Electron-Nuclear Double Resonance Spectrum of an *F*-Center Electron in Alkali Halides (with NaCl Structure)*

T. E. FEUCHTWANG
Department of Physics and Coordinated Science Laboratory, University of Illinois, Urbana, Illinois

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From the de Boer model of the *F* center, one can calculate a spin Hamiltonian to describe the hyperfine interaction of the *F*-center electron with an arbitrary nucleus in the lattice. This Hamiltonian was discussed in the preceding paper. In this paper we shall use this Hamiltonian to construct a spin Hamiltonian describing the hyperfine interaction of the *F* electron with all nuclei in the lattice in the presence of a constant and uniform magnetic field. From this we shall deduce the electron-nuclear double resonance spectrum for the *F* electron. The negative-ion vacancy (in a cubic lattice) is an inversion center, and the magnetic field is a pseudovector. Consequently, nuclei at sites which are mapped into each other by an inversion in the vacancy are physically equivalent. If this fact is accounted for, then the entire electron-nuclear double resonance spectrum may be viewed as a set of spectra, each one of which is associated with the interaction of the *F* electron with a particular pair of physically equivalent nuclei. This contrasts with the present theory which assumes that the *F* electron interacts with individual nuclei. The new theory leads to a marked improvement in the agreement between the calculated and observed spectra. An even more interesting result is that the calculated spectrum is now sensitive to the relative sign of the nuclear *g* factor and the electric quadrupole coupling constant. Thus the experimental data can be used to determine not only the magnitude but also the sign of the electric field gradient at lattice sites close to the *F* center.

I. INTRODUCTION

THE first investigation of the *F* centers in alkali halides by means of the electron-nuclear double resonance (ENDOR) technique was made by Feher.[1] Feher interpreted his results by means of the spin Hamiltonian describing the hyperfine interaction of the *F* electron with a single nucleus in the lattice in the presence of a constant magnetic field. From this Hamiltonian he deduced an effective Hamiltonian depending only on the nuclear spin operator. The "ENDOR" spectrum is then assumed to correspond to the magnetic dipole transitions between the states of this effective Hamiltonian.[2]

The experiments performed at the University of Illinois[3] resulted in spectra with considerably more lines than predicted by Feher's theory. It is the purpose of this paper to show that the observed spectra can be interpreted as magnetic dipole transitions between the states of an effective Hamiltonian which depends on the spin operators of pairs of physically equivalent nuclei. Specifically, this operator includes an indirect spin-spin coupling between the two equivalent nuclei. This Hamiltonian is derived from the complete spin Hamiltonian by means of a generalized perturbation scheme due to Pryce.[4] It should be noted that when the uniform magnetic field is oriented parallel to an axis of rotation symmetry, one or more of the sets of equivalent nuclei may be larger than 2. In principle our technique applies also to these special cases. The algebraic computations involved in these cases are, however, excessive. In practice the orientation of the uniform magnetic field is varied over all distinct orientations in a given crystal plane. Hence, for a given run only a few special orientations will occur for which an analysis considering only pairs of equivalent nuclei is invalid. The effort in analyzing also these special cases is not warranted since no additional physical insight is to be obtained from the analysis of the experimental data involved. We, therefore, shall restrict ourselves to the discussion of the general case involving only pairs of equivalent nuclei.

The most interesting feature of the new effective Hamiltonian is that it predicts the "ENDOR" spectrum to depend not only on the absolute magnitude of the electric quadrupole coupling constant but also on the sign of the product of this constant and of the nuclear *g* factor for the given pair of equivalent nuclei. This implies that the sign of the electric field gradient at lattice sites close to an *F* center can be determined from the "ENDOR" data. This result was invoked in the preceding paper during the discussion of the contribution of the lattice polarization to the electric field gradient at lattice sites close to an *F* center.[5] This feature is a direct consequence of the fact that we include in the treatment of the hyperfine interaction of the *F* electron with the nuclei terms of the second order in the electronic spin operator. This observation follows from the simplified analysis of the hyperfine interaction of the *F* electron with a single nucleus. Such an analysis is presented in Appendix A.

We shall now outline the derivation of the effective Hamiltonian from the complete spin Hamiltonian.

In the presence of a static and uniform magnetic field $\mathbf{H}_0$ the spin Hamiltonian describing the interaction

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[1] G. Feher, Phys. Rev. **105**, 1122 (1957).

[2] See reference 1, Eq. (2).

[3] See W. C. Holton, thesis, University of Illinois, 1960 (unpublished). Also C. P. Slichter, Phys. Rev. Letters **5**, 197 (1960).

[4] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[5] See Sec. III of the preceding paper [Phys. Rev. **126**, 1616 (1962)].

of the F electron and the nuclei of the lattice with each other and with the magnetic field can be written in the form

$$\mathbf{H}(\mathbf{S},\mathbf{I}_\alpha)=\mathbf{H}(\text{electron Zeeman})+\sum_\alpha[\mathbf{H}_\alpha(\text{hyperfine})+\mathbf{H}_\alpha(\text{nucleus Zeeman})]. \quad (1)$$

Here we excluded any direct interaction between the spins of different nuclei. The hyperfine interaction between the F electron and the nuclei of the lattice is written as a sum over the lattice sites of the hyperfine operator introduced in the preceding paper,[6,7]

$$\mathbf{H}_\alpha(\text{hyperfine})=a_\alpha\mathbf{S}\cdot\mathbf{I}_\alpha+2\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}\sum_{m=-2}^{2}(-1)^m b_{m,\alpha}\mathcal{Y}_{-m}^{(2)}(\mathbf{S},\mathbf{I}_\alpha),$$
$$+\frac{2}{3}\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}\sum_{m=-2}^{2}(-1)^m Q_{m,\alpha}\mathcal{Y}_{-m}^{(2)}(\mathbf{I}_\alpha), \quad (2)$$

where the operators $\mathcal{Y}_m^{(2)}(\mathbf{S},\mathbf{I}_\alpha)$ are defined by

$$\mathcal{Y}_0^{(2)}(\mathbf{S},\mathbf{I}_\alpha)=\tfrac{1}{2}(5/4\pi)^{\frac{1}{2}}(3\mathbf{S}_0\mathbf{I}_{0,\alpha}-\mathbf{S}\cdot\mathbf{I}_\alpha),$$
$$\mathcal{Y}_{\pm1}^{(2)}(\mathbf{S},\mathbf{I}_\alpha)=\tfrac{1}{2}(15/4\pi)^{\frac{1}{2}}(\mathbf{S}_0\mathbf{I}_{\pm1,\alpha}+\mathbf{S}_{\pm1}\mathbf{I}_{0,\alpha}),$$
$$\mathcal{Y}_{\pm2}^{(2)}(\mathbf{S},\mathbf{I}_\alpha)=(15/8\pi)^{\frac{1}{2}}(\mathbf{S}_{\pm1}\mathbf{I}_{\pm1,\alpha}),$$

and

$$\mathbf{S}_0=\mathbf{S}_z,\quad \mathbf{S}_{\pm1}=\mp(2)^{-\frac{1}{2}}(\mathbf{S}_x\pm i\mathbf{S}_y).$$

Analogous expressions define $\mathcal{Y}_m^{(2)}(\mathbf{I}_\alpha)$ and $\mathbf{I}_\mu$, $\mu=0,\pm1$.

