On Λ-Type Doubling in $^3\Pi$ States of Diatomic Molecules Intermediate Between Hund's Cases *a* and *b*

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Theoretical formulas based on the work of Van Vleck are developed for the Λ-type doubling in $^3\Pi$ states with coupling intermediate between Hund's cases *a* and *b*. Heretofore only the limiting cases *a* and *b* had been considered for triplet states. It is shown that, in addition to the usual splitting caused by the $\Pi-\Sigma$ interaction, there is a contribution to the doubling of the $^3\Pi_0$ component which arises from the magnetic spin-spin coupling between individual electrons. The expressions for the doubling necessitate the numerical solution of a cubic equation for each value of J but are otherwise simple and easy of application. Comparison with experiment is made in the case of N_2 where good numerical agreement is found. The fine structure of $^3\Sigma$ states which is called ρ-type tripling is also considered. It is shown that this fine structure can arise from perturbation by Π states—a sort of reflection of the Λ-type doubling in these states. Curiously, it is found that the formulas which are derived in this manner give separations depending on the rotational quantum number K in exactly the same way as the formulas of Kramers which were obtained from quite a different origin, *viz.*, spin-spin interaction and coupling of the spin to the rotational magnetic moment of the molecule.

1. Introduction[1]

The general theory of Λ-type doubling in diatomic molecules, including spin effects, has been treated by Van Vleck.[2] He has calculated the width of the Λ-type doublets explicitly for $^2\Pi$ states intermediate between Hund's cases *a* and *b* but for $^3\Pi$ states only in the ideal limiting cases *a* and *b*. The general intermediate case for molecules in $^3\Pi$ states will be treated in this paper.

In both Hund's cases *a* and *b* the axial field due to the separation of the atomic nuclei is pronounced enough to give the component of the electronic orbital angular momentum parallel to the molecular axis a quantized value[3] Λ. In Hund's case *a* the spin-orbit interaction couples the spin to the axis of the molecule so that its parallel component has a quantized value Σ. The sum of Λ and Σ denoted by Ω is the parallel component of the total electronic angular momentum. In Hund's case *b* the effect of the rotation of the molecule on the spin predominates over the spin-orbit coupling and the spin becomes decoupled from the molecular axis. Then of course Σ and Ω cease to have a meaning.

In the absence of molecular rotation the two states (Λ, Σ) and $(-\Lambda, -\Sigma)$ are ordinarily[4] degenerate since they differ only in the sense of rotation about the molecular axis. The rotation of the molecule removes this degeneracy and results in a splitting of the energy levels. This separation is called the Λ-type doubling.

Following Van Vleck we shall consider the interaction between the $^3\Pi$ state in which we are interested and a single $^3\Sigma$ state. We shall later take account of the remaining $^3\Sigma$ states by a summation. This is, of course, equivalent to finding the interaction between the $^3\Pi$ state and all the $^3\Sigma$ states but of neglecting the influence of the $^3\Sigma$ states on one another. The $^3\Delta$ states have a negligible effect on the Λ-type doubling in $^3\Pi$ states and are disregarded.

Van Vleck has given the Hamiltonian matrix elements for the diatomic molecule using an unperturbed representation appropriate to Hund's case *a*. These elements are[5]

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[1] A preliminary report of this work was given in abstract 13 of the Minneapolis meeting of the American Physical Society, June 1935 (Phys. Rev. **48**, 475 (1935)).

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

[3] Strictly, the parallel component alternates rapidly between $+\Lambda$ and $-\Lambda$ and has an average value zero. Its square, however, has the quantized value Λ^2. As is customary, the angular momentum is measured in quantum units $h/2\pi$.

[4] Note, however, the exceptional case of $^3\Pi_0$ where the degeneracy between the two Λ components is removed by the spin-orbit and spin-spin coupling even for $J=0$.

[5] J. H. Van Vleck, reference 2. The first three of Eqs. (1) are, respectively, Van Vleck's Eqs. (32), (31) and (29); the fourth follows immediately from Eqs. (54), (30) and (20) with the modification explained at the foot of page 493 of his article.

$$\begin{aligned}
\mathcal{H}(nv\Lambda\Sigma;\, nv\Lambda\Sigma) &= C(nv\Lambda;\, nv\Lambda)+A(nv\Lambda;\, nv\Lambda)\Lambda\Sigma+B(nv\Lambda;\, nv\Lambda)[J(J+1)-\Omega^2+S(S+1)-\Sigma^2],\\
\mathcal{H}(nv\Lambda\Sigma;\, nv\Lambda\Sigma\pm 1) &= B[J(J+1)-\Omega(\Omega\pm 1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma\pm 1)]^{\frac{1}{2}},\\
\mathcal{H}(nv\Lambda\Sigma;\, n'v'\Lambda\pm 1\Sigma) &= 2(BL_x)(nv\Lambda;\, n'v'\Lambda\pm 1)[(J\pm\Omega+1)(J\mp\Omega)]^{\frac{1}{2}},\\
\mathcal{H}(nv\Lambda\Sigma;\, n'v'\Lambda\pm 1\Sigma\mp 1) &= (AL_x+2BL_x)(nv\Lambda;\, n'v'\Lambda\pm 1)[S(S+1)-\Sigma(\Sigma\mp 1)]^{\frac{1}{2}}.
\end{aligned} \tag{1}$$

Here $\mathcal{H}$ is the total Hamiltonian operator for the diatomic molecule. The elements (1) are complete except for omission of the small centrifugal swelling effect mentioned in footnote 17, a very small term to take account of the magnetic coupling of the **L** and **S** vectors with the field set up by the molecule's end over end rotation, and the terms due to the magnetic spin-spin interaction which will be considered in the next section. The symbol A denotes the coefficient of the spin-orbit coupling which is taken to be of the form $A(\mathbf{L}\cdot\mathbf{S})$. The additive constant C is fixed for an electronic state and serves to give the molecular energy exclusive of multiplet and rotational structure. The arguments of A and $B=h^2/8\pi^2 I$ have not been written in, except in the first Eq. (1). $L_x(nv\Lambda;\, n'v'\Lambda')$ denotes the matrix element of the component of electronic orbital angular momentum in the x direction, perpendicular to the molecular axis, for the stationary molecule. The spin quantum number and the total angular momentum quantum number for the molecule have been designated by S and J, respectively. We have used v for the vibrational quantum number and n to symbolize all the remaining electronic quantum numbers which have not been shown explicitly.

