values and is thus equal to

$$\prod_{\epsilon,\delta}\prod_{j=1}^{4}\lambda_j(\epsilon,\delta)=\prod_{\epsilon,\delta}\{(1+x^2)(1+y^2)-y(1-x^2)(\epsilon+\epsilon^{-1})-x(1-y^2)(\delta+\delta^{-1})\},$$

which is precisely (2.4). Needless to say, in the $n\times n$ case ϵ and δ are nth roots of unity but the system of Eqs. (5.1) remains otherwise unchanged.

In conclusion, it is a pleasure to acknowledge the kind hospitality of The Institute for Advanced Study and to thank many of our friends for the healthy pessimism they showed during the early stages of this work.

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Magnetic Hyperfine Structure in Diatomic Molecules*,†

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A general theory of the magnetic hyperfine structure in diatomic molecules, including states other than $^1\Sigma$ states, is given. The magnetic hyperfine interaction is derived from the Dirac equation for the electron in the molecular potential field. First-order hyperfine structure formulas are given for the various vector coupling schemes characteristic of molecular states. The $^1\Sigma$ magnetic hyperfine structures are obtained from second order hyperfine interactions. Applications to the $N^{14}O^{16}$ and $O^{16}O^{17}$ microwave spectra are discussed.

1. INTRODUCTION

THE general theory of the nuclear hyperfine structure observed in atomic spectra has been worked out and discussed extensively,[1] and even the detailed features of the observed spectra are quite well understood. No such general treatment has apparently been given for diatomic molecules. In the case of diatomic molecules with no resultant electronic spin or orbital angular momentum ($^1\Sigma$), satisfactory phenomenological treatments of the magnetic interaction of the nuclear moment with the electronic currents, in the form of an $\mathbf{I}\cdot\mathbf{J}$ coupling with the molecular angular momentum vector, have been given.[2] Investigation has shown[3] that this effect arises for the most part from the effect in second order of the nondiagonal matrix elements of the nuclear magnetic interaction with the electronic currents. The interaction of the nuclear electric quadrupole moment with the electronic currents in these molecules has also been treated satisfactorily.[4] The development of microwave spectroscopy and molecular beam techniques have made it possible to examine the hyperfine spectra of paramagnetic gas molecules, i.e., molecules in states other than $^1\Sigma$. The present paper is devoted to the general treatment of the hyperfine spectra of diatomic molecules. For molecules with nonzero electronic angular momentum, it may be anticipated that the nuclear moment interaction with the electrons will be of the order of magnitude of atomic magnetic hyperfine couplings, and thus will be very much larger than typical nuclear electric quadrupole couplings. The strength and mode of the vector coupling of the nuclear spin to the various angular momentum vectors in the molecule will therefore be primarily determined by the magnetic interactions, and it will be sufficient in almost all cases to evaluate only the diagonal values of the electric quadrupole interaction, in a vector coupling representation determined by the magnetic interaction. The greater part of the present work will thus deal with the theory of the magnetic interaction of a single nuclear spin with the electronic currents in the various kinds of molecular states.

Typical features of the molecular magnetic hyperfine interactions may be compared with those of atoms. The interaction with electronic spins in the atomic case is treated quite differently in s states ($L=0$) and non-s states.[1] For non-s states, the spin coupling may be written as the interaction of two point magnetic dipoles in the form $3(\mathbf{I}\cdot\mathbf{R})(\mathbf{S}\cdot\mathbf{R})/R^5-(\mathbf{I}\cdot\mathbf{S})/R^3$, where $\mathbf{R}$ is the space vector from nucleus to electron. For s-states, this interaction vanishes (as does the orbital interaction), and the actual hyperfine coupling must be accounted for by a more refined treatment of the magnetic interaction. The most satisfactory method of treating the interaction of the nuclear magnetic moment with the electronic currents is via the Dirac equation for the

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† Assisted in part by the ONR.

[1] E. Fermi, Z. Physik **60**, 320 (1930); G. Breit and F. W. Doermann, Phys. Rev. **36**, 1732 (1930); H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, Haarlem, 1936); E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

[2] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940); H. Zeiger and D. I. Bolef, Phys. Rev. **85**, 788 (1952); D. I. Bolef and H. J. Zeiger, Phys. Rev. **85**, 799 (1952).

[3] H. M. Foley, Phys. Rev. **72**, 504 (1947); G. C. Wick, Phys. Rev. **73**, 51 (1948).

[4] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

electron.[1] Advantage may be taken of the spherical symmetry of the potential field in which the electron moves to reduce the interaction for s-states to the form

$$W_{\rm hfs}=(16/3)\pi g_I\mu_0\mu_N\psi_r^2(0)\mathbf{I}\cdot\mathbf{S}, \tag{1.1}$$

where $\psi_r^2(0)$ is the electron density at the origin (position of the nucleus).

In the case of the diatomic molecule the potential field possesses only axial symmetry and no classification of states according to a total angular momentum quantum number can be made. Thus, there can be no separation of the hyperfine interaction into characteristic s- and non-s forms. Nevertheless, effects similar to the atomic s-state interaction are found. In particular, a $^2\Sigma$ or $^3\Sigma$ molecular state with total rotational angular momentum zero shows a nonvanishing hyperfine structure.

For molecules, there is also the complicating feature of the introduction, in addition to the electronic l and s, of a third vector, the molecular rotational angular momentum. This brings about the well-known molecular coupling states (Hund's case a and case b),[5] and makes possible a number of different nuclear spin couplings. These possible couplings will be treated in detail in later sections.

2. THE MAGNETIC INTERACTION OF NUCLEAR MOMENT AND ELECTRONS

The general form of the interaction of the nuclear magnetic moment with a single electron has been given by Breit and Doermann.[1] Their Hamiltonian was derived by reducing the Dirac equation for the electron in the field of the nucleus from four component form to the approximately correct two component Pauli form. The hyperfine perturbation was obtained from the latter equation. Due to normalization difficulties, their result contains a non-Hermitian term which must be arbitrarily excluded.

We will derive the Pauli equation in a form suitable for our purposes by applying a series of unitary transformations to the Dirac Hamiltonian. This procedure, an extension of the method of Foldy and Wouthuysen,[6] avoids the normalization difficulty. A treatment of this problem using the Dirac equation with explicit consideration of normalization has recently been given by Karnaugh.[7]

We write the Dirac Hamiltonian in the conventional form

$$H_0=\beta mc^2-eV+c\boldsymbol{\alpha}\cdot(\mathbf{p}-(e/c)\mathbf{A}). \tag{2.1}$$

We apply to this Hamiltonian three successive unitary transformations of the form

$$H_i=e^{iS_i}H_{i-1}e^{-iS_i}, \tag{2.2}$$

where, if $\mathcal{E}=-\nabla V$,

$$S_1=-ic\beta\boldsymbol{\alpha}\cdot\{\mathbf{p}-(e/c)\mathbf{A}\}/2(mc^2-eV),$$

$$S_2=\frac{-ic\beta}{2(mc^2-eV)}\left[\frac{-eVc}{(mc^2-eV)}\boldsymbol{\alpha}\cdot\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)-\frac{ie\beta c}{2(mc^2-eV)}\boldsymbol{\alpha}\cdot\boldsymbol{\mathcal{E}}\right],$$

$$S_3=\frac{-ic\beta}{2(mc^2-eV)}\left\{\frac{e^2V^2c^2}{mc^2-eV}\boldsymbol{\alpha}\cdot\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)+\frac{ie^2V\beta c^2}{2(mc^2-eV)}\boldsymbol{\alpha}\cdot\boldsymbol{\mathcal{E}}+\frac{\text{const}\,c^3}{(mc^2-eV)^2}\boldsymbol{\alpha}\cdot\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)\times[\sigma\cdot(p-e/cA)]^2\right\}\varphi=0. \tag{2.3}$$

We are left finally with

$$H_3=\beta mc^2-eV+\frac{\beta c^2}{2mc^2}\left[\boldsymbol{\sigma}\cdot\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)\right]^2+\frac{iec^2}{8(mc^2-eV)^2}\left[\boldsymbol{\sigma}\cdot\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right),\boldsymbol{\sigma}\cdot\boldsymbol{\mathcal{E}}\right] \tag{2.4}$$

+terms of order $1/(mc^2)^3$ and higher. In the above, $[A, B]$ denotes $[AB-BA]$. This Hamiltonian yields the Pauli equation as

$$\left\{E+eV-\frac{1}{2m}\left[\boldsymbol{\sigma}\cdot\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)\right]^2+\frac{c^2e\hbar}{8i(mc^2+eV)^2}\left[\boldsymbol{\sigma}\cdot\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right),\boldsymbol{\sigma}\cdot\boldsymbol{\mathcal{E}}\right]\right\}\varphi=0, \tag{2.5}$$

taking the electron charge to be $-e$. In the third term, the divergent denominator has been set equal to $2mc^2$. A term proportional to μ_N^2 has been neglected. The hyperfine part of (2.5) may be written in terms of the electronic orbital angular momentum L' as

$$\frac{e\hbar}{2mc}\frac{2\boldsymbol{\mu}\cdot\mathbf{L}'}{r_1^3}+\frac{2i\mu_0}{\hbar}\mathbf{S}\cdot[\mathbf{p}\times\mathbf{A}]+\frac{2e^2\hbar}{4m^2c^3}\mathbf{S}\cdot[\boldsymbol{\mathcal{E}}'\times\mathbf{A}], \tag{2.6}$$

in which $S=\sigma/2$, and we have set $E+mc^2+eV=2mc^2$ in the denominator of the first two terms. In the case of an atom, Eq. (2.6) becomes

$$\frac{2g_I\mu_0\mu_N}{r^3}\left\{\left[\mathbf{I}\cdot\mathbf{L}+\frac{3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})}{r^2}-\mathbf{I}\cdot\mathbf{S}\right]+\frac{2mc^2e^2\mathcal{E}_r r}{[E+eV+mc^2]^2}\left[-\frac{(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})}{r^2}+\mathbf{I}\cdot\mathbf{S}\right]\right\}. \tag{2.7}$$

The first term gives the hyperfine levels for non-s states and is zero for s-states. The second term may be

[5] G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), p. 218.