The coefficients $b_{m,\alpha}$ and $Q_{m,\alpha}$ are components of two irreducible spherical tensors of rank two. These components were defined in the preceding paper[8] in the αth local coordinate system. We shall find it convenient to refer all quantities to an external frame, which has its origin at the center of the vacancy and its polar axis parallel to $\mathbf{H}_0$. The Hamiltonian in the external frame has the same form as in the local frame except that the coefficients are now $\tilde{b}_{m,\alpha}$ and $\tilde{Q}_{m,\alpha}$. From the definition of $b_{m,\alpha}$ and $Q_{m,\alpha}$ as spherical tensors, it follows that

$$\tilde{b}_{m,\alpha}=\sum_{n=-2}^{2}D_{nm}^{(2)}(\varphi_\alpha,\theta_\alpha,0)b_{n,\alpha}. \quad (3)$$

(The same transformation law also relates $\tilde{Q}_{m,\alpha}$ to $Q_{n,\alpha}$.) Here $(\theta_\alpha,\varphi_\alpha)$ are the polar angles of $\mathbf{H}_0$ in the αth local coordinate system,

$$D_{nm}^{(2)}(\varphi,\theta,\psi)=e^{-in\varphi}d_{nm}^{(2)}(\theta)e^{-im\psi} \quad (4)$$

is the 5-dimensional irreducible representation of the group of 3-dimensional rotations[9] and

$$d_{nm}^{(2)}(\theta)=\sum_s\frac{(-1)^s[(2+n)!(2-n)!(2+m)!(2-m)!]^{\frac{1}{2}}}{s!(2-s-n)!(2+m-s)!(n+s-m)!}\times[\cos(\theta/2)]^{4+m-n-2s}[-\sin(\theta/2)]^{n-m+2s},$$

where s assumes all integral values allowed by the requirement that no argument of the factorials shall be negative.

In a cubic lattice each site is an inversion center. Furthermore, the magnetic field is a pseudovector. Hence, the Hamiltonian indicated in Eq. (1) is invariant under an inversion in the vacancy (origin). Thus the nuclei at sites α and α' which are mapped into each other by an inversion in the origin are physically equivalent. Consequently the proper zero-order spin functions χ for the entire lattice are products of an electronic spin function $\chi_F=|SM_s\rangle$ and symmetrized pairs of nuclear spin functions,[10]

$$\chi_{\alpha\alpha'}=(2)^{-\frac{1}{2}}[|I_\alpha M_{I,\alpha}\rangle|I_{\alpha'}M'_{I,\alpha'}\rangle \pm|I_\alpha M'_{I,\alpha}\rangle|I_{\alpha'}M_{I,\alpha'}\rangle]. \quad (5)$$

That is,

$$\chi=\chi_F\prod_\alpha\chi_{\alpha\alpha'}. \quad (6)$$

Note that $\chi_{\alpha\alpha'}$ is an eigenfunction of the following operators

$$\mathbf{F}_{z,\alpha}=\mathbf{I}_{z,\alpha}+\mathbf{I}_{z,\alpha'};\ (\mathbf{I}_{z,\alpha})^2+(\mathbf{I}_{z,\alpha'})^2;\ \mathbf{I}_\alpha^2;\ (\mathbf{I}_{\alpha'})^2;\ \text{Parity}. \quad (7)$$

That is, $\chi_{\alpha\alpha'}$ belongs to the eigenvalues

$$M_F=M_{I,\alpha}+M_{I,\alpha'};\ (M_{I,\alpha})^2+(M_{I,\alpha'})^2;\ I_\alpha(I_\alpha+1)=I_{\alpha'}(I_{\alpha'}+1);\ P$$

of the operators indicated above. $\chi_{\alpha\alpha'}$ can be decomposed into a linear combination of eigenfunctions which belong to the same eigenvalues

$$M_F=M_{I,\alpha}+M_{I,\alpha'};\quad I_\alpha(I_\alpha+1)=I_{\alpha'}(I_{\alpha'}+1);\ P$$

of the operators

$$\mathbf{F}_{z,\alpha};\ (\mathbf{I}_\alpha)^2;\ (\mathbf{I}_{\alpha'})^2;\ \text{Parity},$$

and to different eigenvalues of the operator

$$\mathbf{F}_\alpha^2=(\mathbf{I}_\alpha+\mathbf{I}_{\alpha'})^2. \quad (8)$$

Thus in the representation defined by Eq. (6) the Hamiltonian matrix consists of a direct sum of submatrices $H(\alpha,\alpha',P)$. Each such submatrix couples only states χ for which all factors $\chi_{\beta\beta'}$, $\beta\neq\alpha$ are identical and for which the remaining factors $\chi_{\alpha\alpha'}$ have the same

[6] See Eq. (9) in the preceding paper.

[7] The following convention concerning the local coordinate systems is implied in Eq. (1): If sites α and β are mapped into each other under an element of the lattice point group which leaves the vacancy (0,0,0) fixed, then the same transformation maps $x_{i,\alpha}$ into $x_{i,\beta}$, $i=1,2,3$.

[8] See Eqs. (11) and (12) in the preceding paper.

[9] See M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. IV.

[10] When $\mathbf{H}_0$ is oriented parallel to an axis of rotation symmetry there occur larger sets of equivalent sites (per shell). Thus, if $\mathbf{H}_0$ is oriented along the [100] direction the sites (0,1,0), (0,$\bar{1}$,0), (0,0,1), and (0,0,$\bar{1}$) are equivalent. In this case the proper zero-order spin functions are more complicated, and involve factors consisting of linear combinations of four single spin functions which transform according to the irreducible representations of the group C_{4v}. We shall not consider such special cases.

parity. Hence our problem reduces to the diagonalization of the spin Hamiltonian for the interaction of the F electron with two equivalent nuclei at sites α and α' in the presence of a magnetic field $\mathbf{H}_0$.

We shall assume $\mathbf{H}_0$ is strong enough to make the hyperfine and the nuclear Zeeman interactions small perturbation of the electronic Zeeman term. This problem is most conveniently solved in two steps. First, an effective nuclear spin Hamiltonian is constructed. This Hamiltonian is to operate on the manifold of states belonging to one (of the two) degenerate states of the unperturbed electronic Zeeman Hamiltonian. Then the effective Hamiltonian is treated by conventional techniques. Clearly the totality of magnetic dipole transitions with $\Delta M_s=0$ corresponds to the collection of such transitions between the states of the individual effective nuclear Hamiltonians.[11]

The method of calculating such effective Hamiltonians is formally equivalent to the perturbation expansion of the eigenvalues of the full Hamiltonian in terms of the eigenvalues of the unperturbed Hamiltonian. The difference between the conventional expansion and the present formalism is that the terms in the series now consist of operators which operate on the manifold of states belonging to a given (degenerate) eigenvalue of the unperturbed Hamiltonian. Since we wish to include in the effective Hamiltonian the electric quadrupole term of Eq. (2), it is important to include all other terms of comparable order. It turns out that this consideration requires us to retain some of the second-order terms in the perturbation expansion mentioned above.[12] Some of these terms resemble the electron coupled nuclear spin-spin interaction discussed by Ramsey.[13] The importance of this term is due to the fact that it couples nearly degenerate states of the first-order effective Hamiltonian. We shall see that the second-order terms are responsible for two previously mentioned improvements of the present theory over Feher's theory.

