SECOND-ORDER EFFECTS IN ELECTRON–NUCLEAR DOUBLE RESONANCE SPECTRA

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A general expression is obtained for the effective nuclear spin Hamiltonian of a paramagnetic center with hyperfine interaction with several nuclei. The theory of second-order effects in electron-nuclear double resonance (ENDOR) spectra is developed for sufficiently general cases. The theory is compared with experiments made on F centers in LiF, KCl, and KBr, and explains fully the complex structure of the ENDOR lines. By comparing theory with experiment, it is established that the quadrupole-interaction constant Q′ of the K^{39} nucleus of sphere 1 of the F center in KBr is positive, and the analogous constant of the Li^7 nucleus of sphere 1 in LiF vanishes within the limits of experimental error (Q′ < 10 kHz).

INTRODUCTION

THE resolution attainable in the electron-nuclear double resonance (ENDOR) method makes it possible to observe the line structure due to the so-called second-order effects. The latter are taken to mean effects arising in the second approximation (with respect to energy) of perturbation theory with the hyperfine interaction as the perturbation and of the electron Zeeman energy as the zero-order Hamiltonian. These effects, interpreted as the "indirect interaction" of the nuclei, were observed in the ENDOR spectrum by Holton and Blum.[1] Subsequently Feuchtwang[2] presented a detailed theory of the second-order structure of ENDOR lines with allowance for the quadrupole interaction, when the "interaction" of only a pair of nuclei is significant. The theory of [2] was compared with experiment and this comparison yielded the sign of the quadrupole constant of the K^{39} nuclei of sphere 1 of the F center in the KCl crystal. The ENDOR spectra were theoretically and experimentally considered by Kravitz and Piper[3] in the case of the "interaction" of a quartet of spin ½.

However, the formulas of [2] for the ENDOR energies and frequencies do not take full account of the deviation of the nuclear-spin quantization axis from the direction of the external magnetic field H[4] (effective field), and therefore all the terms proportional to b^2/ν_0 (the symbols are explained below) in [2] are incorrect (with the exception of the orientation of H along the symmetry axes), as is the angular dependence in the quadrupole interaction. To be sure, for cases when $|a| \gg |b|$ the terms proportional to b^2/ν_0 are small, but the change of the quadrupole terms in the ENDOR frequencies for a longitudinal orientation of H is appreciable, since it can be of the same order as the effects of the indirect interaction of the nuclei.

In the present paper we consider the theory of second-order effects in ENDOR spectra of paramagnetic centers; this theory takes correct account of the deviation of the nuclear-spin quantization axis from the direction of the external magnetic field. We consider the energies and frequencies for the cases of a pair of "interacting" nuclei and an arbitrary number of pairwise "interacting" nuclei when contact interaction predominates. Account is taken of the asymmetry of the lines in the ENDOR spectrum of a pair of nuclei with $I = {}^3/_2$, due to quadrupole interaction in second-order perturbation theory.

The theory is compared with experiments performed on F centers in LiF, KCl, and KBr. The comparison has shown that the structure of the observed ENDOR lines is fully explained by second-order effects. By comparing the calculated spectrum with the experimental one, in analogy with [2], we determine the sign of the quadrupole constant of the K^{39} nuclei of sphere 1 in KBr (Q′ > 0); it is shown that for Li^7 in sphere 1 of LiF, the quadrupole-interaction constant can be regarded as equal to zero within the limits of experimental accuracy (Q′ < 10 kHz).

THEORY

1. Effective nuclear spin Hamiltonian. We start from the spin Hamiltonian of a paramagnetic center with electron spin S and isotropic electron g-factor in the form

$$\hat{\mathcal{H}} = \nu_0 \hat{S}_z - \sum_j (\nu_n{}^j I_z{}^j + A_1{}^j \hat{S}_1 \hat{I}_1{}^j + A_2{}^j \hat{S}_2 \hat{I}_2{}^j + A_3{}^j \hat{S}_3 \hat{I}_3{}^j + \hat{\mathcal{H}}_Q{}^j). \quad (1)$$