[6] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. 78, 29 (1950).

[7] M. Karnaugh, dissertation, Yale University (1952) (unpublished).

written, after a partial integration, as (1.1). This term is proportional to the charge density at the nucleus, and is nonzero for s-states only.

Expression (2.6) will be the basis for our treatment of the hyperfine spectra of molecules. In the remainder of the paper we will write

$$2mc^2e^2\mathcal{G}_r/[E+eV+mc^2]^2=\delta(r), \qquad (2.8)$$

since the terms with this coefficient (except for neglected relativistic corrections, significant only for heavy nuclei) give appreciable contributions only from the region near the nucleus.

3. MOLECULAR QUANTIZATION

The rigorous theory of the quantum states of diatomic molecules, and in particular the approximate nature of the separation of rotation, vibration, and electronic motion have been discussed by Van Vleck and Kronig.[8] In a first-order theory of molecular hyperfine structure, it is necessary only to know the particular vector coupling representation of the electronic spin and the orbital and rotational angular momenta. The most important of these representations are Hund's case a, in which the spin is strongly coupled to the internuclear axis by the spin orbit interaction, and Hund's case b, in which the spin is decoupled by "gyroscopic" terms in the kinetic energy, and the spin vector is added to the total angular momentum of the molecule. Which of these vector coupling schemes most nearly describes any molecular state depends on the relative magnitudes of the spin orbit coupling and the gyroscopic term (proportional to $\hbar^2/2I$). In both of these cases, the component of electronic angular momentum parallel to the internuclear axis is a good quantum number Λ, and the separation of levels corresponding to different values of Λ is characteristically much greater than the level splittings due to rotation, spin orbit coupling, Λ doubling, or hyperfine structure. In this paper we shall be concerned for the most part with hyperfine and other interactions which are diagonal in Λ. Higher order effects due to matrix elements of the various interactions which are nondiagonal in Λ we consider in Sec. 7.

4. THE MAGNETIC HYPERFINE INTERACTION IN A MOLECULAR COORDINATE SYSTEM

The coordinate system for the molecule consists in the first place of a rectangular coordinate system XYZ fixed in the laboratory and with the center of mass of the molecule at the origin. The orientation of the internuclear axis in this frame is given by the polar and azimuthal angles θ and ψ with respect to the Z axis. The positions of the electrons are described in a rectangular coordinate system $x'y'z'$, fixed in the molecule, with z' along the internuclear axis and x' constrained to remain in the XY plane. In the usual treatment of the molecular problem,[8] an approximate separation of the Hamiltonian into electronic, vibrational, and rotational terms is made, and the wave function is the product of three corresponding factors:

$$\Psi=\psi_e(x', y', z')\psi_V(R)\psi_R(\theta, \psi). \qquad (4.1)$$

(The electron spin may be quantized in the laboratory or in the internal coordinate system according to Hund's case b or case a, respectively.)

We shall express the magnetic hyperfine interaction [expression (2.6)] in the internal coordinate system, replacing $x'y'z'$ by cylindrical coordinates $\rho'\varphi z'$ where $x'=\rho'\cos\varphi$ and $y'=\rho'\sin\varphi$. It is clear that the φ dependence of the electronic wave function is of the form

$$e^{\pm i\Lambda\varphi}/(2\pi)^{\frac{1}{2}}. \qquad (4.2)$$

(The effect of the degeneracy in $\pm\Lambda$ is described in Sec. 6.) To obtain the matrix elements of (2.6) diagonal in Λ we shall first average over φ.‡

In the first term of (2.6): $(2e/2mc)\mathfrak{y}_N\cdot(\mathbf{r}_1\times\mathbf{p})/r_1^3$, $\mathbf{r}_1$ is the vector from the nucleus to the interacting electron. It is convenient to express this in terms of the orbital angular momentum about the center of mass. From Fig. 1, we note that $\mathbf{r}_1=\mathbf{r}-\tau\mathbf{k}'$, where τ is the distance from the center of mass to the nucleus with spin; and $\mathbf{k}'$ is a unit vector in the z' direction. This first term becomes

$$\frac{2g_I\mu_0\mu_N}{r_1^3}\mathbf{I}\cdot\mathbf{L}-\frac{e}{2mc}2\mathfrak{y}\cdot[\tau\mathbf{k}'\times\mathbf{p}], \qquad (4.3)$$

where $\mathbf{L}\hbar=\mathbf{r}\times\mathbf{p}$ and $\mu_0=e\hbar/2mc$.

The second term of (4.3) has no matrix elements diagonal in Λ.

The second term of expression (2.6) may be expanded, and the only terms which do not vanish on averaging

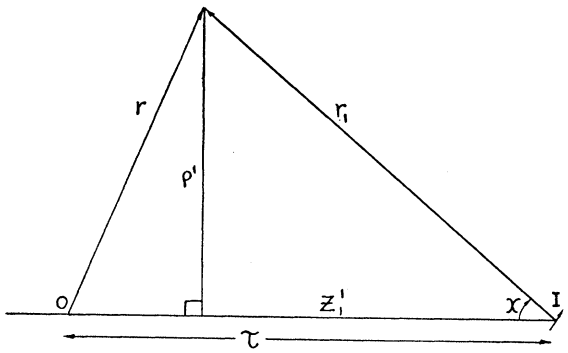

FIG. 1. Coordinates of the electron in the molecular frame of reference. The nucleus is located at I and the center of mass of the molecule at 0.

[8] R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, Cambridge, 1930); J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

‡ Throughout the paper the term "matrix elements" will frequently be used for operators which have been averaged over the electronic coordinates, but remain operators with respect to the spin and rotational coordinates.

over φ are

$$-\frac{\mathfrak{u}\cdot\mathbf{S}}{r_1^3}+\mu_{x'}S_{x'}\frac{3x'^2}{r_1^5}+\mu_{y'}S_{y'}\frac{3y'^2}{r_1^5}+\mu_{z'}S_{z'}\frac{3z_1'^2}{r_1^5}. \quad (4.4)$$

The third term of expression (2.6) contains the factor $\mathbf{S}\cdot\mathcal{E}'\times\mathbf{A}$, which may be written as

$$\mathbf{S}\cdot\left[\mathcal{E}'\times\frac{\mathfrak{u}\times\mathbf{r}_1}{r_1^3}\right]=\frac{\mathcal{E}'\cdot\mathbf{r}_1}{r_1^3}\mathfrak{u}\cdot\mathbf{S}+\mathcal{E}'\cdot\mathfrak{u}\frac{\mathbf{S}\cdot\mathbf{r}_1}{r_1^3}. \quad (4.5)$$

The expansion of Eq. (4.5) in cylindrical coordinates and the integration over φ yields

$$[\mathcal{E}'\times\mathbf{A}]\cdot\mathbf{S}=\frac{\mathcal{E}_{\rho'}'\rho'+\mathcal{E}_{z'}'z'}{r_1^3}\mathfrak{u}\cdot\mathbf{S}$$
$$-\frac{\mathcal{E}_{\rho'}'\rho'}{2r_1^3}(\mu_{x'}S_{x'}+\mu_{y'}S_{y'})-\frac{\mathcal{E}_{z'}'z_1'}{r_1^3}\mu_{z'}S_{z'}, \quad (4.6)$$

where $\mathcal{E}_{\rho'}$ and $\mathcal{E}_{z'}$ are the ρ' and z' components of the electric field produced by all charges except the interacting electron.

We now collect the terms of expressions (4.3), (4.4), and (4.6), and form the complete expression for the effective magnetic hyperfine operator for all matrix elements diagonal in Λ. We designate the angle between the molecular axis and the vector r_1' from the nucleus to the electron by $\chi=\tan^{-1}\rho'/z_1'$ (see Fig. 1), and write $\mathcal{E}'=e\mathcal{E}$. We obtain the operator in the form

$$aI_{z'}L_{z'}+b\mathbf{I}\cdot\mathbf{S}+cI_{z'}S_{z'}, \quad (4.7)$$

where

$$a=2g_I\mu_0\mu_N(1/r_1^3)_{\mathrm{Av}},$$

$$b=2g_I\mu_0\mu_N\left[\frac{e^2 2mc^2}{[E+eV+mc^2]^2}\frac{\mathcal{E}_{\rho'}\rho'/2+\mathcal{E}_{z'}z_1}{r_1^3}-\frac{3\cos^2\chi-1}{2r_1^3}\right]_{\mathrm{Av}}, \quad (4.8)$$

$$c=2g_I\mu_0\mu_N\left[\frac{e^2 2mc^2}{[E+eV+mc^2]^2}\frac{\mathcal{E}_{\rho'}\rho'/2-\mathcal{E}_{z'}z_{1'}}{r_1^3}+\frac{3}{2}\frac{3\cos^2\chi-1}{r_1^3}\right]_{\mathrm{Av}},$$

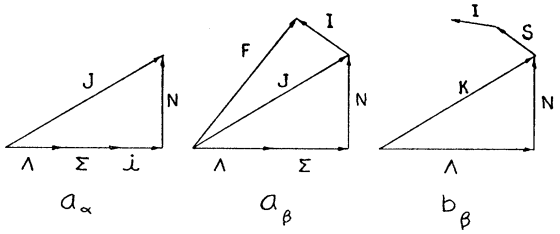

FIG. 2. The three molecular coupling states including nuclear spin. The various coupling possibilities for case b are discussed in Sec. 5 and appear in Fig. 3.

with the signs as indicated (μ_0 positive). This expression (4 7) may be employed to discuss all features of the hyperfine spectra in both Hund's case a and case b arising from matrix elements diagonal in Λ. The quantities in brackets $[\ ]_{\mathrm{Av}}$ are to be averaged over the electronic space coordinates for the particular states. The first term of b or c yields a nonvanishing contribution only in regions closer to the nucleus than the classical radius of the electron, $e^2/2mc^2$. In this region the nonvanishing component of the electron wave function is spherically symmetric (within our approximation). If we write $\mathcal{E}_{\rho'}\rho'=\mathcal{E}_r r_1\sin^2\chi$ and $\mathcal{E}_{z'}z_{1'}=\mathcal{E}_r r_1\cos^2\chi$, upon performing the average (assuming spherical symmetry) we obtain

$$b=2g_I\mu_0\mu_N\left[\frac{2}{3}\frac{\delta(r_1)}{r_1^2}-\frac{3\cos^2\chi-1}{2r_1^3}\right]_{\mathrm{Av}},$$
$$c=3g_I\mu_0\mu_N\left[\frac{3\cos^2\chi-1}{r_1^3}\right]_{\mathrm{Av}}. \quad (4.9)$$

The term in b with coefficient $\delta(r_1)$ arises because of the quasi-relativistic treatment leading to expression (2.6), and represents the departure of the actual hyperfine coupling from that expected from the interaction of two-point dipoles. If the electronic charge distribution were exactly spherical, the term $3\cos^2\chi-1$ would vanish and the term referred to above would give the whole hyperfine structure. In this case Eq. (4.7) reduces to the Fermi formula for s-states, Eq. (1.1). On the other hand, if this "s-term" interaction was absent we should have $3b+c=0$. Thus, the value of $3b+c$ from any observed spectrum is an indication of the presence of some spherical charge density bearing a free spin near the nucleus.