In Sec. II, we shall calculate the effective Hamiltonian for a pair of equivalent nuclei. In Sec. III, we shall approximately diagonalize this Hamiltonian, and calculate the "ENDOR" spectrum associated with a given pair of equivalent nuclei. In Sec. IV the calculated spectrum is compared with a typical experimental spectrum.

II. CALCULATION OF THE EFFECTIVE SPIN HAMILTONIAN (FOR A PAIR OF EQUIVALENT NUCLEI)

In the following derivation we shall omit some intermediate steps in order to preserve the continuity of the main discussion. The more important steps are reproduced in Appendix B.

We shall concern ourselves with those terms of Eq. (1) which relate to the nuclei at sites α and α' which are mapped into each other by an inversion in the vacancy. These terms are rewritten below in a form that exhibits explicitly their dependence on the electron spin operators:

$$\mathbf{H}_\alpha(S,\mathbf{I}_\alpha,\mathbf{I}_{\alpha'})=2\beta H_0\mathbf{S}_z+(-\mathbf{H}_{-1}^{(1)}\mathbf{S}_1+\mathbf{H}_0^{(1)}\mathbf{S}_z-\mathbf{H}_1^{(1)}\mathbf{S}_{-1})+\mathbf{H}_2^{(1)}.^{14} \quad (9)$$

Here (x,y,z) are coordinates in the external frame (in which the z axis is parallel to $\mathbf{H}_0$). The small operators $(H_\mu^{(1)};\mu=-1,0,1,2)$ involve only the nuclear spin operators $\mathbf{I}_\alpha$ and $\mathbf{I}_{\alpha'}$.

Pryce[4] has shown that the eigenvalues and eigenstates of a Hamiltonian $\mathbf{H}=\mathbf{H}^{(0)}+\mathbf{H}^{(1)}$ corresponding to a given degenerate eigenvalue E_m of $\mathbf{H}^{(0)}$ are, to third order in $\mathbf{H}^{(1)}$, given by the corresponding quantities of the effective Hamiltonian $\mathbf{H}'$ defined below.

$$\mathbf{H}'=E_m+\mathbf{P}_m\mathbf{H}^{(1)}\mathbf{P}_m-\sum_{n\neq m}\frac{\mathbf{P}_m\mathbf{H}^{(1)}\mathbf{P}_n\mathbf{H}^{(1)}\mathbf{P}_m}{E_n-E_m}. \quad (10)$$

Here $\mathbf{P}_m$ is the projection operator onto the linear manifold of states belonging to E_m.[15] For the Hamiltonian defined by Eq. (9) the sum in Eq. (10) reduces to a single term since $\mathbf{H}^{(0)}=2\beta H_0\mathbf{S}_z$ has only two eigenstates. Hence, if we combine Eqs. (9) and (10), we obtain the following effective nuclear spin operators:

$$\mathbf{H}_{+,\alpha}(\mathbf{I}_\alpha,\mathbf{I}_{\alpha'})=\beta H_0+\tfrac{1}{2}\mathbf{H}_0^{(1)}+\mathbf{H}_2^{(1)}+(2\beta H_0)^{-1}\mathbf{H}_{-1}^{(1)}\mathbf{H}_1^{(1)}, \quad (11)$$

$$\mathbf{H}_{-,\alpha}(\mathbf{I}_\alpha,\mathbf{I}_{\alpha'})=-\beta H_0-\tfrac{1}{2}\mathbf{H}_0^{(1)}+\mathbf{H}_2^{(1)}-(2\beta H_0)^{-1}\mathbf{H}_1^{(1)}\mathbf{H}_{-1}^{(1)}. \quad (11a)$$

Here Eqs. (11) and (11a) refer to the manifolds of states in which the spin of the F electron is, respectively, parallel and antiparallel to $\mathbf{H}_0$.[16] With the help of Eqs. (1)–(3) we can rewrite Eqs. (11) and (11a) to exhibit the dependence of $H_{\pm,\alpha}$ on the nuclear spin operators $\mathbf{I}_\alpha$, $\mathbf{I}_{\alpha'}$ and $\mathbf{F}=\mathbf{I}_\alpha+\mathbf{I}_{\alpha'}$. From now on we shall suppress the subscript α whenever this is not likely to introduce confusion.

$$\begin{aligned}\mathbf{H}_\pm=&\pm\{\tfrac{1}{2}\Delta+A_\pm\mathbf{F}_z+B[\mathbf{I}_\alpha^2+\mathbf{I}_{\alpha'}^2-(\mathbf{I}_{z,\alpha})^2-(\mathbf{I}_{z,\alpha'})^2]\\&+C\mathbf{F}_z^2\pm\tilde{Q}^0[(\mathbf{I}_{z,\alpha})^2+(\mathbf{I}_{z,\alpha'})^2-(\mathbf{I}_\alpha^2+\mathbf{I}_{\alpha'}^2)/3]\}\\&\pm2B(\mathbf{I}_{1,\alpha}\mathbf{I}_{-1,\alpha'}+\mathbf{I}_{-1,\alpha}\mathbf{I}_{1,\alpha})\mp\sqrt{3}\,\mathrm{Re}(\tilde{b}_{-1}\mathbf{F}_1)\\&+\left\{\frac{2}{3}\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}\sum_{m=\pm1,\pm2}(-1)^m\tilde{Q}_m[\mathcal{Y}_{-m}^{(2)}(\mathbf{I}_\alpha)+\mathcal{Y}_m^{(2)}(\mathbf{I}_\alpha)]\right.\\&\left.+\frac{1}{2\Delta}O_\pm(\mathbf{F}_z,\mathbf{F}_1,\mathbf{F}_{-1})\right\}, \quad (12)\end{aligned}$$

[11] These transitions comprise the "ENDOR" spectrum.

[12] Note that $A_\alpha^2/\beta H_0$ may be $O(Q_{m,\alpha})$ for some m and α. A similar situation occurs in the calculation of the spin Hamiltonian for a paramagnetic ion in a crystal, where it is responsible for the anisotropic electronic g factor. This is discussed by A. Abragam and M. L. Pryce, Proc. Roy. Soc. (London) **205**, 135 (1951).

[13] N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

[14] $\mathbf{S}_{\pm1}=\mp(2)^{\frac{1}{2}}(\mathbf{S}_x\pm i\mathbf{S}_y)$, $\mathbf{S}_0=\mathbf{S}_z$.

[15] Note that $\mathbf{H}'$ operates only on the manifold of states belonging to E_m.

[16] That is with $M_s=\pm\frac{1}{2}$.

TABLE I. Approximate ranges of values for the parameters in Eq. (12).