Here and throughout, all the coupling constants are given in frequency units, ν_0 is the electron Larmor frequency, the z axis is directed along H, the index j numbers the nuclei with spins I^j, ν_n is the nuclear Larmor frequency, and A_p (p = 1, 2, 3) are the components of the tensor of the magnetic hyperfine interaction in the principal coordinate system of the j-th nucleus with axes ξ, η, and ζ. Introducing the notation customarily used in ENDOR work, we obtain

$$\sum_{p=1}^{3} A_p = 3a, \quad A_1 = a - b_1 + 2b_2,$$

$$A_2 = a - b_1 - b_2, \quad A_3 = a + 2b_1 - b_2, \quad (2)$$

where a is the Fermi constant of the isotropic magnetic interaction, and b_1 and b_2 are connected with the tensor of the magnetic hyperfine dipole–dipole interaction and determine the anisotropy of the magnetic hyperfine interaction[1)] (see, e.g., [4]).

[1)] The anisotropy constants b_1 and b_2 introduced here differ from the analogously designated constants b [4], but coincide with those customarily used (see, e.g., the review [5]). The constant b_{kl} of [4] equals $b_1 - b_2$ of [5], and b_{k2} of [4] coincides with b_1 of [5].

We write the operator of the quadrupole interaction in (1) in the form

$$\hat{\mathcal{H}}_Q = Q'(\hat{I}_3^2 - {}^1/_3\hat{I}^2) + Q''(\hat{I}_1^2 - \hat{I}_2^2). \quad (3)$$

We have omitted here the index j; Q' and Q'' are the usual quadrupole-interaction constants.

If the ζ axis is the axial-symmetry axis, then $b_2 = 0$ and $Q'' = 0$. It is assumed throughout that

$$\nu_0 \gg |A_p|, \quad |\nu_n|, \quad |Q'|, \quad |Q''|. \quad (4)$$

The last inequality makes it possible to determine the energy levels and the wave functions by using the method of effective nuclear spin Hamiltonian that depends only on the nuclear-spin operators. The eigenvalues of such a spin Hamiltonian coincide with the eigenvalues of $\hat{\mathcal{H}}$ from (1), with accuracy to second order of perturbation theory, i.e., with accuracy to terms proportional to A_p^2/ν_0 inclusive. In this approximation the wave function of the system is $\psi = \chi_M \chi'$, where χ' is the nuclear spin function, which is the eigenfunction of the effective nuclear spin Hamiltonian, χ_M is the eigenfunction of $\hat{S}_z$, and M is the projection of the electron spin on the z axis. As shown in the Appendix, the effective nuclear spin Hamiltonian can be written in the form

$$\hat{\mathcal{H}}_{ef} = \nu_0 M + \sum_\sigma (M\Delta_M{}^\sigma \hat{F}_n{}^\sigma + \hat{\mathcal{H}}_Q{}^\sigma + \hat{\mathcal{H}}_{2ef}^\sigma). \quad (5)$$

The index σ numbers here the groups of nuclei. In each group σ there are k_σ nuclei with identical coupling constants Δ_M and unit vectors n. For each nucleus[4] we have (we omit the index j)

$$\Delta_M = \Big[\sum_{p=1} \Big(A_p - \frac{\nu_n}{M}\Big)^2 \alpha_p{}^2\Big]^{1/2}, \quad (6)$$

α_p are the direction cosines of H in the (ξ, η, ζ) system of the j-th nucleus, and $\mathbf{n} = \mathbf{n}(M)$ is a vector whose direction is determined by the direction cosines,[4]

$$\delta_p = \frac{A_p - \nu_n/M}{\Delta_M}\alpha_p, \quad (7)$$

$\hat{\mathcal{H}}_Q^\sigma = \sum_{j=1}^{k_\sigma} \hat{\mathcal{H}}_Q^j$, $\hat{\mathbf{F}}^\sigma = \sum_{j=1}^{k_\sigma} \hat{\mathbf{I}}^j$ is the operator of the total spin of k_σ nuclei, $\hat{F}_n$ is the operator of the projection of the unit vector $\mathbf{n}(M)$, and m_σ is its eigenvalue. The effective second-order spin Hamiltonian is

$$\hat{\mathcal{H}}_{2ef}^\sigma = \frac{(S_+)^{(2)}_{M,M-1}}{\nu_0}\hat{\Gamma}_{+-}{}^\sigma - \frac{(S_+)^{(2)}_{M+1,M}}{\nu_0}\hat{\Gamma}_{-+}{}^\sigma, \quad (8)$$

where

$$\hat{\Gamma}_{\pm\mp}{}^\sigma = \frac{1}{4}\sum_{p,q}\sum_{j,j'}^{k_\sigma} A_p{}^j A_q{}^{j'}(\beta_p{}^j \mp i\gamma_p{}^j)(\beta_q{}^{j'} \pm i\gamma_q{}^{j'})\hat{I}_p{}^j\hat{I}_q{}^{j'}, \quad (9)$$