If more than one electron contributes to the total orbital or spin angular momentum, the hyperfine interaction operator has the form of expression (4.7), but the coefficient [Eq. (4.9)] contains a term from each interacting electron.

5. COUPLINGS AND MATRIX ELEMENTS

We consider now the vector coupling possibilities of a single nuclear spin to the various angular momenta of the molecule. In principle, representations can occur in which the nuclear spin is quantized either in the laboratory coordinate system or in the internal coordinate system of the molecule. Now a coupling of the nuclear moment to the internuclear axis will come about through the magnetic interaction with the electronic orbital angular momentum (and with the electron spin in Hund's case a). This interaction is the analog of the coupling of the electron spin to the molecular axis which leads to Hund's case a, but is about 1000 times smaller in magnitude since the magnetic moment of the nucleus is much smaller than that of the electron. The "gyroscopic" terms which act to decouple the spin from the axis are of the same order of magnitude for molecular

and electronic spins since they depend on the spins rather than the magnetic moments of the particles. We may distinguish the following important cases of vector coupling as (a) case a_α: Hund's case a with the nuclear spin space quantized with respect to the internuclear axis. (This includes the case where $S=0$); (b) case a_β: Hund's case a with the nuclear spin space quantized in the laboratory frame. (This includes the case where $S=0$); (c) case b_β: Hund's case b with the nuclear spin space quantized in the laboratory frame. The vector coupling possibilities are shown in Fig. 2. The several possible coupling schemes for case b are discussed later in this section.

Actually, because of the weak magnetic coupling of the nuclear spin to the molecular axis, case a_α is expected to be of extremely rare occurrence, and in the interests of brevity will not be considered here.[9]

Case a

The magnetic hyperfine operator (4.7) may be written as

$$aI_{z'}L_{z'}+b(I_{x'}S_{x'}+I_{y'}S_{y'})+(b+c)I_{z'}S_{z'}. \quad (5.1)$$

The second term has only nonzero matrix elements which are off-diagonal in Ω, and hence, in a molecule which is in a good case a state, the effects of this term will be very small and are neglected here. For a discussion of this term in cases intermediate between Hund's case a and case b and in $^1\Sigma$ states, see Sec. 7. Thus, the part of expression (5.1) diagonal in Λ becomes

$$[a\Lambda+(b+c)\Sigma]I_{z'}=d\mathbf{I}\cdot\mathbf{k}', \quad (5.2)$$

where $d=a\Lambda+(b+c)\Sigma$, and $\mathbf{k}'$ is the unit coordinate vector along the molecular axis. The magnetic hyperfine structure problem in case a_β is thus reduced to the calculation of the diagonal value of Eq. (5.2) in a representation in which the electronic wave function is that designated as Hund's case a, and the nuclear spin is quantized in the fixed laboratory system. To express this result, we require the matrix elements of the components of the unit coordinate vector $\mathbf{k}'$ in the fixed system. In Appendix I are given such matrix elements for the vectors of the internal molecular coordinate system. We write the matrix of (5.2) first in the "decoupled" representation in which JIm_Jm_I are good quantum numbers. Expansion of the scalar product and reference to Appendix I yield for the matrix elements diagonal in J

$$d\frac{\Omega}{J(J+1)}\mathbf{I}\cdot\mathbf{J}. \quad (5.3)$$

It should be pointed out that the coefficient of the I, J coupling varies with J. We may make use of the addition formulas of Condon and Shortley[10] to obtain the matrix elements in the weak field $IJFm_F$ representation:

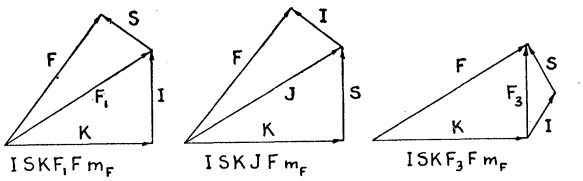

FIG. 3. The three simple coupling cases in case b_β. The "good" quantum numbers are indicated in each case.

$$(JIFm_F|\mathbf{I}\cdot\mathbf{k}'|JIFm_F)=\Omega\frac{F(F+1)-J(J+1)-I(I+1)}{2J(J+1)},$$

$$(IJFm_F|\mathbf{I}\cdot\mathbf{k}'|IJ-1Fm_F) \quad (5.4)$$
$$=\pm\frac{1}{2}\frac{(J^2-\Omega^2)^{\frac{1}{2}}}{J(4J^2-1)^{\frac{1}{2}}}[(F+J-I)(F+I-J+1)\times(F+I+J+1)(J+I-F)]^{\frac{1}{2}}.$$

The $J\rightarrow J+1$ matrix element follows from the Hermitian property of the matrix. It is expected that the effects of matrix elements nondiagonal in J will be small (inasmuch as the rotational energy is very much greater than the hyperfine structure) and may be taken into account as a second order perturbation.

Case b_β

Here both I and S are space quantized in the laboratory coordinate system. We may write expression (5.1) as

$$a\Lambda(\mathbf{I}\cdot\mathbf{k}')+b(\mathbf{I}\cdot\mathbf{S})+c(\mathbf{I}\cdot\mathbf{k}')(\mathbf{S}\cdot\mathbf{k}'). \quad (5.5)$$

In a completely "decoupled" representation (good quantum numbers are $ISKm_Im_Sm_K$) the matrix elements of $\mathbf{I}\cdot\mathbf{k}'$, $\mathbf{S}\cdot\mathbf{k}'$, $\mathbf{I}\cdot\mathbf{S}$ may be evaluated directly from Appendix I, and the last term calculated by matrix multiplication. The zero field problem is rather complicated, however, inasmuch as it involves the coupling of the three vectors I, K, S. The simplest possibilities are (see also Fig. 3)

$$K+I=F_1, \quad K+S=J, \quad I+S=F_3,$$
$$F_1+S=F, \quad J+I=F, \quad F_3+K=F.$$

We shall refer to these three representations as the F_1, J, and F_3 representations, respectively. The good quantum numbers are indicated in Fig. 3 for each case.

The part of the Hamiltonian of the system which must be discussed in the determination of the appropriate representation for this case includes the hyperfine couplings of expression (5.5) and the electron spin orbit interaction contained in the third term of Eq.

[9] R. A. Frosch, dissertation, Columbia University (1952) (unpublished).

[10] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), pp. 69, 71.

(2.5). The appropriate part of this term may be written

$$\frac{e^2\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot[\boldsymbol{\mathcal{E}}\times\mathbf{p}]=-2i\mu_0^2\Big\{\mathcal{E}_{\rho'}\frac{\partial}{\partial z'}(S_{x'}\sin\varphi-S_{y'}\cos\varphi)$$
$$+\mathcal{E}_{z'}\Big[-\frac{1}{\rho'}\frac{\partial}{\partial\varphi}(S_{x'}\cos\varphi+S_{y'}\sin\varphi)$$
$$+\frac{\partial}{\partial\rho'}(-S_{x'}\sin\varphi+S_{y'}\cos\varphi)\Big]+S_{z'}\frac{\mathcal{E}_{\rho'}}{\rho'}\frac{\partial}{\partial\varphi}\Big\},\quad(5.6)$$

where $S=\sigma/2$. Only the last term of (5.6) yields matrix elements diagonal in Λ. In case b, S is quantized in the laboratory frame, and it is appropriate to write the part of (5.6) diagonal in Λ as

$$2\mu_0^2\Lambda\Big(\frac{\mathcal{E}_{\rho'}}{\rho'}\Big)_{\text{Av}}\mathbf{S}\cdot\mathbf{k}'=2\mu_0^2\Big(\frac{\mathcal{E}_{\rho'}}{\rho'}\Big)_{\text{Av}}\Lambda^2\frac{\mathbf{S}\cdot\mathbf{K}}{K(K+1)},\quad(5.7)$$

for the term diagonal in K. Thus the electron spin orbit interaction represents a coupling of S to K. For states with $\Lambda\neq0$, expression (5.7) will in general be much larger than the hyperfine coupling term (5.5), and thus the J representation will be approximately correct. For Σ states, however, (5.7) vanishes, and the remaining effects of the spin orbit coupling are obtained from the second-order effects of the matrix elements of (5.6) between Σ and Π states. This coupling of S to K, known as ρ doubling for $^2\Sigma$ states,[8] may be shown to be of the form

$$\text{const }\mu_0B\frac{(\Sigma|L_\perp|\Pi)}{h\nu_{\Sigma\Pi}}[K(K+1)]^{\frac{1}{2}}S_\perp+\text{const }\mu_0^2(S_\perp)^2,\quad(5.8)$$

where $S_\perp$ is the appropriate one of $S_{x'}\pm iS_{y'}$, and similarly for $L_\perp$. The first term of (5.8) becomes finally constant $\mathbf{S}\cdot\mathbf{K}$. The second term may be written as constant $(S^2-(\mathbf{S}\cdot\mathbf{k}')^2)$ and is a somewhat complicated coupling of S to K, as is seen from the discussion of expression (7.8) in Sec. 7. These couplings are of much smaller magnitude than (5.7) and are possibly of the same magnitude as the hyperfine interaction. A similar formula obtains for $^3\Sigma$ states.[11]

Although the hyperfine level pattern can in principle be obtained from any of the three representations F_1, J, F_3 by writing out the complete matrix of the hyperfine interaction (5.5) and the spin orbit coupling (5.6) in this representation and solving the secular determinant directly, it is usually much more convenient to choose a representation in which the diagonal values of (5.5) and (5.6) are large compared to off-diagonal elements. In this case the energy levels may be obtained by second order perturbation theory.