Nuclei in shell number[a]	$\Delta=2\beta H_0$[b]	a	b_0	$g_N\beta_N H_0$	$A_\pm$	B	C	$\tilde{Q}_0$
1, 2	≈ 9000	10–100	1–15	0.6–1.3	$\approx a/2$ (5–50)	$\approx a^2/4\Delta$ (0.003–0.3)	$\approx 9b_0^2/4\Delta$ (0.002–0.06)	$\approx Q_0$ (0.02–0.2)
3	≈ 9000	$\lesssim 1$	$\lesssim 1$	0.6–1.3	$\approx a/2+b_0\mp g_N\beta_N H_0=O(1)$	$[(a-b_0)/4\Delta](a+2b_0)$		

[a] The shell number $n=(R_\alpha/a)^2$, where R_α = distance from αth site to the vacancy, a = interionic distance.
[b] Energies are in Mc/sec.

where the following abbreviations were used:

$$\Delta=2\beta H_0=\text{the electronic Zeeman splitting,} \tag{13}$$

$$A_\pm=\tfrac{1}{2}a+\tilde{b}_0\mp\beta_N g_N H_0\mp B, \tag{14}$$

$$B=(1/4\Delta)[(a-\tilde{b}_0)^2-6|\tilde{b}_2|^2], \tag{15}$$

$$C=(3/2\Delta)|\tilde{b}_1|^2, \tag{16}$$

$$O_+=(a-\tilde{b}_0)\times\sqrt{3}[\tilde{b}_1\mathbf{F}_{-1}\mathbf{F}_z+\tilde{b}_{-1}\mathbf{F}_z\mathbf{F}_1-\sqrt{2}(\tilde{b}_{-2}\mathbf{F}_{-1}^2+\tilde{b}_2\mathbf{F}_1^2)]-3\sqrt{2}(\tilde{b}_1\tilde{b}_2\mathbf{F}_1\mathbf{F}_z+\tilde{b}_{-1}\tilde{b}_{-2}\mathbf{F}_z\mathbf{F}_{-1}), \tag{17}$$

$$O_-=(a-\tilde{b}_0)\times\sqrt{3}[\tilde{b}_{-1}\mathbf{F}_1\mathbf{F}_z+\tilde{b}_1\mathbf{F}_z\mathbf{F}_{-1}-\sqrt{2}(\tilde{b}_{-2}\mathbf{F}_{-1}^2+\tilde{b}_2\mathbf{F}_1^2)]-3\sqrt{2}(\tilde{b}_{-1}\tilde{b}_{-2}\mathbf{F}_{-1}\mathbf{F}_z+\tilde{b}_1\tilde{b}_2\mathbf{F}_z\mathbf{F}_1). \tag{18}$$

In Eq. (12) the terms in the first set of curly braces are diagonal in the representation defined by Eq. (5).[17] The next term couples sets of nearly degenerate (zero-order) states having equal values of $M_F=M_{I,\alpha}+M_{I,\alpha'}$. Note that this term can be written as

$$\pm 2B(\mathbf{I}_\alpha\cdot\mathbf{I}_{\alpha'}-\mathbf{I}_{z,\alpha}\mathbf{I}_{z,\alpha'}). \tag{19}$$

Here the second term is diagonal in the present representation and the first term is a spin-spin coupling of of the type discussed by Ramsey.[13] One may interpret this coupling as arising from the fact that both nuclear dipoles align themselves in the field of the F electron. The second-order character of this effect is evident and is reflected in the formal calculation of the coupling constant B.

III. CALCULATION OF THE ELECTRON NUCLEAR DOUBLE RESONANCE SPECTRUM (OF A PAIR OF EQUIVALENT NUCLEI)

In this section we shall approximately diagonalize the operator indication in Eq. (12). In view of the remarks made at the end of the preceding section, we shall concern ourselves primarily with the terms in the first set of curly braces and the term immediately following these. The remaining terms in Eq. (12) have zero expectation in the representation to be used. We shall consider the contribution of $\sqrt{3}\,\mathrm{Re}(\tilde{b}_{-1}\mathbf{F}_1)$ to second order in a perturbation expansion. The terms in the second set of curly braces will be neglected.

In order to justify the procedure outlined above, we shall consider the range of values for the parameters in Eq. (12). For this purpose we shall use the approximation

$$\tilde{b}_{m,\alpha}\approx D_{0m}^{(2)}(\varphi_\alpha,\theta_\alpha,0)b_{0,\alpha}=(4\pi/5)^{\frac{1}{2}}Y_m^{(2)}(-\theta_\alpha,0)b_{0,\alpha}. \tag{20}$$

This relation is an immediate consequence of Eq. (3), and the fact that, for $m\neq 0$, $b_{m,\alpha}$ either vanishes (for symmetry reasons) or is very small.[18] The experimental data indicate that in the first two shells $(b_0/a)=O(1/10)$ while in the farther shells, for some lattices $(b_0/a)=O(1)$. Furthermore $(g_N\beta_N H_0/a)=$ is $O(1/10$–$1/100)$ for the first two shells and $O(1)$ for the farther shells. Consequently, the ranges of the parameters in Eq. (12) are quite different for the first two shells from those in the farther shells. Table I summarizes the available experimental information.

In the representation defined by Eq. (5), and to be denoted henceforth by $(MM'\pm)$, the expectation of $(\mathbf{H}_\pm\mp\Delta/2)$ is easily calculated to be

$$\pm\{A_\pm M_F+B[2I(I+1)-(M^2+M'^2)]+CM_F^2\pm\tilde{Q}_0[(M^2+M'^2)-\tfrac{2}{3}I(I+1)]+PB[I(I+1)-MM'](\delta_{M,M'-1}+\delta_{M,M'+1})\},^{19} \tag{21}$$

where $P=\pm 1$ depending on whether the spin function is even or odd under permutation of sites α and α'. Of the operators which contribute to the above expectation value, only the last one, i.e.,

$$\mp 2B(\mathbf{I}_{1,\alpha}\mathbf{I}_{-1,\alpha'}+\mathbf{I}_{-1,\alpha}\mathbf{I}_{1,\alpha'})$$

has off-diagonal terms, namely those coupling states having the same values of M_F and P. There are several pairs of such states. According to Table I, A is sufficiently larger than B, C, and $\tilde{Q}_0$ for us to treat these pairs of states as nearly degenerate. It is a simple matter to diagonalize the several 2×2 submatrices and calculate the correspondingly corrected set of nuclear spin functions. These functions are eigenfunctions of the operators $\mathbf{F}_z$ and parity, they are not eigenfunctions of $\mathbf{F}^2$.

The next term in Eq. (12) is

$$\sqrt{3}\,\mathrm{Re}(\tilde{b}_{-1}\mathbf{F}_1)=\tfrac{3}{8}b_0\sin(2\theta_\alpha)(\mathbf{I}_+ + \mathbf{I}_-). \tag{22}$$

This operator couples states of equal P and differing in M_F by ± 1. In second-order perturbation theory, these contribute corrections to the energy of order $\frac{9}{64}b_0^2/A$.

[17] See the observation made following Eq. (6).

[18] This point is discussed in Sec. II of the preceding paper.

[19] In deriving this result we use as the zero-order Hamiltonian $\mathbf{H}_\pm^{(0)}=\pm A_\pm\mathbf{F}_z$.

TABLE II. The approximate eigenstates and eigenvalues of H_-.