2. MATRIX ELEMENTS FOR THE SPIN-SPIN INTERACTION

The matrix elements (1) given by Van Vleck do not include terms which arise from the magnetic coupling of the individual spins. These elements are diagonal in Ω and hence were of no importance in the cases which he considered with the exception of the doubling for $^3\Pi_0$ states.

The spin-spin coupling energy can be taken in the form[6]

$$\mathcal{H}_{ss}=4\beta^2\sum_{j>i}[-3(\boldsymbol{s}_i\cdot\boldsymbol{r}_{ij})(\boldsymbol{s}_j\cdot\boldsymbol{r}_{ij})+(\boldsymbol{s}_i\cdot\boldsymbol{s}_j)r_{ij}{}^2]/r_{ij}{}^5, \tag{2}$$

where β is the Bohr magneton and i, j refer to the various electrons. The matrix elements of (2) in our axial representation are all seen to be diagonal in Ω but may have $\Delta\Lambda=\Delta\Sigma=0$, $\Delta\Lambda=-\Delta\Sigma=\pm 1$, or $\Delta\Lambda=-\Delta\Sigma=\pm 2$. The elements diagonal in Λ and Σ are not of interest for the Λ-type doubling. These elements give rise to the fine structure of the $^3\Sigma$ state which has been considered by Kramers[7] and which will be mentioned later in section 6. The elements with $\Delta\Lambda=-\Delta\Sigma=\pm 1$ yield small terms connecting the Π and Σ states. However, as these elements are much smaller than those of (1) of the same type already connecting the Π and Σ states, they can safely be ignored. On the other hand, the elements for which $\Delta\Lambda=-\Delta\Sigma=\pm 2$ have no counterpart in (1) and though small cannot be disregarded since they connect the initially degenerate $^3\Pi_0$ states which have $\Lambda=-\Sigma=+1$ and -1. These states will be designated $+{}^3\Pi_0$ and $-{}^3\Pi_0$, respectively. The part of (2) which yields elements between them is

$$-3\beta^2\sum_{j>i}[s_i{}^+s_j{}^+(r_{ij}{}^-)^2+s_i{}^-s_j{}^-(r_{ij}{}^+)^2]/r_{ij}{}^5,$$

where $$s_i{}^\pm=s_{x_i}\pm is_{x_i},$$

and $$r_{ij}{}^\pm=x_{ij}\pm iy_{ij}=(x_i\pm iy_i)-(x_j\pm iy_j).$$

The z axis is here taken along the axis of the molecule.

Let us suppose, for simplicity, that there are only two electrons outside of closed shells and consider the interaction of the states $+{}^3\Pi_0$ and $-{}^3\Pi_0$. We may take the orbital parts of the wave functions to be[8]

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[6] See, for example, H. A. Kramers, Zeits. f. Physik **53**, 422 (1929).

[7] H. A. Kramers, reference 6.

[8] The minus sign appearing in ψ_- is inserted to take care of the behavior of the spin functions on reflection in a plane containing the nuclei. With this convention in phases, the complete wave function for the $+\Pi$ state transforms into that for the $-\Pi$ state on the above reflection. Cf. J. H. Van Vleck, Phys. Rev. **40**, 544 (1932), especially page 559.

$$-\psi_{-}=\psi_{+}^{*}=(8\pi^{2})^{-\frac{1}{2}}[u_{\sigma}(r_{1},\theta_{1})u_{\pi}(r_{2},\theta_{2})e^{-i\phi_{2}}-u_{\sigma}(r_{2},\theta_{2})u_{\pi}(r_{1},\theta_{1})e^{-i\phi_{1}}],$$

where ψ_+ and ψ_- refer, respectively, to the states $+{}^3\Pi_0$ and $-{}^3\Pi_0$. Here $u_\sigma(r, \theta)$ is the wave function appropriate to a single electron having λ or m_l equal to zero. The similar function $u_\pi(r, \theta)e^{i\phi}$ has $\lambda = m_l = +1$. The arguments r, θ, ϕ of these functions are the usual polar variables with the azimuthal angle ϕ measured in the positive sense around the z axis from the xz plane. Throughout we use an asterisk to denote the complex conjugate. The functions $u(r, \theta)$ without the ϕ-factor can be supposed real. The expression r_{12}^+ is now the same as $r_1 \sin\theta_1 e^{i\phi_1} - r_2 \sin\theta_2 e^{i\phi_2}$. We then have

$$\mathcal{H}_{ss}(+{}^3\Pi_0;\,-{}^3\Pi_0) = -3\beta^2\int\cdots\int\psi_+^*(r_1\sin\theta_1 e^{i\phi_1}-r_2\sin\theta_2 e^{i\phi_2})^2(r_{12})^{-5}\psi_- dv_1 dv_2,$$

since the spin factors reduce to unity. The integrand is everywhere finite on account of the nodes in the wave functions ψ wherever the electrons coincide. Now the interelectronic distance r_{12} involves the azimuthal angles ϕ_1 and ϕ_2 only through a factor $\cos(\phi_1-\phi_2)$. Similarly, the rest of the integrand depends on $\phi_1-\phi_2$ but not on $\phi_1+\phi_2$. Hence we can transform to these linear combinations as new azimuthal variables and perform the integration over $\phi_1+\phi_2$. We then find

$$\mathcal{H}_{ss}(+{}^3\Pi_0;\,-{}^3\Pi_0) = (3/2\pi)\beta^2\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\int_0^\pi\sin\theta_1d\theta_1\int_0^\pi\sin\theta_2d\theta_2\int_0^\pi[(U^2-V^2)/r_{12}^5]d(\phi_1-\phi_2)$$

