perturbations" and "predissociation" which have been treated by Kronig,[6] and which we do not aim to discuss in the present paper although the mathematics is very similar to that we use. We may, however, note that this perturbation effect explains nicely why Hulthén observes a pronounced sigma doubling of the $^2P_{3/2}$ state in HgH at a certain critical j although in general the doubling in this state is inconsequential except for great j.

In case (a) the asymmetrical doubling behavior of the various components, in which the lowest value of σ gives the widest sigma doubling, furnishes a valuable criterion for determining whether a spin multiplet is "normal" or "inverted" if not known otherwise. This idea was suggested to me by Professor Mulliken. The sigma doubling shows, for instance, unequivocably that the BO spin doublet is inverted, a point not quite certain otherwise. In C_2 and N_2 it identifies the P_0-P_0 bands but does not tell whether the N_2 multiplets are regular or inverted as existing spectroscopic data does not ioslate the energy contributions of the initial and final states.

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[55] These causes may explain why Mulliken finds C_1-C_2 to be 25 per cent greater for one spin component of OH than for the other. In particular there is here not ideal case (b) so that traces of case (a) dissymmetry may have begun to show.

We shall not discuss in detail the experimental confirmation of the formula for rho-type doubling, but experiment seems to confirm nicely the theoretical type of variation with j and the prediction that the constant of proportionality a' be of roughly the same magnitude as the doubling constant a for case (a) P states.[56]

The writer wishes to express his hearty thanks to Professor Mulliken for much useful information on the experimental data and to Professor Kemble for valuable suggestions on rho-type doubling.

Department of Physics,
University of Wisconsin,
January 31, 1929.

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[56] The experimental values of the constant a' in ^2S doublets are often very close to the constant a in the ^2P ones. (See Fig. 4 of ref. [52]) (The distinction in sign given by 71 is not detectable.) An exact equality is not to be expected, as the hypothesis of pure precession is not accurate, and also we have neglected the part of rho-type doubling due to magnetic moment developed by nuclear orbital motions, so that we ought to add in the contribution given by Eqs. (67–68). We have not included (68) in (71) as (71) aims only at orders of magnitude. However, experimental evidence for nearly equal a' and a may be taken to mean strong interaction between a given P and S state.