States[a,b]	Values of[c] M_F	P	F	Energies[d]
1. $(-\frac{3}{2}-\frac{3}{2}+)$	-3	$+$	3	$3A_--3B+9C+2\tilde{Q}_0+3D_-$
2. $(-\frac{3}{2}-\frac{1}{2}+)$	-2	$+$	3	$2A_--8B+4C\quad+2D_-$
3. $(1+\alpha^2)^{-\frac{1}{2}}[(-\frac{3}{2}\,\frac{1}{2}+)+\alpha(-\frac{1}{2}-\frac{1}{2}+)]$	-1	$+$	1, 3	$A_--6B+\ C-\ \tilde{Q}_0+\ D_-+\epsilon$
4. $(1+\alpha^2)^{-\frac{1}{2}}[\alpha(-\frac{3}{2}\,\frac{1}{2}+)-(-\frac{1}{2}-\frac{1}{2}+)]$	-1	$+$	1, 3	$A_--6B+\ C-\ \tilde{Q}_0+\ D_--\epsilon$
5. $(1+\beta^2)^{-\frac{1}{2}}[(-\frac{3}{2}\,\frac{3}{2}+)+\beta(-\frac{1}{2}\,\frac{1}{2}+)]$	0	$+$	1, 3	$-7B\qquad\qquad+\eta$
6. $(1+\beta^2)^{-\frac{1}{2}}[\beta(-\frac{3}{2}\,\frac{3}{2}+)-(-\frac{1}{2}\,\frac{1}{2}+)]$	0	$+$	1, 3	$-7B\qquad\qquad-\eta$
7. $(1+\alpha^2)^{-\frac{1}{2}}[\alpha(\frac{3}{2}-\frac{1}{2}+)-(\frac{1}{2}\,\frac{1}{2}+)]$	1	$+$	1, 3	$-\ A_--6B+\ C-\ \tilde{Q}_0-\ D_--\epsilon$
8. $(1+\alpha^2)^{-\frac{1}{2}}[(\frac{3}{2}-\frac{1}{2}+)+\alpha(\frac{1}{2}\,\frac{1}{2}+)]$	1	$+$	1, 3	$-\ A_--6B+\ C-\ \tilde{Q}_0-\ D_-+\epsilon$
9. $(\frac{3}{2}\,\frac{1}{2}+)$	2	$+$	3	$-2A_--8B+4C\quad-2D_-$
10. $(\frac{3}{2}\,\frac{3}{2}+)$	3	$+$	3	$-3A_--3B+9C+2\tilde{Q}_0-3D_-$
11. $(-\frac{3}{2}-\frac{1}{2}-)$	-2	$-$	2	$2A_--2B+4C\quad+2D_-$
12. $(-\frac{3}{2}\,\frac{1}{2}-)$	-1	$-$	2	$A_--5B+\ C\quad+\ D_-$
13. $(1-\gamma^2)^{-\frac{1}{2}}[(-\frac{3}{2}\,\frac{3}{2}-)+\gamma(-\frac{1}{2}\,\frac{1}{2}-)]$	0	$-$	0, 2	$-3B\qquad\qquad+\zeta$
14. $(1+\gamma^2)^{-\frac{1}{2}}[\gamma(-\frac{3}{2}\,\frac{3}{2}-)-(-\frac{1}{2}\,\frac{1}{2}-)]$	0	$-$	0, 2	$-3B\qquad\qquad-\zeta$
15. $(\frac{3}{2}-\frac{1}{2}-)$	1	$-$	2	$-\ A_--5B+\ C\quad-\ D_-$
16. $(\frac{3}{2}\,\frac{1}{2}-)$	2	$-$	2	$-2A_--2B+4C\quad-2D_-$

[a] Here we use the observation $(MM'\pm)=(2)^{-\frac{1}{2}}(|I_\alpha M_{I,\alpha}\rangle|I_{\alpha'}M'_{I,\alpha'}\rangle\pm|I_\alpha M'_{I,\alpha}\rangle|I_{\alpha'}M_{I,\alpha'}\rangle)$ and consider in particular nuclei with spin $I=3/2$.
[b] The parameters α, β, and γ are calculated by solving 2nd order secular equations, they are:

$$\alpha=(\tilde{Q}_0+B-\epsilon)/2(6)^{\frac{1}{2}}B,\quad \beta=(2\tilde{Q}_0+4B-\eta)/3B,\quad \gamma=(2\tilde{Q}_0-\zeta)/3B,$$

where

$$\epsilon=[(\tilde{Q}_0+B)^2+24B^2]^{\frac{1}{2}},\quad \eta=[(2\tilde{Q}_0+4B)^2+9B^2]^{\frac{1}{2}},\quad \zeta=[4\tilde{Q}_0^2+9B^2]^{\frac{1}{2}}.$$

Note that α, β, and γ vanish when B vanishes; and when $\tilde{Q}_0$ vanishes,

$$\alpha=-(2/3)^{\frac{1}{2}},\quad \beta=-1/3,\quad \gamma=-1.$$

These are the appropriate values for a representation in which **F** is diagonal: (3), (5), and (8) correspond to $F=1$; (4), (6), and (7) to $F=3$; (13) correspond to $F=0$; (14) to $F=2$.
[c] When two values are indicated for F, the corresponding function is a linear combination of the two functions for which those are the eigenvalues of **F**.
[d] The parameters ϵ, η, and ζ are defined in footnote b.

It is simple to show that the actual corrections are

$$\pm D_\pm M_F=\tfrac{9}{64}(b_0^2/A_\pm)\sin^2(2\theta_\alpha)(\pm 2M_F). \qquad (23)$$

This correction is in some instances well within the experimental resolution. All other terms in Eq. (12) are negligible.

The "ENDOR" spectrum represents magnetic dipole transitions subject to the constraint (selection rule) $\Delta M_s=0$. Magnetic dipole transitions are most conveniently specified in a representation with sharp angular momentum operators **J** and $\mathbf{J}_z$. In the present case the appropriate operators are **F** and $\mathbf{F}_z$ defined above. In applying the selection rules $\Delta F=\pm 1$, 0 and $\Delta M_F=\pm 1$, we shall have to take account of the fact that our representation does include states which are not sharp in **F**, and hence, we shall have a slightly increased number of transitions due to the mixture of states belonging to different eigenvalues of **F**. We shall ignore the fact that the operator defined in Eq. (22) mixes, in second order, states of different M_F since the additional (weakly) allowed transitions introduced by this effect correspond to much lower frequencies than the rest of the spectrum.[20] In Table II we list for a nucleus of spin $I=3/2$, the states of $\mathbf{H}_-$ and their energies, within the abovementioned approximation.[21]

In Table III we list the corresponding calculated "ENDOR" frequencies.

It is easily verified that the transitions within the manifold of states associated with $\mathbf{H}_+$, i.e., with $M_s=1/2$ lead to a spectrum which can be obtained from the one for $\mathbf{H}_-$ by replacing A_- by A_+ and $\tilde{Q}_0$ by $-\tilde{Q}_0$.