$$=\alpha({}^3\Pi),\quad\text{say,}\tag{3}$$

where U and V are both real and are equal, respectively, to

$$[u_\sigma(r_1,\theta_1)u_\pi(r_2,\theta_2)r_1\sin\theta_1+u_\sigma(r_2,\theta_2)u_\pi(r_1,\theta_1)r_2\sin\theta_2]\cos(\phi_1-\phi_2)$$
$$-u_\sigma(r_1,\theta_1)u_\pi(r_2,\theta_2)r_2\sin\theta_2-u_\sigma(r_2,\theta_2)u_\pi(r_1,\theta_1)r_1\sin\theta_1$$

and

$$[u_\sigma(r_1,\theta_1)u_\pi(r_2,\theta_2)r_1\sin\theta_1-u_\sigma(r_2,\theta_2)u_\pi(r_1,\theta_1)r_2\sin\theta_2]\sin(\phi_1-\phi_2).$$

Sign of $\alpha({}^3\Pi)$. It can be easily shown that if the factor r_{12}^{-5} is omitted in (3), then the resulting integral is positive. The effect of reinserting this factor will clearly be to accentuate the contribution to the integral from those regions of configuration space where the electrons are very close together. The contribution from these regions is always positive. This can be shown by holding one electron fast and expanding the integrand of (3) in a Taylor's series in the coordinates of the other electron about the position of the first. If one retains only the nonvanishing terms of lowest order and then integrates over the volume or surface of a small sphere around the fixed electron, one finds that the result is always positive whatever the position of the fixed electron. Hence, if the functions u_σ and u_π vary slowly enough in space so that the region in which the first term of the Taylor's expansion is accurate, includes the region of important contribution to the integral, then the integral will surely be positive.

3. The Λ-Type Doubling

From Eqs. (1) and (3) we obtain the necessary matrix elements for our problem. The resulting ninth order Hamiltonian matrix, for the interaction of the Π with one Σ state, can be reduced to one of fourth and one of fifth order by applying the well-known Wang transformation whose matrix elements are given by Van Vleck.[9] This reduction corresponds to a transformation to wave functions with the Kronig (+) or (−) symmetry or antisymmetry on reflection of space and spin coordinates of all particles in the origin. Such symmetry property the original functions with constant angular

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[9] J. H. Van Vleck, reference 2, p. 495.

momentum about the molecular axis did not have. This is tantamount to using sine and cosine rather than exponential azimuthal factors in the wave functions. After the reduction, the Hamiltonian matrices are

$$\begin{array}{c||ccccc||}
{}^3\Pi_2 & B_\pi(x-3)+A_\pi & B_\pi(2x-4)^{\frac{1}{2}} & 0 & 2\eta(x-2)^{\frac{1}{2}} & 0 \\
{}^3\Pi_1 & B_\pi(2x-4)^{\frac{1}{2}} & B_\pi(x+1) & B_\pi(2x)^{\frac{1}{2}} & 2^{\frac{1}{2}}(\xi+2\eta) & [1-(-1)^\Sigma]\eta(2x)^{\frac{1}{2}} \\
{}^3\Pi_0 & 0 & B_\pi(2x)^{\frac{1}{2}} & B_\pi(x+1)-A_\pi+\alpha & -(-1)^\Sigma 2\eta x^{\frac{1}{2}} & [1-(-1)^\Sigma](\xi+2\eta) \\
{}^3\Sigma_1 & 2\eta^*(x-2)^{\frac{1}{2}} & 2^{\frac{1}{2}}(\xi+2\eta)^* & -(-1)^\Sigma 2\eta^* x^{\frac{1}{2}} & B_\Sigma x-h\nu(\Pi;\Sigma) & [1-(-1)^\Sigma]B_\Sigma x^{\frac{1}{2}} \\
{}^3\Sigma_0 & 0 & [1-(-1)^\Sigma]\eta^*(2x)^{\frac{1}{2}} & [1-(-1)^\Sigma](\xi+2\eta)^* & [1-(-1)^\Sigma]B_\Sigma x^{\frac{1}{2}} & B_\Sigma(x+2)-h\nu(\Pi;\Sigma)
\end{array} \tag{4a}$$

and

$$\begin{array}{c||ccccc||}
{}^3\Pi_2 & B_\pi(x-3)+A_\pi & B_\pi(2x-4)^{\frac{1}{2}} & 0 & 2\eta(x-2)^{\frac{1}{2}} & 0 \\
{}^3\Pi_1 & B_\pi(2x-4)^{\frac{1}{2}} & B_\pi(x+1) & B_\pi(2x)^{\frac{1}{2}} & 2^{\frac{1}{2}}(\xi+2\eta) & [-1-(-1)^\Sigma]\eta(2x)^{\frac{1}{2}} \\
{}^3\Pi_0 & 0 & B_\pi(2x)^{\frac{1}{2}} & B_\pi(x+1)-A_\pi-\alpha & (-1)^\Sigma 2\eta x^{\frac{1}{2}} & [-1-(-1)^\Sigma](\xi+2\eta) \\
{}^3\Sigma_1 & 2\eta^*(x-2)^{\frac{1}{2}} & 2^{\frac{1}{2}}(\xi+2\eta)^* & (-1)^\Sigma 2\eta^* x^{\frac{1}{2}} & B_\Sigma x-h\nu(\Pi;\Sigma) & [-1-(-1)^\Sigma]B_\Sigma x^{\frac{1}{2}} \\
{}^3\Sigma_0 & 0 & [-1-(-1)^\Sigma]\eta^*(2x)^{\frac{1}{2}} & [-1-(-1)^\Sigma](\xi+2\eta)^* & [-1-(-1)^\Sigma]B_\Sigma x^{\frac{1}{2}} & B_\Sigma(x+2)-h\nu(\Pi;\Sigma)
\end{array} \tag{4b}$$

with the abbreviations $x=J(J+1)$, $\xi=(AL_x)(\Pi;\Sigma)$ and $\eta=(BL_x)(\Pi;\Sigma)$. In writing the matrices (4) we have used the relation $(L_x)(+\Pi;\Sigma)=-(-1)^\Sigma(L_x)(-\Pi;\Sigma)$, where $+\Pi$ and $-\Pi$ refer to the states with $\Lambda=+1$ and -1, respectively, and where the exponent Σ is zero or one according as the Σ state is Σ^+ or Σ^-. A Σ state is defined as Σ^+ or Σ^- according as its wave function remains unchanged or reverses sign on reflection of the electronic space coordinates in a plane containing the nuclei.