Hyperfine Matrix Elements in Case b_β

We give here the complete matrix elements (diagonal in Λ) of the operators $\mathbf{I}\cdot\mathbf{k}'$, $\mathbf{I}\cdot\mathbf{S}$, $\mathbf{S}\cdot\mathbf{k}'$, from which the hyperfine energy levels may be calculated by matrix multiplication according to (5.5), for the following cases:

(a) F_3 representation: $\mathbf{I}\cdot\mathbf{S}$, $\mathbf{I}\cdot\mathbf{k}'$, $\mathbf{S}\cdot\mathbf{k}'$, for all I, S, K,
(b) J representation: $\mathbf{I}\cdot\mathbf{S}$, $\mathbf{I}\cdot\mathbf{k}'$, for all I, S, K; and $\mathbf{S}\cdot\mathbf{k}'$, for $S=\frac{1}{2}$, 1 and all I, K,
(c) F_1 representation: $\mathbf{I}\cdot\mathbf{S}$, $\mathbf{S}\cdot\mathbf{k}'$, for all I, S, K; and $\mathbf{I}\cdot\mathbf{k}'$, for $I=\frac{1}{2}$, 1 and all S, K.

Diagonal values of $\mathbf{S}\cdot\mathbf{k}'$ in the J representation and of $\mathbf{I}\cdot\mathbf{k}'$ (for all S and I, respectively) may be written down directly from the vector model. We have made use of the results of Racah,[12] Condon and Shortley,[10] and Bardeen and Townes[4] in calculating these matrix elematrix elements. Details of the method are given in the dissertation of Frosch.[9] The actual formulas for the energy levels and spectral line frequencies in these representations are rather complicated, and it has not appeared worth while to work out the complete formulas, which may be obtained from the matrix elements below. One example is worked out in Sec. 10. The notation $(|A/B|)$ refers to the element of A or of B. When a double sign appears either the upper or the lower sign is to be taken throughout. Unlisted matrix elements are either zero or follow directly from the Hermitian properties of the matrices in the usual manner. We note, first of all, that in all representations

$$\begin{aligned}&(K\vdots\mathbf{k}'\vdots K)=\Lambda/K(K+1),\\&(K\vdots\mathbf{k}'\vdots K-1)=(K^2-\Lambda^2)^{\frac{1}{2}}/K(4K^2-1)^{\frac{1}{2}},\\&(IS\vdots\mathbf{I}/\mathbf{S}\vdots IS)=(KS\vdots\mathbf{I}/\mathbf{S}\vdots KS)=(KI\vdots\mathbf{I}/\mathbf{S}\vdots KI)=1.\end{aligned}\quad(5.9)$$

Now

$$(KF_3F|\mathbf{I}\cdot\mathbf{S}|KF_3F)=\tfrac{1}{2}[F_3(F_3+1)-I(I+1)-S(S+1)].\quad(5.10)$$

We note

$$\begin{aligned}(SIF_3\vdots\mathbf{I}\vdots SIF_3)&=\frac{F_3(F_3+1)-S(S+1)+I(I+1)}{2F_3(F_3+1)},\\(SIF_3\vdots\mathbf{I}\vdots SIF_3-1)&=\pm\frac{[(F_3-S+I)(F_3+S+I+1)(S+I-F_3+1)(F_3+S-I)]^{\frac{1}{2}}}{2F_3[(2F_3-1)(2F_3+1)]^{\frac{1}{2}}}.\end{aligned}\quad(5.11)$$

[11] M. H. Hebb, Phys. Rev. **49**, 610 (1936).
[12] G. Racah, Phys. Rev. **61**, 186 (1942); **62**, 438 (1942); **63**, 237, 368 (Eq. 4) (1943).

The similar quantities for S are obtained by interchanging I and S and inverting the double sign. Then,

$$\begin{aligned}
&(F_3KF|\mathbf{I}\cdot\mathbf{k}'/\mathbf{S}\cdot\mathbf{k}'|F_3KF)=\tfrac{1}{2}(K\vdots\mathbf{k}'\vdots K)(F_3\vdots\mathbf{I}/\mathbf{S}\vdots F_3)\{F(F+1)-F_3(F_3+1)-K(K+1)\},\\
&(F_3KF|\mathbf{I}\cdot\mathbf{k}'/\mathbf{S}\cdot\mathbf{k}'|F_3K-1F)=\pm\tfrac{1}{2}(K\vdots\mathbf{k}'\vdots K-1)(F_3\vdots\mathbf{I}/\mathbf{S}\vdots F_3)\\
&\qquad\times[(F+K-F_3)(F+F_3-K+1)(F+F_3+K+1)(F_3+K-F)]^{\frac{1}{2}},\\
&(F_3KF|\mathbf{I}\cdot\mathbf{k}'/\mathbf{S}\cdot\mathbf{k}'|F_3-1KF)=\mp\tfrac{1}{2}(K\vdots\mathbf{k}'\vdots K)(F_3\vdots\mathbf{I}/\mathbf{S}\vdots F_3-1)\\
&\qquad\times[(F+F_3-K)(F+K-F_3+1)(F+F_3+K+1)(F_3+K-F)]^{\frac{1}{2}},\\
&(F_3KF|\mathbf{I}\cdot\mathbf{k}'/\mathbf{S}\cdot\mathbf{k}'|F_3-1K-1F)=-\tfrac{1}{2}(K\vdots\mathbf{k}'\vdots K-1)(F_3\vdots\mathbf{I}/\mathbf{S}\vdots F_3-1)\\
&\qquad\times[(F_3+K+F+1)(F_3+K+F)(F_3+K-F)(F_3+K-F-1)]^{\frac{1}{2}},\\
&(F_3KF|\mathbf{I}\cdot\mathbf{k}'/\mathbf{S}\cdot\mathbf{k}'|F_3+1K-1F)=\tfrac{1}{2}(K\vdots\mathbf{k}'\vdots K-1)(F_3\vdots\mathbf{I}/\mathbf{S}\vdots F_3+1)\\
&\qquad\times[(F+K-F_3-1)(F+K-F_3)(F+F_3-K+1)(F+F_3-K+2)]^{\frac{1}{2}},
\end{aligned}\tag{5.12}$$

In the J representation,

$$\begin{aligned}
&(JIF|\mathbf{I}\cdot\mathbf{S}|JIF)=\tfrac{1}{2}(I\vdots\mathbf{I}\vdots I)(J\vdots\mathbf{S}\vdots J)\{F(F+1)-J(J+1)-I(I+1)\},\\
&(JIF|\mathbf{I}\cdot\mathbf{S}|J-1IF)=\mp\tfrac{1}{2}(I\vdots\mathbf{I}\vdots I)(J\vdots\mathbf{S}\vdots J-1)[(F+J-I)(F+I-J+1)(F+J+I+1)(J+I-F)]^{\frac{1}{2}},
\end{aligned}\tag{5.13}$$

where

$$\begin{aligned}
&(KSJ\vdots\mathbf{S}\vdots KSJ)=(KS\vdots\mathbf{S}\vdots KS)\frac{J(J+1)-K(K+1)+S(S+1)}{2J(J+1)},\\
&(KSJ\vdots\mathbf{S}\vdots KSJ-1)=\mp(KS\vdots\mathbf{S}\vdots KS)\cdot\frac{[(J-K+S)(J+K+S+1)(K+S-J+1)(J+K-S)]^{\frac{1}{2}}}{2J[(2J+1)(2J-1)]^{\frac{1}{2}}},
\end{aligned}\tag{5.14}$$

Now,

$$\begin{aligned}
&(JIF|\mathbf{I}\cdot\mathbf{k}'|JIF)=\tfrac{1}{2}(J\vdots\mathbf{k}'\vdots J)\{F(F+1)-J(J+1)-I(I+1)\},\\
&(JIF|\mathbf{I}\cdot\mathbf{k}'|J-1IF)=\pm\tfrac{1}{2}(J\vdots\mathbf{k}'\vdots J-1)[(F+J-I)(F+I-J+1)(F+I+J+1)(J+I-F)]^{\frac{1}{2}},
\end{aligned}\tag{5.15}$$

where

$$\begin{aligned}
&(KJ\vdots\mathbf{k}'\vdots KJ)=(K\vdots\mathbf{k}'\vdots K)\frac{J(J+1)-S(S+1)+K(K+1)}{2J(J+1)},\\
&(KJ\vdots\mathbf{k}'\vdots K-1J)=\pm(K\vdots\mathbf{k}'\vdots K-1)\frac{[(J-S+K)(J+S+K+1)(S+K-J)(J+S-K+1)]^{\frac{1}{2}}}{2J(J+1)},\\
&(KJ\vdots\mathbf{k}'\vdots KJ-1)=\mp(K\vdots\mathbf{k}'\vdots K)\frac{[(J-S+K)(J+S+K+1)(S+K-J+1)(J+S-K)]^{\frac{1}{2}}}{2J[(2J+1)(2J-1)]^{\frac{1}{2}}},\\
&(KJ\vdots\mathbf{k}'\vdots K-1J-1)=(K\vdots\mathbf{k}'\vdots K-1)\frac{[(J-S+K)(J+S+K+1)(J-S+K-1)(J+S+K)]^{\frac{1}{2}}}{2J[(2J+1)(2J-1)]^{\frac{1}{2}}},\\
&(KJ\vdots\mathbf{k}'\vdots K-1J+1)=-(K\vdots\mathbf{k}'\vdots K-1)\frac{[(S+K-J)(J+S-K+1)(S+K-J-1)(J+S-K+2)]^{\frac{1}{2}}}{2(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}}.
\end{aligned}\tag{5.16}$$