Now $A_--A_+=2g_N\beta_N H_0$, i.e., replacing A_- by A_+ leads to a shift in the mean frequency of the spectrum without affecting the distribution of the lines about this mean frequency. The spectrum listed in Table III is manifestly sensitive to a reversal in the sign of $\tilde{Q}_0$. Hence, the two subspectra associated with a given pair of equivalent nuclei differ in the distribution of the individual frequencies about their mean frequency. Thus a definite assignment of a subspectrum to one of the two operators $\mathbf{H}_\pm$, permits the determination of $\tilde{Q}_0$. Such an assignment is possible on the basis of the mean frequency $A_\pm+D_\pm$ i.e., the subspectrum with higher mean frequency is associated with $\mathbf{H}_-$ if $g_N>0$ and with $\mathbf{H}_+$ if $g_N<0$. Thus, we conclude that the calculated spectrum for a given pair of equivalent nuclei is sensitive to the relative sign of g_N and $\tilde{Q}_0$. However, the sign of g_N is known from independent experiments. Hence, the present theory permits the determination of the sign of $\tilde{Q}_0$ from the experimental "ENDOR" data. This is in contrast with the theory which neglects the terms proportional to B, C, and

[20] See footnote c of Table III.
[21] Our conclusions are insensitive to the actual value of I, but $I=\frac{3}{2}$ is the simplest nontrivial case.

$D_{\pm}$. For, in this approximation, the individual subspectra are insensitive to the sign of $\tilde{Q}_0$, and differ only in their mean frequency.

From Eq. (3) it follows that

$$\tilde{Q}_0=\sum_{m=-2}^{2} D_{m0}^{(2)}(\varphi_\alpha,\theta_\alpha,0)Q_{m,\alpha}, \tag{24}$$

hence, if the sign and magnitude of $\tilde{Q}_0$ are known as a function of the polar angles $(\theta_\alpha,\varphi_\alpha)$, one can completely determine the electric quadrupole coupling tensor $\mathbf{Q}_\alpha$ in the local coordinate system of the αth nucleus.

IV. COMPARISON OF THE THEORY WITH EXPERIMENTAL DATA

In order to check the theory developed in the preceding sections, the two distributions of frequencies, corresponding to the two choices of sign for $\tilde{Q}_0$, were calculated for a subspectrum associated with two K^{39} nuclei in KCl. The uniform magnetic field, $\mathbf{H}_0$, was oriented in the [110] direction. The subspectrum chosen was that associated with $\mathbf{H}_-$ for a pair of nuclei in the first shell, with their (local) z axis normal to $\mathbf{H}_0$. This subspectrum is reproduced in Fig. 1. The parameters a, b_0, and $|\tilde{Q}_0|$ as well as the orientation of the nuclei with respect to the external magnetic field were determined in the usual way, with the help of Feher's spin Hamiltonian.[22] The two calculated spectra are compared in Table IV with the observed one. It is evident that for $\tilde{Q}_0<0$, the agreement is well within the experimental error. For $\tilde{Q}_0>0$, the agreement is very poor.

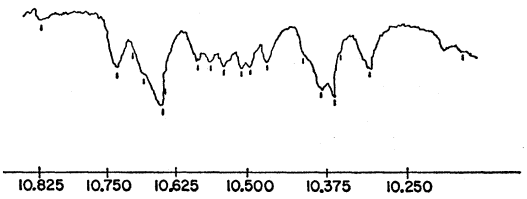

FIG. 1. Observed "ENDOR" subspectrum associated with two K^{39} nuclei in the first shell of KCl with their (local) z axis oriented to the external field H_0. The field $\mathbf{H}_0$ is along the [110] direction. The lines indicated by a short vertical dash are associated with $\mathbf{H}_-$ and were used in Table IV. The frequency is indicated in kMc/sec.

It is remarkable that except for a pair of lines separated by a frequency interval smaller than the experimental resolution, all calculated lines could be identified in the observed spectrum. This is all the more remarkable for the two weakly allowed transitions[23] leading to the extreme frequencies $(A_-\pm 0.359)$ Mc/sec, which in fact overlap adjacent subspectra.[24]

The negative sign of $\tilde{Q}_0$ implies that $Q_{0,110}$ is positive. In the preceding paper this result was interpreted in terms of the displacement of the ions around the F center into the vacancy.[25]

TABLE III. The (approximate) calculated "ENDOR" spectrum.

Transition[a,b]	Frequency[c,d]
1. $2\rightarrow 1$	$A_-+5B+5C+2\tilde{Q}_0+D_-$
2. $3\rightarrow 2^*$	$A_--2B+3C+\tilde{Q}_0+D_--\epsilon$
3. $4\rightarrow 2$	$A_--2B+3C+\tilde{Q}_0+D_-+\epsilon$
4. $5\rightarrow 3$	$A_-+B+C-\tilde{Q}_0+D_-+\epsilon-\eta$
5. $6\rightarrow 3^*$	$A_-+B+C-\tilde{Q}_0+D_-+\epsilon+\eta$
6. $5\rightarrow 4^*$	$A_-+B+C-\tilde{Q}_0+D_--\epsilon-\eta$
7. $6\rightarrow 4$	$A_-+B+C-\tilde{Q}_0+D_--\epsilon+\eta$
8. $7\rightarrow 5^*$	$A_--B-C+\tilde{Q}_0+D_-+\epsilon+\eta$
9. $8\rightarrow 5$	$A_--B-C+\tilde{Q}_0+D_--\epsilon+\eta$
10. $7\rightarrow 6$	$A_--B-C+\tilde{Q}_0+D_-+\epsilon-\eta$
11. $8\rightarrow 6^*$	$A_--B-C+\tilde{Q}_0+D_--\epsilon-\eta$
12. $9\rightarrow 7$	$A_-+2B-3C-\tilde{Q}_0+D_--\epsilon$
13. $9\rightarrow 8^*$	$A_-+2B-3C-\tilde{Q}_0+D_-+\epsilon$
14. $10\rightarrow 9$	$A_-+5B-5C-2\tilde{Q}_0+D_-$
15. $12\rightarrow 11$	$A_-+3B+3C+D_-$
16. $13\rightarrow 12^*$	$A_--2B+C+D_--\zeta$
17. $14\rightarrow 12$	$A_--2B+C+D_-+\zeta$
18. $15\rightarrow 13^*$	$A_-+2B-C+D_-+\zeta$
19. $15\rightarrow 14$	$A_-+2B-C+D_--\zeta$
20. $16\rightarrow 15$	$A_--3B-3C+D_-$

[a] Corresponding to $\Delta M_F=-1$, the set corresponding to $\Delta M_F=1$ leads to the same set of frequencies.
[b] The starred transitions are only "weakly" allowed. They are strictly "forbidden" in the two limiting cases when B or $\tilde{Q}_0$ vanish.
[c] Here we did not include the transitions allowed by the mixture of states of different M_F resulting from the second-order corrections due to the off-diagonal terms of the operator indicated in Eq. (22). These transitions lead to frequencies which are lower than those listed by A_-+D_-.
[d] Recall that magnetic dipole transitions conserve parity.

TABLE IV. Comparison of the calculated with an observed "ENDOR" spectrum.