It is to be clearly understood that for a given ${}^3\Sigma$ state, elements relating to the ${}^3\Sigma_0$ component appear in only one of the matrices (4); i.e., the single ${}^3\Sigma_0$ state factors with (4a) when Σ is Σ^- and with (4b) when Σ is Σ^+. On account of the factors $[\pm 1-(-1)^\Sigma]$ in (4) all the off-diagonal elements for the ${}^3\Sigma_0$ state vanish for one of these matrices and the corresponding diagonal element for this state is to be rejected. Hence one of the matrices (4) always reduces to one of fourth order. Indeed we could have written (4) directly as one fifth and one fourth order matrix but then the terms $\pm\alpha$ would have appeared with a coefficient $(-1)^\Sigma$ and the correspondence of the matrices (4) to the $(\pm)$ linear combinations of the original wave functions would have depended on the symmetry of the Σ state. As we have actually written (4), the wave functions which are associated with the first matrix (4a) are even linear combinations of the original functions and hence are even on reflection of orbital and spin coordinates in a plane containing the nuclei, while those associated with the second matrix (4b) are odd. Thus the complete wave functions for (4a) are $(+)$ or $(-)$ and those for (4b) are $(-)$ or $(+)$ according as J is even or odd.

It may be mentioned here that the secular determinant which corresponds to the Π portion of (4) yields the following cubic equation whose roots are $W({}^3\Pi_2)$, $W({}^3\Pi_1)$ and $W({}^3\Pi_0)$ exclusive of the Λ-type doubling effects:

$$\begin{vmatrix}
B_\pi(x-3)+A_\pi-W & B_\pi(2x-4)^{\frac{1}{2}} & 0 \\
B_\pi(2x-4)^{\frac{1}{2}} & B_\pi(x+1)-W & B_\pi(2x)^{\frac{1}{2}} \\
0 & B_\pi(2x)^{\frac{1}{2}} & B_\pi(x+1)-A_\pi-W
\end{vmatrix}=0 \tag{5}$$

with $x=J(J+1)$. This equation was given by Hill and Van Vleck[10] and recently used by Budó[11] for determining the ${}^3\Pi$ energy levels in the intermediate case $a-b$.

One sees on passing to Hund's case a by taking B/A equal to zero that the two matrices (4), aside from the extra diagonal element relating to the ${}^3\Sigma_0$ state, become identical in first order. The presence

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[10] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928), page 261.

[11] A. Budó, Zeits. f. Physik **96**, 219 (1935).

of the diagonal spin-spin terms $\pm\alpha$ for the $^3\Pi_0$ states and of the spin-orbit interaction term connecting the $^3\Pi_0$ and $^3\Sigma_0$ states in only one of the matrices (4) shows us that, as noted by Van Vleck,[12] there is a Λ-type doubling for the $^3\Pi_0$ component even in case a. Using first-order perturbation theory we find for this doubling

$$^3\Pi_0 \text{ case } a\colon\quad h\Delta\nu_0=(-1)^{J+1}[W(^3\Pi_{0+})-W(^3\Pi_{0-})]=\gamma-2\alpha+\kappa \tag{6}$$

with $\gamma=4\Sigma(-1)^{\Sigma}|(AL_x)(\Pi;\Sigma)|^2/h\nu(\Pi;\Sigma)$ and α as defined in section 2. Here κ is the contribution to the $^3\Pi_0$ doubling which arises from interaction of the $^3\Pi$ with $^1\Sigma$ and $^5\Sigma$ states. Van Vleck[12] has shown that this interaction, for case a coupling, yields a separation of the $^3\Pi_0$ states which is independent of J, but leaves $^3\Pi_1$ and $^3\Pi_2$ levels unaffected. The doubling which occurs when $\Omega=0$ thus has a different origin than the usual doubling introduced by the rotational distortion. The subscripts $\pm$ in Eq. (6), refer to the $(\pm)$ symmetry defined at the beginning of this section and are not to be confused with the notation of Section 2.

In the ideal limiting case b, obtained by setting A/B equal to zero and omitting the spin-spin terms $\pm\alpha$, we find that the quintic secular determinant corresponding to (4) factors into two quadratics and a linear term and that the quartic related to (4) reduces to a single quadratic and a pair of linear factors. These may be collected and expressed as

$$\begin{gathered}[W-h\nu(\Pi;\Sigma)-B_\Sigma K(K+1)][W+B_\pi-B_\pi K(K+1)]-8|(BL_x)(\Pi;\Sigma)|^2K(K+1)=0\\ \text{and}\qquad W+B_\pi-B_\pi K(K+1)=0\end{gathered} \tag{7}$$

with $K=J-1$, J and $J+1$. K is the usual rotational quantum number exclusive of spin which is characteristic of case b. As is to be expected in case b the spin has completely disappeared and Eqs. (7) are valid for Π and Σ states of any multiplicity. Hence the Λ-type doubling which is now the same for all three components with the same value of K is

$$^3\Pi_2,\ ^3\Pi_1,\ ^3\Pi_0 \text{ case } b\colon\quad h\Delta\nu=\epsilon K(K+1)\quad\text{where}\quad \epsilon=8\sum(-1)^{\Sigma}|(BL_x)(\Pi;\Sigma)|^2/h\nu(\Pi;\Sigma). \tag{8}$$

The behavior of the energy levels in the transition from case a to case b may be seen from Fig. 1 which is constructed according to the following rules:[13] (1). In case a the higher state of the Λ-type doublet is alternately $(+)$ and $(-)$ with respect to Kronig symmetry as J increases by unity. (2). In case b the higher state of the Λ-type doublet is alternately $(+)$ and $(-)$ as K increases by unity. (3). The state $J=0$ passes over into one of the states $K=1$ without a crossing of the levels. (4). The three multiplet components with the same value of J in case a pass over into three states in case b with K equal to $J-1$, J and $J+1$. In the special case $J=1$ there are only two pairs of states in case a but the value of $K=J-1=0$ in case b is missing. (5). No states having the same value of J and the same Kronig symmetry can cross.