For $S=\frac{1}{2}$,

$$(KJ=K-\tfrac{1}{2}|\mathbf{S}\cdot\mathbf{k}'|K-1J=K-\tfrac{1}{2})=\pm(K^2-\Lambda^2)^{\frac{1}{2}}/2K,\tag{5.17}$$

and for $S=1$,

$$\begin{aligned}
&(KJ=K|\mathbf{S}\cdot\mathbf{k}'|K-1J=K)=\pm\frac{(K^2-\Lambda^2)^{\frac{1}{2}}}{K(2K+1)^{\frac{1}{2}}}(K+1)^{\frac{1}{2}},\\
&(KJ=K-1|\mathbf{S}\cdot\mathbf{k}'|K-1J=K-1)=\pm\frac{(K^2-\Lambda^2)^{\frac{1}{2}}}{K(2K-1)^{\frac{1}{2}}}(K-1)^{\frac{1}{2}}.
\end{aligned}\tag{5.18}$$

In general, for all S, the diagonal elements are

$$(KJ|\mathbf{S}\cdot\mathbf{k}'|KJ)=\frac{\Lambda\{J(J+1)-K(K+1)-S(S+1)\}}{2K(K+1)}.\tag{5.19}$$

In the F_1 representation the matrix elements are to be obtained from those in the J representation by interchanging I and S, and letting J become F_1.

In the case of triplet states, where two electron spins add to a resultant $S=1$, in addition to the matrix elements given above there are also some elements between the triplet states and singlet states of the same

values of Λ. These connect states with considerable energy difference, and are considered as higher order effects. The appropriate matrix elements of the hyperfine operators may be obtained using the methods outlined by Frosch,[9] in conjunction with the formulas of Condon and Shortley.[10]

The effect of the "s-state" part of the magnetic hyperfine interaction obtained specifically from the relativistic treatment, discussed in Sec. 4, becomes especially apparent in the case of the zero rotational state of a Σ electronic level ($K=0$, $\Lambda=0$). The appropriate representation is F_3, and the diagonal hyperfine energy level formula is

$$\tfrac{1}{6}(3b+c)\{F(F+1)-S(S+1)-I(I+1)\}. \quad (5.20)$$

In Sec. 4, it was shown that the nonvanishing of the coefficient of this expression is directly related to the presence of a distribution of electron spin moment near the nucleus similar to that of an atomic s-state.

Matrix elements in the partially decoupled representation in a weak magnetic field (quantum numbers $ISKF_1m_{F1}m_S$, $ISKJm_Jm_I$, $ISKF_3m_{F3}m_K$) may also be obtained from the above operators using the formulas of Condon and Shortley.[10]

6. THE EFFECT OF THE LAMBDA-DOUBLING

The treatment of hyperfine interactions in the previous section has been concerned only with matrix elements diagonal in Λ. Before discussing the effects due to interactions connecting electronic states of very different energies, it is appropriate to consider the effect of the near degeneracy of states of value $\pm\Omega$ ($\pm\Lambda$ in case b). This degeneracy is raised in some order of the perturbation theory by the action of a part of the kinetic energy of rotation which was neglected in the separation of rotation and electronic motion.[8] The matrix elements of this operator are given in Sec. 7, expression (7.9). The correct linear combinations of the degenerate wave functions are the symmetric and antisymmetric functions, e.g., $[f(\Lambda\Sigma)\pm f(-\Lambda-\Sigma)]/(2)^{\frac{1}{2}}$ in Hund's case a. For both case a and case b, we write these as $[f(+)\pm f(-)]/(2)^{\frac{1}{2}}$. The matrix elements of the hyperfine operator now may be written as

(a) Diagonal in Λ doubling state:

$$\begin{pmatrix}\text{symmetric}\\ \text{antisym.}\end{pmatrix}\Big|H_{\text{hfs}}\Big|\begin{pmatrix}\text{symmetric}\\ \text{antisym.}\end{pmatrix}=\tfrac{1}{2}\{(+|H|+)+(-|H|-)\pm 2(-|H|+)\}; \quad (6.1)$$

(b) Off-diagonal in Λ doubling state:

$$\begin{pmatrix}\text{symmetric}\\ \text{antisym.}\end{pmatrix}\Big|H_{\text{hfs}}\Big|\begin{pmatrix}\text{antisym.}\\ \text{symmetric}\end{pmatrix}=\tfrac{1}{2}\{(+|H|+)-(-|H|-)\}, \quad (6.2)$$

where the matrix elements $(+|H|+)$ etc., are obtained from the $f(+)$, $f(-)$ states, in which Λ is a good quantum number. The matrix elements $(+|H|+)$ and $(-|H|-)$ are thus diagonal in Λ and are among those already derived in Sec. 5. For case a_β, the hyperfine matrix elements diagonal in Λ and Ω are of the form

$$[a\Lambda+(b+c)\Sigma](\mathbf{I}\cdot\mathbf{k}'). \quad (6.3)$$

The matrix elements of this operator which are also diagonal in J are the same for the states $\pm\Omega$ whose degeneracy is removed in Λ doubling. The matrix elements nondiagonal in J are of opposite signs for $\pm\Omega$ so that $(+|H|+)=-(-|H|-)$ for $\Delta J=\pm 1$.

In addition to the magnetic hyperfine elements diagonal in Λ of Sec. 5, there are also matrix elements connecting states differing in Λ by $\Delta\Lambda=\pm 1,\pm 2$. Thus, there are interactions between the degenerate states for Π states only. Some of the matrix elements are diagonal and some off diagonal in J, and they yield the various quantities of Eq. (6.1). The hyperfine matrix elements nondiagonal in Λ and Ω are worked out in Sec. 7, and we employ here expression (7.3) written as

$$(+|H|-)=(+\Pi|t|-\Pi)(S_{x'}+iS_{y'})\mathbf{I}\cdot(\mathbf{x}'+i\mathbf{y}'). \quad (6.4)$$

We shall give here explicit formulas for the hyperfine splitting for a case a_β $^2\Pi_{\frac{1}{2}}$ molecular state, neglecting the hyperfine matrix elements nondiagonal in J. The matrix elements for $\Delta J=\pm 1$ may be worked out from Sec. 5 and the Appendix. Thus, we have for the symmetric and antisymmetric Λ doubling states

$$W_{S/A}=(+|H|+)\pm(+|H|-),$$

with

$$(+|H|+)=\left(a-\frac{b+c}{2}\right)\frac{\mathbf{I}\cdot\mathbf{J}}{2J(J+1)},$$

$$(+|H|-)=\frac{d(J+\frac{1}{2})}{2J(J+1)}\mathbf{I}\cdot\mathbf{J}, \quad (6.5)$$

where

$$d=(+\Pi|t|-\Pi)=-\frac{g_I\mu_0\mu_N}{2}\left[\left(\frac{\delta(r_1)}{r_1^2}-\frac{3}{r_1^3}\right)\sin^2\chi\right]_{\text{Av}}.$$

Electronic wave functions which contribute to this $+\Pi\rightarrow-\Pi$ matrix element will vanish near the nucleus sufficiently rapidly so that the first term of the above expression for d will be negligible compared to the second.

For case b molecular states the same symmetry properties of the matrix elements obtain as in case a_β and the discussion given above applies for case b with the rotational angular momentum K replacing J. Expressions similar to Eq. (6.5) may be developed from the formulas of Sec. 7, with the important difference that in case b the electron spin is quantized in the laboratory rather than in the molecular frame.

7. SECOND-ORDER EFFECTS

In this section are considered effects which arise from those matrix elements of the magnetic hyperfine inter-

action [Eq. (2.6)] which are off diagonal in Λ, or off diagonal in Λ in Hund's case a. Levels which correspond to different values of the axial orbital angular momentum Λ, or in case a to differentel ectron spin components, are in general separated by energy intervals which are very large compared to the hyperfine interaction energy. The special features due to the $\pm\Omega$ degeneracy (Λ doubling) are treated in Sec. 6. These second-order effects in the general case give only small corrections to the first-order hyperfine structure, the theory of which is developed in Secs. 4 and 5. There are, however, several special cases in which these effects are of importance. In addition to the Λ doubling effects, there is the large class of molecular states with no first-order hyperfine structure, e.g., $^1\Sigma$ states, in which these second-order effects (and the nuclear electric quadrupole perturbation) constitute the whole of the hyperfine structure. The treatment of the hyperfine level structure in molecular cases intermediate between Hund's case a and case b also involves some of these off diagonal matrix elements.