Observed lines[a,b] $f-10530.5$ kc/sec		Calculated spectrum[b,c] $(f-A_-/h)$ kc/sec $\tilde{Q}_0<0$	$\tilde{Q}_0>0$
− 13.5	13.5	17.5	3
− 30.5	35.5	36	10
− 58.5	58.5	62	36
−124.5	127.5	132	132
−139.5	140.5	143	171
−158.5	159.5	154	206
−175.5	175.5	171	219
−216.5	210.5	219 222.5	236 243
−358.5	344.5	359	452

[a] The calculated spectra are manifestly symmetric about their mean frequency, hence only upper half is listed. The observed spectrum is not quite symmetric and hence the two corresponding frequencies are listed side by side.
[b] The observed lines were read to the closest kc/sec, and because of the choice of mean frequency, they are listed to the closest 0.5 kc/sec. The experimental resolution was, however, only about ±5 kc/sec. The calculated frequencies were rounded off to the closest 0.5 kc/sec.
[c] $\Delta=9250$ Mc/sec, $a=20.66$ Mc/sec, $b_0=0.91$ Mc/sec, $|\tilde{Q}_0|=0.096$ Mc/sec.

[22] This Hamiltonian lead to a spectrum:

$$hf=\pm g_N\beta_N H_0+\tfrac{1}{2}[a+b_0(3\cos^2\theta_\alpha-1)]+\tfrac{1}{2}Q_0(3\cos^2\theta_\alpha-1)(M_I-\tfrac{1}{2})$$

and permits rough determination of the parameters associated with a particular pair of nuclei from the angular dependence of hf. This determination can be improved with the present theory. Thus, we obtained for $\frac{1}{2}Q_0$, 0.096 Mc/sec rather than the previously quoted value of 0.1 Mc/sec.
[23] See footnote b, Table III.
[24] See Fig. 1.
[25] See Sec. IV of the preceding paper.

V. CONCLUSIONS

Using a generalized perturbation scheme, an effective nuclear spin Hamiltonian was derived. This Hamiltonian explicitly accounts for the symmetry properties of an F center in lattices with the structure of NaCl. It gives a detailed description of the "ENDOR" spectrum associated with a given pair of equivalent nuclei, which agrees very well with the observed spectra. The theory was shown to permit an unambiguous determination of the sign of the electric quadrupole coupling constant in the hyperfine interaction between the F electron and nuclei of the lattice.

The theory permits a much closer determination of the quadrupole coupling tensor from the "ENDOR" data than Feher's Hamiltonian did. Consequently this theory enables us to extract from the data more detailed information on the field gradient in the neighborhood of F centers than was previously possible. As was pointed out in the preceding paper, this information could in turn be used in determining the displacement of the ions around an F center.

ACKNOWLEDGMENT

The writer wishes to thank Professor C. P. Slichter for suggesting the problem, and following the work with continued interest.

APPENDIX A

It is worth noting that the sensitivity of the "ENDOR" spectrum to the sign of the product of the nuclear g factor and the electric quadrupole coupling constant does not depend on the fact that in each shell the nuclei occur in physically equivalent pairs. The effect occurs already when one considers the spectrum associated with the interaction of the F electron and a single nucleus, provided one considers second-order terms in the electron spin operator. Thus, consider Feher's simplified spin Hamiltonian[2]

$$\begin{aligned}\mathbf{H}(\mathbf{S},\mathbf{I}_\alpha)&=2\beta H_0\mathbf{S}_z+a_\alpha\mathbf{S}\cdot\mathbf{I}+\mathbf{b}_{0,\alpha}(3\mathbf{S}_z\mathbf{I}_{z,\alpha}-\mathbf{S}\cdot\mathbf{I}_z)\\&\quad+\tfrac{1}{3}Q_{0,\alpha}(3\mathbf{I}_{z,\alpha}{}^2-\mathbf{I}_\alpha{}^2)-\beta_N g_{N,\alpha}H_0\mathbf{I}_{z,\alpha}\\&=2\beta H_0\mathbf{S}_z+(a_\alpha+2b_{0,\alpha})\mathbf{I}_{z,\alpha}\mathbf{S}_z\\&\quad-\beta_N g_{N,\alpha}H_0\mathbf{I}_{z,\alpha}+\tfrac{1}{3}Q_{0,\alpha}(3\mathbf{I}_{z,\alpha}{}^2-\mathbf{I}_\alpha{}^2)\\&\quad+(a-b_0)(\mathbf{S}_{+1}\mathbf{I}_{-1,\alpha}+\mathbf{S}_{-1}\mathbf{I}_{+1,\alpha}).\end{aligned}\tag{A1}$$

In a representation in which $\mathbf{S}^2$, $\mathbf{S}_z$, $\mathbf{I}_\alpha{}^2$, $\mathbf{I}_{z,\alpha}{}^2$ are all diagonal, the last term couples the pairs of states $|S,\ M_s-1,\ I,M_I\rangle$ and $|S,M_s,I,\ M_I-1\rangle$. It is a simple matter to calculate the eigenvalues of $\mathbf{H}(\mathbf{S},\mathbf{I}_\alpha)$ to second order in $\mathbf{S}$ and first order in $\mathbf{I}_\alpha$

$$\begin{aligned}E_\pm(M_I)&=\pm\{\beta H_0+[\tfrac{1}{2}a+b_0\mp\beta_N g_N H_0]M_I\\&\quad\pm Q_0[M_I{}^2-\tfrac{1}{3}I(I+1)]+[(a-b_0)^2/8\beta H_0]\\&\quad\times[I(I+1)-M_I(M_I\pm1)]\},\end{aligned}\tag{A2}$$

where the upper and lower signs refer, respectively, to the levels associated with $M_s=\pm\frac{1}{2}$. We may rewrite Eq. (A2) to bring it into a form closer to that used in the text, [Eq. (21)],

$$\begin{aligned}E_\pm(M_I)&=\pm\{\tfrac{1}{2}\Delta+A_\pm M_I\pm Q_0[M_I{}^2-\tfrac{1}{3}I(I+1)]\\&\quad+B[I(I+1)-M_I{}^2]\},\end{aligned}\tag{A3}$$

where

$$\begin{aligned}\Delta&=2\beta H_0,\\A_\pm&=\tfrac{1}{2}a+b_0\mp\beta_N g_N H_0\mp B,\\B&=(a-b_0)^2/4\Delta.\end{aligned}\tag{A4}$$

The levels defined by Eq. (A3) are depicted schematically in Fig. 2, for the case where $g_N>0$, $I=\frac{3}{2}$.

The effect of the second-order term $B[I(I+1)-M_I{}^2]$ can be visualized as a "repulsion" between the pairs of coupled levels. The effect on the "ENDOR" spectrum is depicted in Fig. 2(b): the separation between the three lines, associated with that value of M_s that leads to a lower mean frequency, is smaller or larger than the separation between the lines of the other set, depending on whether $g_{N,\alpha}Q_{0,\alpha}$ is greater than or less than zero.