4. The Λ-Type Doubling in the General Intermediate Case

In the intermediate case the elements connecting different $^3\Pi$ components are comparable with the $^3\Pi$ multiplet separations. However the elements connecting $^3\Pi$ and $^3\Sigma$ components are small in comparison with the $\Pi-\Sigma$ separation unless the Σ state accidentally lies very close to the Π state. The latter situation is exceptional and we shall proceed on the assumption that the Σ state is well removed. We then have a case of "near degeneracy"[14] for the Π states. The technique for such problems is to solve exactly the part of the problem relating to the nearly degenerate levels and then to handle the effect of the remaining states using perturbation methods. This means that we must diagonalize the

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[12] J. H. Van Vleck, Phys. Rev. **40**, 544 (1932), Section 4; also reference 2, Section 7.

[13] In drawing Fig. 1, it has been assumed that the constants C_0 and γ have the same sign. Otherwise, the symmetries of the $^3\Pi_0$ and $^3\Pi_1$ components in case a may be reversed.

[14] Cf. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, p. 137.

third order matrix consisting of the Π portion of either of the matrices (4) disregarding the small terms $\pm\alpha$, i.e., solve the matrix equation $S^{-1}\mathcal{H}S = W$ for S and W. Here $\mathcal{H}$ is the Π portion of the matrix (4), W is the diagonal matrix consisting of the eigenvalues of $\mathcal{H}$, and S is a unitary transformation matrix. Explicitly we have to solve the following system of linear homogeneous equations for the elements of S:[15]

$$\begin{aligned}
[B_\pi(x-3)+A_\pi-W({}^3\Pi_i)]S({}^3\Pi_2;\,{}^3\Pi_i)+B_\pi(2x-4)^{\frac{1}{2}}S({}^3\Pi_1;\,{}^3\Pi_i)&=0,\\
B_\pi(2x-4)^{\frac{1}{2}}S({}^3\Pi_2;\,{}^3\Pi_i)+[B_\pi(x+1)-W({}^3\Pi_i)]S({}^3\Pi_1;\,{}^3\Pi_i)+B_\pi(2x)^{\frac{1}{2}}S({}^3\Pi_0;\,{}^3\Pi_i)&=0,\\
B_\pi(2x)^{\frac{1}{2}}S({}^3\Pi_1;\,{}^3\Pi_i)+[B_\pi(x+1)-A_\pi-W({}^3\Pi_i)]S({}^3\Pi_0;\,{}^3\Pi_i)&=0
\end{aligned}\tag{9}$$

with $i=2, 1, 0$. The usual conditions for the consistency of these nine equations, *viz.*, that the three determinants (one for each of $i=2, 1, 0$) of the coefficients of the elements of S shall vanish, gives us the familiar secular Eq. (5) which determines the W's except for Λ-type doubling effects. Let us suppose that Eq. (5) has been solved and that the transformation matrix S has been determined from (9). We then apply this transformation to the two matrices (4), first, however, piecing out the matrix S in the usual way with unit diagonal elements and zeros off the diagonal until it has the proper dimensions. The transformed matrices now have no large off-diagonal elements connecting the various ${}^3\Pi$ components. Because of the presence of the terms $\pm\alpha$ in (4) but not in the matrix which S is designed to diagonalize one finds that after the transformation the matrices (4) do have elements connecting the ${}^3\Pi$ components. These elements all involve α as a factor and hence are small in comparison with the ${}^3\Pi$ multiplet widths. Our "near degeneracy" difficulties are then removed and all the off-diagonal elements can be treated by perturbation theory.

We could immediately write down the energies of the three levels for each of the matrices (4). These expressions are rather cumbersome and, as we are chiefly interested in the widths of the Λ-type doublets, we shall give only the differences between corresponding eigenvalues of (4a) and (4b). On summing over Σ states these are

$$\begin{aligned}
h\Delta\nu_i = {} & C_0[S({}^3\Pi_0;\,{}^3\Pi_i)]^2+C_1[2J(J+1)]^{\frac{1}{2}}S({}^3\Pi_1;\,{}^3\Pi_i)S({}^3\Pi_0;\,{}^3\Pi_i)\\
& +C_2\{J(J+1)[S({}^3\Pi_1;\,{}^3\Pi_i)]^2+2[(J-1)J(J+1)(J+2)]^{\frac{1}{2}}S({}^3\Pi_2;\,{}^3\Pi_i)S({}^3\Pi_0;\,{}^3\Pi_i)\},
\end{aligned}\tag{10}$$

where $i=2, 1, 0$ for the three components. Here $C_0=\gamma+\delta+2\epsilon-2\alpha+\kappa$, $C_1=\delta+4\epsilon$, $C_2=\epsilon$. The constants α, γ, ϵ are given by Eqs. (3), (6), (8), respectively, while κ is explained below Eq. (6) and

$$\delta = 16\times\text{real part of }\Sigma(-1)^{\Sigma}(AL_x)(\Pi;\,\Sigma)(BL_x)(\Sigma;\,\Pi)/h\nu(\Pi;\,\Sigma).$$

5. APPLICATION TO THE FIRST POSITIVE BANDS OF THE NITROGEN MOLECULE

The most extensive data on the structure of a ${}^3\Pi$ state have been obtained by Naudé[16] from the analysis of the first positive bands of nitrogen ($B^3\Pi-A^3\Sigma$). He has analyzed both the fifth and sixth vibrational levels of the ${}^3\Pi$ upper state. We shall however consider here only the latter. In order to apply the theory of section 4 we must

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[15] In writing the elements of S, we have made no distinction between initial and final indices. It is to be understood that the first index refers to the case *a* representation while the second refers to the final representation intermediate between cases *a* and *b*.