The matrix elements of the first term of Eq. (2.6),

$$\frac{e}{mc}\frac{\boldsymbol{\mu}\cdot\mathbf{L}'}{r_1^3}, \tag{7.1}$$

may be written

$$2g_I\mu_0\mu_N\left(\Lambda\left|\frac{1}{r_1^3}[I_{x'}L_{x'}+I_{y'}L_{y'}]\right|\Lambda\pm1\right). \tag{7.2}$$

The magnetic interaction of the nuclear spin moment with the electron spin moment [Eq. (2.6)] yields matrix elements off diagonal both with respect to Λ and with respect to Σ. The elements off diagonal in Λ arise from the terms in (2.6) of the form $(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})$, which appear both in the ordinary spin-spin interaction and in the 'relativistic' term. The terms which contribute off diagonal matrix elements may be expanded in the molecular frame of reference as

$$\begin{aligned}2g_I\mu_0\mu_N&\left[\frac{3}{r_1^3}-\frac{\delta(r_1)}{r_1^3}\right]\\&\times\left\{\frac{\sin^2\chi}{4}[e^{-2i\varphi}(I_{x'}+iI_{y'})(S_{x'}+iS_{y'})\right.\\&+e^{2i\varphi}(I_{x'}-iI_{y'})(S_{x'}-iS_{y'})]\\&+\sin\chi\cos\chi[e^{-i\varphi}[(I_{x'}+iI_{y'})S_{z'}\\&+(S_{x'}+iS_{y'})I_{z'}]+e^{i\varphi}[(I_{x'}-iI_{y'})S_{z'}\\&\left.+(S_{x'}-iS_{y'})I_{z'}]]\right\}.\end{aligned} \tag{7.3}$$

Clearly, the first term, with factors $e^{\pm2i\varphi}$, in this expression connects states of $\Delta\Lambda=\pm2$. These terms are discussed in connection with the Λ doubling of Π states in Sec. 6.

Terms in the hyperfine coupling which are off diagonal in Σ only are of interest in cases intermediate between Hund's case a and case b. Such matrix elements arise from the spin components perpendicular to the symmetry axis (in $\mathbf{I}\cdot\mathbf{S}$) in Eq. (4.7). In a Hund's case a representation, the operator may be written conveniently in the form

$$\begin{aligned}F(\rho,\chi)&\tfrac{1}{2}\{(I_{x'}-iI_{y'})(S_{x'}+iS_{y'})\\&+(I_{x'}+iI_{y'})(S_{x'}-iS_{y'})\}\\&=F(\rho\chi)\tfrac{1}{2}\{\mathbf{I}\cdot(\mathbf{x}'-i\mathbf{y}')(S_{x'}+iS_{y'})\\&\quad+\mathbf{I}\cdot(\mathbf{x}'+i\mathbf{y}')(S_{x'}-iS_{y'})\}.\end{aligned} \tag{7.4}$$

The $S_{x'}\pm iS_{y'}$ operator acts only on the internal electron spin wave function, and the matrix elements of $(\mathbf{x}'\pm i\mathbf{y}')/2$ are, with respect to the rotational wave function, the same as those of a unit vector $\mathbf{i}'$, and are given in Appendix I. Thus, the matrix elements of expression (7.4) connecting $\Sigma\rightarrow\Sigma+1$ and $\Omega\rightarrow\Omega+1$ have the form

$$A(\mathbf{I}\cdot\mathbf{i}')[(S+\Sigma)(S-\Sigma+1)]^{\frac{1}{2}}. \tag{7.5}$$

For a good case a state, the effect of these matrix elements between members of a multiplet may be taken into account as a second-order perturbation. For a real intermediate case these matrix elements would be subjected to the appropriate transformation from case a.

There is another interaction with matrix elements off diagonal in Λ which should be mentioned here. This is the interaction of the electric quadrupole moment of the nucleus with the electrons. This interaction has been discussed extensively by Casimir,[1] and its matrix elements diagonal in Λ have been given by many authors.[2-4] In our notation, this interaction may be written

$$\begin{aligned}\frac{eQ}{I(2I-1)}&\left\{\frac{3\cos^2\chi-1}{2r_1^3}\frac{3I_{z'}^2-I^2}{2}+\frac{3}{4}\frac{\sin\chi\cos\chi}{r_1^3}\right.\\&\times[[I_{z'}(I_{x'}-iI_{y'})+(I_{x'}-I_{y'})I_{z'}]e^{i\varphi}\\&+[I_{z'}(I_{x'}+iI_{y'})+(I_{x'}+iI_{y'})I_{z'}]e^{-i\varphi}]\\&\left.+\frac{3}{8}\frac{\sin^2\chi}{r_1^3}[e^{2i\varphi}(I_{x'}-iI_{y'})^2+e^{-2i\varphi}(I_{x'}+iI_{y'})^2]\right\},\end{aligned} \tag{7.6}$$

where Q is the electric quadrupole moment of the nucleus as defined by Bardeen and Townes.[4] The terms in $e^{\pm2i\varphi}$ may affect the Λ doubling in case b.

Except for the case of Λ doubling described in Sec. 6, the matrix elements of (7.2) or (7.3) would by themselves yield negligible effects in a second-order calculation. There are, however, certain "molecular" matrix elements which are off diagonal in Λ and which, when taken in cross terms with (7.2) or (7.3) yield observable hyperfine structures, even in $^1\Sigma$ states.

We shall give here the effects in $^1\Sigma$ states which arise in second order from the interactions with the electron orbital currents, expression (7.2). The spin effects of

Eq. (7.3) are of the same general form. Semiclassical treatments (large values of J) have been given previously.[3] We write (7.2) in the form

$$\tfrac{1}{2}a[(L_{x'}+iL_{y'})(I_{x'}-iI_{y'})+(L_{x'}-iL_{y'})(I_{x'}+iI_{y'})]. \tag{7.7}$$

This term in second order yields§

$$\frac{a^2}{4}\sum_{\Pi}\frac{(\Sigma|L'_\perp|\Pi)^2}{\Delta E_{\Sigma\Pi}}[(\mathbf{I}\cdot\mathbf{k}')^2-I(I+1)], \tag{7.8}$$

in which the summation is extended over all Π states to which there is a nonvanishing $(\Sigma|L_\perp|\Pi)$ matrix element. The dependence on F of the expression in square brackets is given by $C(C+1)$ with $C=F(F+1)-I(I+1)-J(J+1)$. This is of exactly the same form as the hyperfine level perturbation developed by an electric quadrupole moment. The quantity $\sum_\Pi(\Sigma|L_\perp|\Pi)^2/\Delta E_{\Sigma\Pi}$ cannot, in general, be evaluated. For a very simple model with the total orbital angular momentum a good quantum number (Van Vleck's hypothesis of pure precession),[8] the value $L(L+1)/\Delta E_{\Sigma\Pi}$, is obtained for this quantity. The order of magnitude of this effect is $E_{\text{hfs}}^2/\Delta E_{\Sigma\Pi}$, which will be quite negligible in almost all cases.

The perturbation terms in the molecular Hamiltonian which arise from the nonseparability of electronic and rotational motion, and which lead to the "Λ doubling" observed in molecular spectra give nonvanishing matrix elements between Σ and Π states and these may form cross terms with the magnetic hyperfine operator (7.2). The Λ doubling operator is[8]

$$B(\Sigma|L_\perp|\Pi)[J(J+1)]^{\frac{1}{2}} =2B\left(\Sigma\left|L_{y'}+\frac{\tau p_{x'}}{\hbar}\right|\Pi\right)[J(J+1)]^{\frac{1}{2}}. \tag{7.9}$$

Another molecular operator with similar properties is the interaction of the electrons with an external magnetic field. For $^1\Sigma$ molecules there is no first-order interaction, but there exists the operator

$$\mu_0(L_{x'}\mathbf{x}'+L_{y'}\mathbf{y}')\cdot\mathbf{H}, \tag{7.10}$$

which has matrix elements of the form $\mu_0(\Sigma|L_\perp|\Pi)\mathbf{i}'\cdot\mathbf{H}$. The cross term of the first term of (7.9) with (7.2) is

$$\sum_\Pi 4aB\frac{(\Sigma|L'_\perp|\Pi)^2}{i\Delta E_{\Sigma\Pi}}[J(J+1)]^{\frac{1}{2}}(\mathbf{I}\cdot\mathbf{i}') =\sum_\Pi\frac{(\Sigma|L'_\perp|\Pi)^2}{\Delta E_{\Sigma\Pi}}2aB(\mathbf{I}\cdot\mathbf{J}). \tag{7.11}$$

This term accounts for most of the observed $\mathbf{I}\cdot\mathbf{J}$ interaction in $^1\Sigma$ states. There is a small contribution from the 'direct' $\mathbf{I}\cdot\mathbf{J}$ interaction of the nuclear motion discussed in Sec. 8. For the case of a positive nuclear moment the term above is positive.

The cross term of the second term of (7.9) with (7.1') gives a negligible hyperfine level shift. We will now examine the second-order cross term involving the matrix elements of the second term of (7.9) with those of $L_{y'}$ We have

$$\frac{e}{mc}\tau\mu_{y'} \times\sum_\Pi\frac{(\Sigma|p_{x'}|\Pi)(\Pi|L_{y'}/r_1^3|\Sigma) +(\Sigma|L_{y'}/r_1^3|\Pi)(\Pi|p_{x'}|\Sigma)}{\Delta E_{\Sigma\Pi}}. \tag{7.12}$$

The summation is extended to all excited Π states. Now, since

$$\frac{p_{kn}}{m}=\frac{i}{\hbar}[E_k-E_n]r_{kn}, \tag{7.13}$$

this expression becomes

$$\frac{e}{mc}\tau\mu_{y'}\frac{im}{\hbar}\left(\Sigma\frac{|L_{y'}x'-x'L_{y'}|}{r_1^3}\Sigma\right), \tag{7.14}$$

and since $[L_{y'},x']=-iz_1'$ we have for the cross term

$$\frac{e}{c}\frac{2B}{\hbar}\mu_{y'}\tau[J(J+1)]^{\frac{1}{2}}\left(\frac{z_1'}{r_1^3}\right)_{\text{Av}}=\frac{B}{\hbar c}\mathcal{E}_e(\mathfrak{y}\cdot\mathbf{J})\tau, \tag{7.15}$$

noting that the matrix elements of $\mathfrak{y}\cdot\mathbf{y}'$ are just $\mu_N(\mathbf{I}\cdot\mathbf{J})/2[J(J+1)]^{\frac{1}{2}}$. $\mathcal{E}_e$ is the magnitude of the electronic field produced by the electrons at the nucleus. The first term of Eq. (7.2) gives a contribution equal to (7.15), giving finally

$$2(B/\hbar c)\mathcal{E}_e(\mathfrak{y}\cdot\mathbf{J})\tau. \tag{7.16}$$

This term is just canceled by an equal contribution from the rotational motion of the nuclei (see Sec. 8).