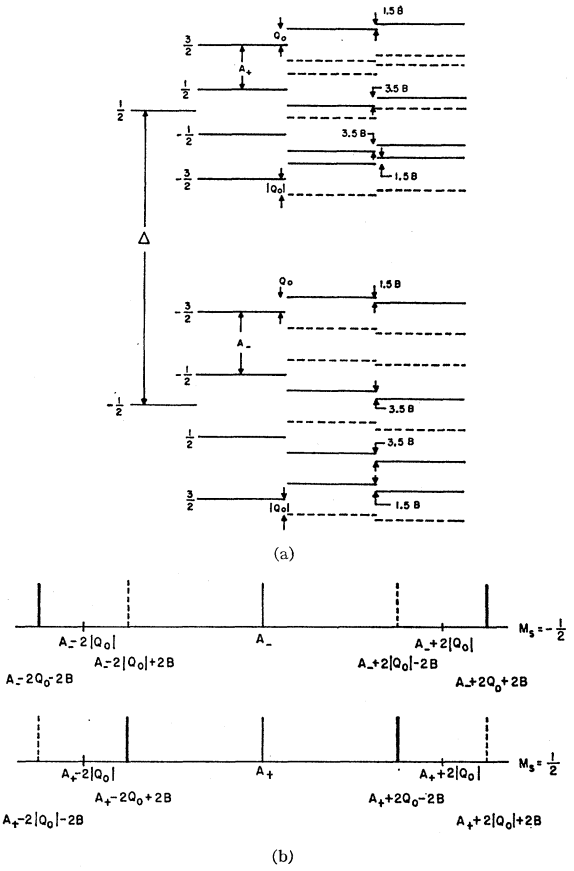

FIG. 2. (a) Schematic representation of the energy levels defined by Eq. (A3). Solid lines, $Q_0>0$; dashed lines, $Q_0<0$. (b) Schematic representation of the ENDOR lines ($\Delta M_s=0$, $\Delta M_I=\pm1$) predicted by Eq. (A3). The extreme lines associated with Q_0 greater than or less than zero denoted, respectively, by solid and dashed lines. If g_N greater than or less than zero, then A_- is, respectively, greater than or less than A_+.

APPENDIX B

List of intermediate steps omitted from Sec. II.

The operators $\mathbf{H}_\mu^{(1)}$ introduced in Eq. (9) are listed below

$$\begin{aligned}
&\mathbf{H}_0^{(1)}\mathbf{S}_z=[(a+2\tilde{b}_0)\mathbf{F}_z-\sqrt{3}(\tilde{b}_1\mathbf{F}_{-1}+\tilde{b}_{-1}\mathbf{F}_{+1})]\mathbf{S}_z,\\
&-\mathbf{H}_{\pm1}^{(1)}\mathbf{S}_{\mp1}=-[(a-\tilde{b}_0)\mathbf{F}_{\pm1}+\sqrt{3}\tilde{b}_{\pm1}\mathbf{F}_z\\
&\qquad\qquad -(\tfrac{3}{8})^{\frac{1}{2}}\tilde{b}_{\pm2}\mathbf{F}_{\mp1}]\mathbf{S}_{\mp1},\\
&\mathbf{H}_2^{(1)}=-\beta_N g_N\mathbf{F}_z+\frac{2}{3}\left(\frac{4\pi}{5}\right)^{\frac{1}{2}}\sum_{m=-2}^{2}(-1)^m\tilde{Q}_m\\
&\qquad\times[\mathcal{Y}_{-m}^{(2)}(\mathbf{I}_\alpha)+\mathcal{Y}_{-m}^{(2)}(\mathbf{I}_{\alpha'})].
\end{aligned}\tag{B1}$$

In applying Eq. (10) to obtain the effective nuclear spin Hamiltonian, we have to take the expectation of the operator

$$\begin{aligned}
&\mathbf{P}_m\mathbf{H}^{(1)}\mathbf{P}_n\mathbf{H}^{(1)}\mathbf{P}_m\\
&\quad=\mathbf{P}_m(-\mathbf{H}_{-1}^{(1)}\mathbf{S}_{+1}+\mathbf{H}_0^{(1)}\mathbf{S}_z-\mathbf{H}_{-1}^{(1)}\mathbf{S}_{-1}+H_2^{(1)})\\
&\qquad\times\mathbf{P}_n(-\mathbf{H}_{-1}^{(1)}\mathbf{S}_{+1}+\mathbf{H}_0^{(1)}\mathbf{S}_z\\
&\qquad\quad-\mathbf{H}_{+1}^{(1)}\mathbf{S}_{-1}+\mathbf{H}_2^{(1)})\mathbf{P}_m,
\end{aligned}\tag{B2}$$

in one of the two states of

$$\mathbf{H}^{(0)}=2\beta H_0\mathbf{S}_z.\tag{B3}$$

Here $\mathbf{P}_m$ is the operator projecting out the chosen state, say χ_A and $\mathbf{P}_n$ is the operator projecting out the remaining state χ_B. Since $\mathbf{H}_0^{(1)}\mathbf{S}_z+\mathbf{H}_2^{(1)}$ is diagonal in χ_A, (B2) reduces to

$$\begin{aligned}
&\mathbf{P}_m(\mathbf{H}_{-1}^{(1)}\mathbf{S}_{+1}+\mathbf{H}_{+1}^{(1)}\mathbf{S}_{-1})\\
&\qquad\times\mathbf{P}_n(\mathbf{H}_{-1}^{(1)}\mathbf{S}_{+1}+\mathbf{H}_{+1}^{(1)}\mathbf{S}_{-1})\mathbf{P}_m\\
&\qquad=|P_n(\mathbf{H}_{-1}^{(1)}\mathbf{S}_{+1}+\mathbf{H}_{+1}^{(1)}\mathbf{S}_{-1})\mathbf{P}_m|^2.
\end{aligned}\tag{B4}$$

The expectation of (B4) in the state χ_A is evidently

$$|\langle\chi_B|\mathbf{H}_{-1}^{(1)}\mathbf{S}_{+1}+\mathbf{H}_{+1}^{(1)}\mathbf{S}_{-1}|\chi_A\rangle|^2=\tfrac{1}{2}\mathbf{H}_{\mp1}^{(1)}\mathbf{H}_{\pm1}^{(1)},\tag{B5}$$

where the upper and lower signs apply, respectively, to the case where $\chi_A=|M_s\rangle=\pm\frac{1}{2}$. Here we used the fact that $\{\chi_A,\chi_B\}$ form a complete set in the space of electron spin functions, and that $\mathbf{H}_{\pm1}^{(1)}$ do not operate on these functions.

To obtain Eq. (11), we only have to divide (B5) by the single energy denominator

$$E_A-E_B=\pm2\beta H_0.\tag{B6}$$

To obtain Eqs. (12)–(18) we have only to substitute Eqs. (B1) into Eq. (B7)

$$\begin{aligned}
\mathbf{H}_{\pm,\alpha}(\mathbf{I}_\alpha,\mathbf{I}_{\alpha'})&=\pm\beta H_0\pm\tfrac{1}{2}\mathbf{H}_0^{(1)}+\mathbf{H}_2^{(1)}\\
&\quad\pm\tfrac{1}{2}(2\beta H_0)^{-1}\mathbf{H}_{\mp1}^{(1)}\mathbf{H}_{\pm1}^{(1)}.
\end{aligned}\tag{B7}$$

In this calculation it should be remembered that

$$\tilde{b}_m=(\tilde{b}_{-m})^*\tag{B8}$$

and that

$$\mathbf{I}_\alpha\cdot\mathbf{I}_{\alpha'}=\sum_{m=-1}^{1}(-1)^m\mathbf{I}_{m,\alpha}\mathbf{I}_{-m,\alpha'}.\tag{B9}$$