[16] S. M. Naudé, Proc. Roy. Soc. **A136**, 114 (1932). Naudé notes at the foot of page 136 that the signs of the Λ-type separations which he gives in Table XIII have only a relative meaning. If one wishes to determine the absolute signs of these separations one must redefine the quantities given by his Eqs. (14) and (15) to be consistent with the corresponding definitions (12), (13), (16) and (17). The two definitions to replace (14) and (15) are, respectively:

$$\begin{aligned}
\Delta_1F_{2ba}'(J) &= F_{2b}'(J+1)-F_{2a}'(J) = {}^SR_{21}(J)-{}^RQ_{21}(J)\\
&= Q_2(J+1)-P_2(J+1) = {}^Q\mathrm{R}_{23}(J)-{}^PQ_{23}(J)\\
\Delta_1F_{2ab}'(J) &= F_{2a}'(J)-F_{2b}'(J-1) = {}^RQ_{21}(J)-{}^QP_{21}(J)\\
&= R_2(J-1)-Q_2(J-1) = {}^PQ_{23}(J)-{}^OP_{23}(J).
\end{aligned}$$

It is then seen that the Λ-type doubling for the ${}^3\Pi_1$ component is of the same sign as that for the ${}^3\Pi_2$ and ${}^3\Pi_0$ components. This modification requires a slight change in Naudé's Fig. 2. All transitions originating in the ${}^3\Pi_1$ component should be shown as coming from the opposite members of the Λ-type doublets. The designation of the *a* and *b* levels and of the symmetries of the states which he gives is correct. In addition, the three transitions $R_2(0)$, $P_2(1)$ and ${}^PQ_{23}(0)$, all of which relate to nonexistent states, should be deleted from Table III.

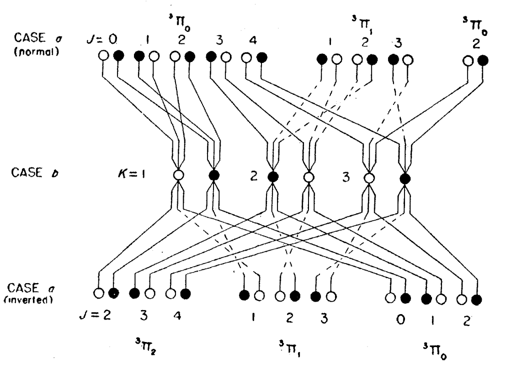

FIG. 1. Schematic diagram of the case $a-b$ energy level correlations. The circles and dots designate levels of different (±) symmetry. The state in the upper right corner is $^3\Pi_2$ instead of $^3\Pi_0$ as shown.

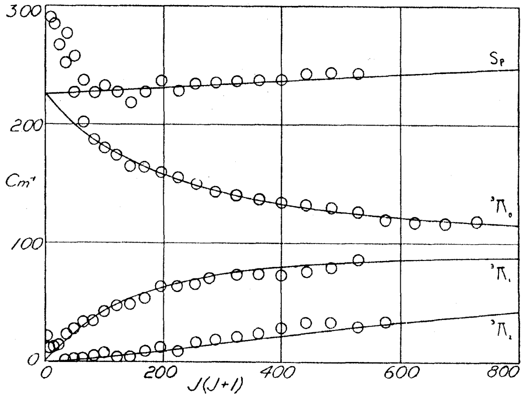

FIG. 2. Λ-type doubling of $B^3\Pi$ levels of N_2. The experimental data are shown by the small circles and the calculated doublet values by the full lines. The upper curve labeled *Sp* is the sum of the Λ-type doublet widths for the three multiplet components. The vertical scale should read 0.0, 1.0, 2.0, 3.0 cm^{-1}.

determine the two constants B, A for this state.[17] The constant B for the $^3\Pi$ state may be found by comparing the spur or diagonal sum of the third order Π part of (4) with the experimental term values of the three components of the Π state. This spur has the form $[3J(J+1)-1]B_\pi$. The first term gives the value of B_π and the second fixes the arbitrary term value origin with relation to our origin of energy. The value of A_π can then be obtained, in the manner employed by Gilbert,[18] from the constant part of the expression $(1/3)(Sp\ R)^2 - Sp\ RR' = 4B_\pi{}^2J(J+1)+(4/3)B_\pi{}^2 - 4B_\pi A_\pi + A_\pi{}^2$, where $Sp\ R$ is the diagonal sum just mentioned and $Sp\ RR'$ is the sum of products of the $^3\Pi$ roots taken two at a time. This equation can be deduced readily from Eq. (5). The values of B_π and A_π adopted in this paper are 1.512 cm^{-1} and 42.2 cm^{-1}, respectively.

Before we can apply Eqs. (10) we must determine the transformation matrix S which was introduced in section 4. This necessitates solution of the cubic secular Eq. (5). It has been found simplest to make this solution numerically for each value of J; although the experimental term values, adjusted as to origin as explained above, may be taken as approximate roots. The transformation coefficients[19] are then readily found with the help of Eqs. (9).