The cross term of (7.2) with (7.10) is

$$\sum_\Pi a\mu_0\frac{(\Sigma|L_\perp|\Pi)^2}{\Delta E_{\Sigma\Pi}}(I_{x'}-iI_{y'})(H_{x'}+iH_{y'}) =\sum_\Pi a\mu_0\frac{(\Sigma|aL_\perp|\Pi)^2}{\Delta E_{\Sigma\Pi}}[\mathbf{I}\cdot\mathbf{H}-(\mathbf{I}\cdot\mathbf{k}')(\mathbf{H}\cdot\mathbf{k}')]. \tag{7.17}$$

This expression represents the effect of the diamagnetic shielding of the nucleus by the electrons in the presence of an external magnetic field. This effect has been discussed extensively by Ramsey[13] and will not be considered further here.

For completeness we consider the cross term of (7.9)

§ In Eqs. (7.8), (7.11), and (7.17) the matrix elements have been written as if the radial integrals could be factored from the angular momentum operators.

[13] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

and (7.10):

$$\sum_{\Pi} 2B\frac{(\Sigma|L_\perp|\Pi)^2}{i\Delta E_{\Sigma\Pi}}\mu_0[J(J+1)]^{\frac{1}{2}}(\mathbf{x}'-i\mathbf{y}')\cdot\mathbf{H} = 2\mu_0 B\sum_{\Pi}\frac{(\Sigma|L_\perp|\Pi)^2}{\Delta E_{\Pi}}(\mathbf{J}\cdot\mathbf{H}), \quad (7.18)$$

which yields the electronic contribution to the molecular rotational magnetic moment:

$$2\mu_0 B\sum_{\Pi}\frac{(\Sigma|L_\perp|\Pi)^2}{\Delta E_{\Sigma\Pi}}\mathbf{J}. \quad (7.19)$$

8. NUCLEAR SPIN-ROTATION INTERACTION IN $^1\Sigma$ STATES

In addition to the second-order electronic $\mathbf{I}\cdot\mathbf{J}$ interaction of Sec. 7, there is also the interaction of the nuclear magnetic moment with the magnetic field produced by the rotation of the heavy particles themselves. This interaction term is

$$-Z_2\frac{e}{M_0c}\mathfrak{y}_1\cdot\frac{[\varrho\times\mathbf{p}]}{\rho^3}, \quad (8.1)$$

where M_0 is the reduced mass, ρ the distance between the nuclei, and $p=p_2=-p_1$. Account must be taken here of the relative motion of the two nuclei. Following the procedure of Sec. 7, we write (8.1) in the form

$$Z_2e\frac{\mathfrak{y}_1\cdot[\tau\mathbf{k}'\times\mathbf{p}]}{c\rho^3M_0}+Z_2e\frac{\mathfrak{y}_1\cdot[\varrho_2\times\mathbf{p}]}{M_0c\rho^3} = \mathcal{E}_N\frac{\tau\mathfrak{y}_1\cdot\mathbf{J}h}{M_0\rho^2c}+\mathcal{E}_N\frac{\rho_2\hbar}{cM_0\rho^2}\mathfrak{y}_1\cdot\mathbf{J}, \quad (8.2)$$

where $\mathcal{E}_N$ is the electric field produced at the position of nucleus 1 by nucleus 2. ρ_2 is the distance from the center of mass nucleus 2. The first term of (8.2) added to (7.16) gives just

$$\frac{\tau\hbar}{M_0\rho^2c}\times[\text{total electric field at 1}]. \quad (8.3)$$

The electric field at the equilibrium position of a nucleus is zero. The second term of (8.2) is to be added to (7.11) and contributes to the $\mathbf{I}\cdot\mathbf{J}$ interaction.

9. INTERACTION WITH AN EXTERNAL FIELD: SELECTION RULES AND INTENSITIES

The contribution of each electron to the electronic dipole moment is the vector $e\mathbf{r}'$ with components $e\mathbf{x}'$, $e\mathbf{y}'$, and $e\mathbf{z}'$ in the molecular coordinate system.

The magnetic dipole moment operator in case a_β is the sum of two parts:

(1) The electronic contribution, a vector in the molecular frame of reference with components:
$(\mu_0L_{x'}+2\mu_0S_{x'})\mathbf{x}'$;
$(\mu_0L_{y'}+2\mu_0S_{y'})\mathbf{y}'$;
and $(\mu_0L_{z'}+2\mu_0S_{z'})\mathbf{z}$.

(2) The nuclear moment vector $g_I\mu_N\mathbf{I}$ in the laboratory system.

In case b_β, the magnetic moment is the sum of:

(1) $\mu_0L_{x'}\mathbf{x}'$; $\mu_0L_{y'}\mathbf{y}'$; $\mu_0\Lambda\mathbf{z}'$ in the molecular coordinate system.

(2) The vector $2\mu_0\mathbf{S}+g_I\mu_N\mathbf{I}$ in the laboratory system.

Diagonal values of the magnetic moment operator yield the first order Zeeman effect. Nondiagonal values of the electric and magnetic dipole operators give the selection rules and the intensities in electric and magnetic dipole transitions, as well as higher order Zeeman and Stark effects. The diagonal matrix elements of the magnetic interaction in case a are

$$(\Lambda+2\Sigma)\mu_0\frac{\Omega}{J(J+1)}m_JH+g_I\mu_Nm_IH \quad (9.1)$$

in strong fields, and

$$(\Lambda+2\Sigma)\mu_0\frac{\Omega}{J(J+1)}\frac{F(F+1)+J(J+1)-I(I+1)}{2F(F+1)} +g_I\mu_N\frac{F(F+1)-J(J+1)+I(I+1)}{2F(F+1)} \quad (9.2)$$

in very weak fields. The presence of Λ doubling does not affect these diagonal values. In case b the diagonal magnetic interaction is

$$\mu_0\frac{\Lambda^2}{K(K+1)}\frac{J(J+1)-S(S+1)+K(K+1)}{2J(J+1)}m_J +2\mu_0\frac{J(J+1)-K(K+1)+S(S+1)}{2J(J+1)}m_J +g_I\mu_Nm_I \quad (9.3)$$

in strong fields, and in weak fields for the J representation (Sec. 5) it is

$$\left\{\mu_0\frac{\Lambda^2}{K(K+1)}\frac{J(J+1)-S(S+1)+K(K+1)}{2J(J+1)} +2\mu_0\frac{J(J+1)-K(K+1)+S(S+1)}{2J(J+1)}\right\} \times\left\{\frac{F(F+1)-I(I+1)+J(J+1)}{2F(F+1)}\right\}m_F +g_I\mu_N\frac{F(F+1)-J(J+1)+I(I+1)}{2F(F+1)}m_F. \quad (9.4)$$

The off diagonal matrix elements of the electric or magnetic dipole moment components may be worked out from the matrix elements of the direction cosines of the molecular coordinate system given in the Appendix, together with the formulas taking into account the vector coupling.[10] In the interest of brevity the results will not be given here.[9]

Some examples of the use of the off diagonal matrix elements have been given in Sec. 7. The selection rules for the diatomic molecule are well known[5] and need only be extended to include the usual rule, $\Delta F=0, \pm 1$.

10. APPLICATIONS

The oxygen and nitrogen oxide molecules appear to be the only examples so far observed of a first-order magnetic hyperfine spectrum.

$O^{16}O^{17}$

The coupling of the electron spin to the molecular rotation in a $^3\Sigma$ state has been shown[11] to arise in part from the second-order effect of the spin orbit interaction orbital angular momentum components perpendicular to the axis, and the Λ doubling interaction [expression (7.9)]. Matrix elements of these operators between $^3\Sigma$ and $^3\Pi$ states yield in second-order energy perturbations in the $^3\Sigma$ level of the form discussed in Sec. 6 Eq. (5.8). Kramers[14] has shown that, in addition to these second-order terms, there is the spin-spin interaction of the electrons, which contributes terms of the same form as the above. The final energy positions of the levels $J=K+1$, K, $K-1$ are then

$$\begin{aligned} W_{K+1}&=W_0-2\lambda\frac{K+1}{2K+3}+\mu(K+1),\\ W_K&=W_0,\\ W_{K-1}&=W_0-2\lambda\frac{K}{2K-1}-\mu K, \end{aligned} \tag{10.1}$$

for $\lambda \ll B$. A more exact formula has been given by Schlapp[15] for the case $B\cong\lambda$.

The first-order magnetic hyperfine structure for a $^3\Sigma$ state is given by the case b_β expression (5.5):

$$b\mathbf{I}\cdot\mathbf{S}+c(\mathbf{I}\cdot\mathbf{k}')(\mathbf{S}\cdot\mathbf{k}'). \tag{10.2}$$

This quantity must be expressed in the F_1, J, or F_3 representation. For O_2 we have $\lambda=1.984$ cm^{-1} and $\mu=-0.0084$ cm^{-1}.[5] Thus, it appears likely that the coupling of S to K will be greater than the hyperfine interaction, and the J representation is appropriate. The diagonal expressions for the hyperfine levels in this representation are

$$W_{FJK}=\frac{F(F+1)-J(J+1)-I(I+1)}{2J(J+1)} \times\begin{cases}(K+2)[b+c/(2K+3)] & \text{for } J=K+1\\ b+c & \text{for } J=K\\ (K-1)[-b+c/(2K-1)] & \text{for } J=K-1.\end{cases} \tag{10.3}$$

Higher order corrections, proportional to b^2, and c^2, etc., may be obtained from the matrix elements of (10.2) according to the methods given in Sec. 5. A comparison of (10.3) with the spectrum of $O^{16}O^{17}$ will be published separately by Dr. S. L. Miller.

$N^{14}O^{16}$

Beringer and Castle[16] have observed the microwave spectrum of NO gas in rather strong magnetic fields. Margenau and Henry, and Henry[17] have given theoretical analyses of the spectrum. Their results are derived from an incomplete Hamiltonian.