Eqs. (10) which give the Λ-type doubling, contain three adjustable constants C_0, C_1, C_2. The values of these constants[20] which give the best fit with the experimental data are $C_0 = 2.27$ cm^{-1}, $C_1 = 0.0095$ cm^{-1}, $C_2 = 0.00026$ cm^{-1}. The calculated Λ-type doubling is shown by the curves in Fig. 2. The corresponding experimental points are indicated by circles. The agreement with experiment is satisfactory except for very small values of J for the $^3\Pi_0$ component and for the spur (sum of doubling widths for the three components). This latter should have the particularly simple form $C_0 + C_2J(J+1)$. It may be pointed out that the experimental error is considerably larger for the first few values of J than for later values. However this is undoubtedly not the reason for the deviation whose explanation is possibly to be found in a resonance effect due to a very near Σ state for these values of J. Such an effect has been noted by Van Vleck in the case of Hulthén's observations on HgH.[21]

One sees on examining Fig. 2 that the character of the doubling for small J is appropriate to

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[17] We have neglected entirely the small term in the energy which comes from the centrifugal swelling of the molecule. Since the binding of the two atoms is in first approximation harmonic, the energy term introduced by the swelling is of the form $DJ^2(J+1)^2$ where D is a small negative coefficient. In our case, we have taken $D = -3\times10^{-6}$ cm^{-1}. In order to apply the theory as we give it, this small term should be subtracted from the experimental data. However, neither the constants A, B nor the Λ-type doubling are exceedingly sensitive to this correction.

[18] See following paper in this issue.

[19] To save space, the table of transformation matrix elements has been omitted. This table for the case $B/A = 0.0358$, $J = 2-25$ may be obtained from the writer.

[20] At this point, we are considering only the relative signs of the C's. That the signs are here all the same simply reflects the fact that for the same value of J the upper members of the doublets for the three multiplet components are all either (+) or (−).

[21] See page 505 of reference 2.

case a (i.e., large constant doubling for $^3\Pi_0$, small doubling proportional to $J(J+1)$ for $^3\Pi_1$ and negligible doubling for the $^3\Pi_2$ component) but that, as J increases and the rotational distortion comes into effect, the doubling tends to become characteristic of case b (i.e., equal doubling increasing as $K(K+1)$ for the three components).

Theoretical consideration of the constants C_0, C_1 *and* C_2. Heretofore, we have regarded the quantities C_0, C_1 and C_2 and hence $(\gamma-2\alpha+\kappa)$, δ and ϵ as adjustable constants at our disposal. We can examine the constants γ, δ and ϵ theoretically if we assume that Van Vleck's *hypothesis of pure precession*[22] is a good approximation. This condition states that the electronic orbital angular momentum of the molecule is a vector of fixed magnitude which precesses uniformly about the molecular axis, and further that A and B are diagonal matrices. Then each of the sums γ, δ, ϵ reduces to a single term for which $L_x(\Pi;\Sigma) = \frac{1}{2}[L(L+1)]^{\frac{1}{2}}$. We then have from Eqs. (6), (8) and (10)

$$\gamma=A^2L(L+1)/\nu,\quad \delta=4ABL(L+1)/\nu,\quad \epsilon=2B^2L(L+1)/\nu. \tag{11}$$

If we now use the values of A and B found for the Π state and take $L=1$, we find that the effective frequencies deduced with the aid of Eqs. (11) from the experimental values of δ and ϵ are respectively 6×10^4 cm^{-1} and 3.5×10^4 cm^{-1}, in sufficiently good agreement considering the approximate nature of Eqs. (11). The mean of these values, say 5×10^4 cm^{-1}, substituted back into the first Eq. (11) yields $|\gamma|=0.07$ cm^{-1}. Thus $\kappa-2\alpha$ must constitute practically all of C_0. Now α seems to have the wrong sign to account for the observed Λ-type doubling in N_2 (cf. following paragraph and also end of Section 2) so that we must suppose C_0 to arise here chiefly from the interaction of the $^3\Pi$ state with neighboring $^1\Sigma$ and $^5\Sigma$ states. As explained earlier, this interaction is capable of producing a separation of the $^3\Pi_0$ levels but, with pure case a coupling, is powerless to split $^3\Pi_1$ or $^3\Pi_2$.

Experimental sign of C_0 *in* N_2. It is evident from the Eqs. (6) and (10), that the sign of C_0 is positive or negative according as the $(-)$ or $(+)$ levels are higher for even J. Experimentally the $(+)$ or $(-)$ character of the $B\ {}^3\Pi$ levels in N_2 is found through the symmetry of the $A\ {}^3\Sigma$ state together with the rule that for electric dipole radiation $(+)$ combines only with $(-)$. The alternating intensities found by Naudé in the first positive bands fix the A state either as $^3\Sigma_u^+$ or $^3\Sigma_g^-$. The former makes C_0 positive while the latter yields a negative value of C_0. Mulliken[24] has concluded from configuration theory that the A state is more probably $^3\Sigma_u^+$ than $^3\Sigma_g^-$. This is in agreement with the recent calculations of Recknagel[25] which place the $^3\Sigma_g^-$ state much higher than $^3\Sigma_u^+$. Also Herzberg and Sponer[26] find that the dissociation products of the A state are probably $^4S+^2D$, from which it is possible to obtain $^3\Sigma_u^+$ but not $^3\Sigma_g^-$. Finally the $^3\Sigma_u^+$ interpretation is strengthened by Kaplan's[27] observation of bands connecting the A state with the $^1\Sigma_g$ ground state of the molecule. If these bands are due to electric dipole radiation $(u-g)$ one is forced to accept the $^3\Sigma_u^+$ assignment for the A state. On the other hand, it might be possible to interpret the Kaplan bands as magnetic dipole radiation[28] $(g-g,\ u-u)$ which would allow $^3\Sigma_g^-$. However it appears almost certain that the A state is $^3\Sigma_u^+$ and that C_0 is positive.

We should expect the Λ-type doubling constant γ due to the $\Pi-\Sigma$ interaction to increase more rapidly than the spin-spin doubling constant 2α as we go to heavier molecules, so that probably it is permissible to consider only the former in such a molecule[23] as I_2. This follows from the fact that γ increases as A^2 and hence as $Z^8{}_{\text{eff}}$. On the other hand, α is of order $\beta^2\overline{(1/r^3)}$, where β is the Bohr magneton and r is the electron-electron distance. Hence α should increase about as fast as $Z^3{}_{\text{eff}}$.