In the experiments of Beringer and Castle, the Λ doubling was not resolved. Its effects are not included in our analysis. (The writers have been informed by Professor Beringer[18] that in a considerably more accurate experiment, the Λ doubling and the related hyperfine structure effects in NO have been resolved. For this reason only, a summary of the analysis of the previous results will be given here.)

The ground state of NO is represented quite well by Hund's case a. In this representation the hyperfine Hamiltonian including all effects diagonal in Λ is

$$[a\Lambda+(b+c)\Sigma](\mathbf{I}\cdot\mathbf{k}')+b(I_{x'}S_{x'}+I_{y'}S_{y'}). \tag{10.4}$$

The second term gives matrix elements only between $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ states (see Sec. 7). This effect is expected to be small, and in fact it was possible to account for the observed spectrum without including it.

The energy levels in a strong magnetic field ($\sim$8500 gauss) were obtained in the following way: The Zeeman matrix, including elements of the Zeeman Hamiltonian connecting $J=3/2$ and $J=5/2$ was solved exactly. (The effect of the $J=7/2$ level on $J=3/2$ states was found to be negligible.) The resulting states were then corrected by a second-order calculation of the effects of the states of $^2\Pi_{\frac{1}{2}}$. This calculation employed the matrix elements of the magnetic field between $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$ states, and the rotational distortion of the spin multiplets[8] (incipient case b). The final linear combination of eigenfunctions was employed to obtain the magnetic hyperfine structure from (10.4). An agreement with the observed spectrum to 0.05 percent was obtained employing $(a\Lambda+(b+c)\Sigma)=0.002607$ cm^{-1}.

[14] H. A. Kramers, Z. Physik **53**, 422 (1929).
[15] R. Schlapp, Phys. Rev. **51**, 342 (1937).
[16] R. Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950).
[17] H. Margenau and A. F. Henry, Phys. Rev. **78**, 587 (1950); A. F. Henry, Phys. Rev. **80**, 549 (1950).
[18] R. Beringer (private communication to the authors).

APPENDIX

We require matrix elements of operators of the form,

$$e^{\mp ik\varphi}\mathbf{I}\cdot(\mathbf{x}'\pm i\mathbf{y}'), \tag{A1}$$

where $k=0$, 1, 2. Since the wave functions are of the form,

$$\Theta_{J\Omega M}(\theta)e^{i\Lambda\varphi}e^{iM\psi}, \tag{A2}$$

the integrals giving matrix elements are of the form,

$$\int\Theta_{J\Omega M}{}^{*}e^{-i\Lambda\varphi}e^{-iM\psi}e^{\mp ik\varphi}\mathbf{I}\cdot(\mathbf{x}'\pm i\mathbf{y}')\Theta_{J'\Omega'M'}e^{i(\Lambda\pm k)\varphi}e^{iM'\psi}d\tau. \tag{A3}$$

If we perform the φ integral, we are left with the quantity,

$$\int\Theta_{J\Omega M}{}^{*}e^{-iM\psi}\mathbf{I}\cdot(\mathbf{x}'\pm i\mathbf{y}')\Theta_{J'\Omega'M'}e^{iM'\psi}\sin\theta d\theta d\psi, \tag{A4}$$

to evaluate. In this connection it is convenient to define a Cartesian coordinate system with unit vectors $\mathbf{i}'\mathbf{j}'\mathbf{k}'$, related to the fixed space frame through the usual Eulerian angles (see Fig. 4). In this Eulerian system, the $\mathbf{x}'$ axis is along the line of nodes, and the $\mathbf{y}'$ axis is related to it in the usual right-handed way. The electron is located on the $\mathbf{i}'$ axis. We may write

$$\mathbf{i}'=\mathbf{x}'\cos\varphi+\mathbf{y}'\sin\varphi=(\mathbf{x}'+i\mathbf{y}')(e^{-i\varphi}/2)+(\mathbf{x}'-i\mathbf{y}')(e^{i\varphi}/2), \tag{A5}$$

and hence, we see that

$$(\Omega|\mathbf{i}'|\Omega\pm1)=\tfrac{1}{2}\int\Theta_{J\Omega M}{}^{*}\times e^{-iM\psi}(\mathbf{x}'\pm i\mathbf{y}')\Theta_{J'\Omega\pm1M'}e^{iM'\psi}\sin\theta d\theta d\psi. \tag{A6}$$

The unit vectors $\mathbf{i}'\mathbf{j}'\mathbf{k}'$ are $\mathbf{T}$ vectors in the notation of Condon and Shortley,[10] that is, they commute with the components of $\mathbf{J}$ in the laboratory system according to $[J_x, T_y]=i\hbar T_z$, etc. Then, their matrix elements are of the form,

$$\begin{aligned}
(\alpha Jm|\mathbf{T}|\alpha'J+1m\pm1)&=\mp(\alpha J\vdots\mathbf{T}\vdots\alpha'J+1)\times\tfrac{1}{2}[(J\pm m+1)(J\pm m+2)]^{\frac{1}{2}}(\mathbf{i}\pm i\mathbf{j}),\\
(\alpha Jm|\mathbf{T}|\alpha'J+1m)&=(\alpha J\vdots\mathbf{T}\vdots\alpha'J+1)\times[(J+1)^2-m^2]^{\frac{1}{2}}\mathbf{k},\\
(\alpha Jm|\mathbf{T}|\alpha'Jm\pm1)&=(\alpha J\vdots\mathbf{T}\vdots\alpha'J)\times\tfrac{1}{2}[(J\mp m)(J\pm m+1)]^{\frac{1}{2}}(\mathbf{i}\pm i\mathbf{j}),\\
(\alpha Jm|\mathbf{T}|\alpha'Jm)&=(\alpha J\vdots\mathbf{T}\vdots\alpha'J)m\mathbf{k},\\
(\alpha Jm|\mathbf{T}|\alpha'J-1m\pm1)&=\pm(\alpha J\vdots\mathbf{T}\vdots\alpha'J-1)\times\tfrac{1}{2}[(J\mp m)(J\mp m-1)]^{\frac{1}{2}}(\mathbf{i}\pm i\mathbf{j}),\\
(\alpha Jm|\mathbf{T}|\alpha'J-1m)&=(\alpha J\vdots\mathbf{T}\vdots\alpha'J-1)(J^2-m^2)^{\frac{1}{2}}\mathbf{k},
\end{aligned} \tag{A7}$$

in which $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are the XYZ unit vectors in the laboratory system. From King, Hainer, and Cross[19] we obtain, with a change of phase to conform to the choice of

[19] Cross, Hainer, and King, J. Chem. Phys. **12**, 210 (1944).

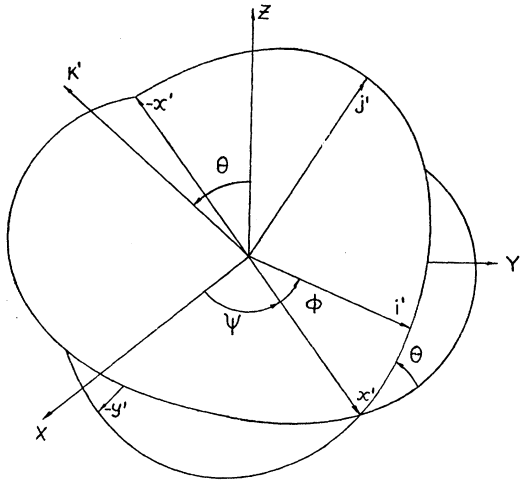

FIG. 4. The Eulerian coordinate system $\mathbf{i}'\mathbf{j}'\mathbf{k}'$ with θ and ψ as chosen by King, Hainer, and Cross. The plus and minus $\mathbf{x}'$ and minus $\mathbf{y}'$ axes are marked. For proper phase and angles as chosen by Condon and Shortley and Van Vleck one should let $\mathbf{j}\rightarrow\mathbf{i}$, $\mathbf{i}\rightarrow-\mathbf{j}$, and $\psi\rightarrow\psi+\pi$. ψ then is the angle between the $\mathbf{i}$ axis and the projection of $\mathbf{k}'$ on the $\mathbf{ij}$ plane.

angles of Van Vleck[8] and the phases of Condon and Shortley,[10]

$$\begin{aligned}
(J\Omega\vdots\mathbf{k}'\vdots J+1\Omega)&=\frac{[(J+\Omega+1)(J-\Omega+1)]^{\frac{1}{2}}}{(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}},\\
(J\Omega\vdots\mathbf{k}'\vdots J\Omega)&=\frac{\Omega}{J(J+1)},\\
(J\Omega\vdots\mathbf{k}'\vdots J-1\Omega)&=\frac{(J^2-\Omega^2)^{\frac{1}{2}}}{J(4J^2-1)^{\frac{1}{2}}},
\end{aligned} \tag{A8}$$

$$(J\Omega\vdots\mathbf{j}'/\mp i\mathbf{i}'\vdots J+1\Omega\pm1)=\mp\frac{[(J\pm\Omega+1)(J\pm\Omega+2)]^{\frac{1}{2}}}{2(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}},$$

$$(J\Omega\vdots\mathbf{j}'/\mp i\mathbf{i}'\vdots J\Omega\pm1)=\frac{[(J\mp\Omega)(J\pm\Omega+1)]^{\frac{1}{2}}}{2J(J+1)},$$

$$(J\Omega\vdots\mathbf{j}'/\mp i\mathbf{i}'\vdots J-1\Omega\pm1)=\pm\frac{[(J\mp\Omega)(J\mp\Omega-1)]^{\frac{1}{2}}}{2J(4J^2-1)^{\frac{1}{2}}}.$$

It should also be noted that, in the rotating frame,

$$(\Sigma|S_{y'}\pm iS_{x'}|\Sigma\pm1)=[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}, \tag{A9}$$

and, in the laboratory frame,

$$(m_S|S_X\mp iS_Y|m_S\pm1)=[S(S+1)-m_S(m_S\pm1)]^{\frac{1}{2}}, \tag{A10}$$

etc.