6. Rho-Type Tripling in $^3\Sigma$ States

When $\Lambda=0$ the spin-orbit energy is small and hence $^3\Sigma$ states conform closely to Hund's case b. The energy of a $^3\Sigma$ state is given approximately by one of the roots of Eqs. (7), summed over different Π states and is

$$W=B_\Sigma K(K+1) - 8K(K+1)\sum_\pi |(BL_x)(\Pi;\Sigma)|^2/h\nu(\Pi;\Sigma)$$

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[22] Cf. pp. 488, 9 of reference 2, also R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

[23] Van Vleck, Phys. Rev. **40**, 544 (1932).

[24] R. S. Mulliken, Rev. Mod. Phys. **4**, 1, 53 (1932).

[25] A. Recknagel, Zeits. f. Physik **87**, 375 (1934).

[26] G. Herzberg and H. Sponer, Zeits. f. physik. Chemie B**26**, 1 (1934).

[27] J. Kaplan, Phys. Rev. **45**, 675, 898 (1934).

[28] Cf. J. H. Van Vleck, Astrophys. J. **80**, 161 (1934).

on neglecting terms higher than the first power in $1/h\nu(\Pi;\Sigma)$. Actually ${}^3\Sigma$ states do not satisfy exactly the conditions of case *b* and there is a slight separation of states with like K but unlike J. This separation Mulliken[29] calls ρ-type doubling for ${}^2\Sigma$ states and we shall use the term ρ-type tripling for the same splitting in the triplet case. The energy levels are given more accurately by the secular determinantal equations related to (4) with the diagonal elements of the determinants, $B_\pi[J(J+1)-3]+A_\pi-W$, $B_\pi[J(J+1)+1]-W$ and $B_\pi[J(J+1)+1]-A_\pi-W$, for the Π states replaced by $h\nu(\Pi;\Sigma)$. If we expand these equations in powers of $1/h\nu(\Pi;\Sigma)$ and neglect terms of higher power than the first, we find that the three solutions for the same value of K are

$$\begin{aligned} W_0&=B_\Sigma' K(K+1),\\ W_+&=W_0-\lambda[2(K+1)/(2K+3)]+\mu(K+1),\\ W_-&=W_0-\lambda[(2K)/(2K-1)]-\mu K, \end{aligned}\tag{12}$$

where

$$B_\Sigma'=B_\Sigma-8\sum_\pi|(BL_x)(\Pi;\Sigma)|^2/h\nu(\Pi;\Sigma),$$

$$\lambda=\sum_\pi|(AL_x)(\Pi;\Sigma)|^2/h\nu(\Pi;\Sigma),$$

$$\mu=8\times\text{real part of}$$

$$\sum_\pi(AL_x)(\Pi;\Sigma)(BL_x)(\Sigma;\Pi)/h\nu(\Pi;\Sigma),$$

and where W_+, W_0, W_- refer to states for which $J=K+1$, K, $K-1$, respectively.

Kramers[7] has considered the splitting of ${}^3\Sigma$ states arising from two causes: (1) the magnetic interaction between the individual electron spins, which he shows is equivalent to a coupling energy proportional to $(3\cos^2\chi-1)$ where χ is the angle between the resultant spin and the axis of the molecule; and (2) the coupling mentioned in section 1 between the spin of the molecule and the magnetic field set up by the molecular rotation. These two effects give a splitting of exactly the same form as that obtained from Eqs. (12); the first effect corresponds to terms of (12) in λ and the second to those in μ. It is very interesting that two completely different mechanisms should give formulas of the same structure.

Naudé[16] has shown that the ρ-type tripling in N_2 is in excellent agreement with Kramers' formulas (9) and hence with our Eqs. (12). Actually, of course, the coefficients λ and μ in (12) should be replaced by the sums of Kramers' coefficients and ours, *viz.*, by $\lambda+(3/2)A'$ and $\mu-B'$, respectively, in order to include both effects. Here we have affixed primes to Kramers' A and B to distinguish them from the usual spin-orbit constant A and the rotational constant B which we use. The experimental values given by Naudé are then $\lambda+(3/2)A'=1.3$ cm^{-1} and $\mu-B'=0.003$ cm^{-1}.

Comparison of μ and B'. The considerations given by Van Vleck[30] for the analogous case of ${}^2\Sigma$ states apply directly here and show that μ is definitely larger than B', except for very light atoms. Also Wick[31] has recently determined the magnetic moment of hydrogen due to molecular rotation and his results confirm the order of magnitude assumed by Van Vleck for this quantity.

Both Kramers' formulas and ours are approximate in that they neglect squares and higher powers of the ratio of the ${}^3\Sigma$ fine structure to the rotational separations. If this ratio is not small, the approximation is no longer valid and Kramers' Eqs. (8) must then be replaced by

$$\begin{aligned} \Omega_{K+1}&=-A'/2+B(2K+3)\\ &\qquad-[9A'^2/4-3A'B+(2K+3)^2B^2]^{\frac{1}{2}},\\ \Omega_K&=A',\\ \Omega_{K-1}&=-A'/2-B(2K-1)\\ &\qquad+[9A'/4-3A'B+(2K-1)^2B^2]^{\frac{1}{2}}. \end{aligned}\tag{13}$$

As explained above, A' is the constant Kramers denotes by A and B is $h^2/8\pi^2I$ and not the same as Kramers' constant B. These exact formulas were essentially derived by Hill and Van Vleck (Eqs. (40), (41), (42) of reference 10). To obtain them explicity one writes $k=S=1$, $j=K$ and replaces A by $3A'$ in Hill and Van Vleck's Eq. (42). Then the three of these equations which relate to the same value of K immediately yield our Eqs. (13).

The writer wishes to take this opportunity of expressing his sincere appreciation to Professor Van Vleck, under whom this work was done, for helpful guidance and criticism.

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

[30] See pp. 499, 500 of reference 2.

[31] G. C. Wick, Zeits. f. Physik **85**, 25 (1933).