(p, q = 1, 2, 3, as before, number the principal axes of the hyperfine interaction tensor). Actually the values of A_p^j and $A_q^{j'}$ do not depend on the numbers j and j' of the nuclei contained in the group σ. β_p^j and γ_p^j are the direction cosines of the axes x and y, which are perpendicular to the z axis (to the field H) in the (ξ, η, ζ) system of the j-th nucleus. Formally, the part of the operator (8) with $j \neq j'$ can be regarded as the operator of the indirect interaction of the nuclei.

We note that the form of the operator (9) presupposes beforehand (see the Appendix) that the energy levels of the individual groups of nuclei are sufficiently well separated, i.e., $|M\Delta_M^\sigma - M\Delta_M^{\sigma'}| \gg A_p^2/\nu_0$. If this inequality is not satisfied, then the groups σ and σ' must be combined into a single group which gives almost degenerate energy levels if $\hat{\mathcal{H}}_0$ and $\hat{\mathcal{H}}_{2ef}$ are neglected.

To determine the eigenvalues and eigenfunctions of the Hamiltonian $\hat{\mathcal{H}}_{ef}$ from (5), we shall henceforth assume that

$$|M\Delta_M| \gg |Q'|, \ |Q''|, \quad (10)$$

so that $(\hat{\mathcal{H}}_Q^\sigma + \hat{\mathcal{H}}_{2ef}^\sigma)$ can be regarded as a perturbation to $M\Delta_M\hat{F}_n^\sigma$.[2)]

It follows from (5) that the energy of the system is equal to $\nu_0 M + \sum_\sigma E^\sigma$, and $\chi' = \prod_\sigma \chi^\sigma$, where E^σ is the energy of the nuclei of group σ, and χ^σ is their spin function.

2. Effective field. If we omit $\hat{\mathcal{H}}_Q$ and $\hat{\mathcal{H}}_{2ef}$ from (5), then the nuclear spin Hamiltonian[4]

$$\hat{\mathcal{H}}_{1ef} - \nu_0 M = \sum_j (M\Delta_M{}^j \hat{I}_n{}^j) \quad (11)$$

breaks up into a sum of single-particle Hamiltonians, so that the hyperfine energy is equal to the sum of the energies of each nucleus, and the wave function is $\chi' = \prod_j \chi^j$. The expression $M\Delta_M/g_n^j\beta_n$ has the meaning of the effective magnetic field acting on the nucleus j in the direction along $\mathbf{n}(M)$ (g_n and β_n are respectively the nuclear g factor and the nuclear magneton). The energy is obtained by replacing I_n^j in (11) by the quantum number m_n^j; χ^j is an eigenfunction of $\hat{I}_n^j$.[4]

Addition of the quadrupole interaction does not change the additivity of the energy of the hyperfine interaction and the multiplicativity of the functions. To obtain the energy levels with allowance for the quadrupole interaction it is necessary to separate the diagonal part of the corresponding operator. The latter, as can be readily shown, is

$$\hat{\mathcal{H}}_{Q1}{}^j = \bar{Q}_0{}^j(\hat{I}_n{}^2 - {}^1/_3\hat{I}^2)^j, \quad (12)$$

where[3)]

$$\bar{Q}_0{}^j = {}^1/_2(3\delta_3{}^2 - 1)(Q' + Q'') + (3\delta_1{}^2 - 1)Q''. \quad (13)$$

The quadrupole contribution to the hyperfine interaction of the j-th nucleus equals $Q_0^j(m_n^j)^2$. The angular dependence of the quadrupole parts of the energy is determined by the orientation of the effective field relative to the symmetry axes of the j-th nucleus.

The ENDOR frequencies ($\Delta M = 0$, $\Delta m_n^j = \pm 1$, $\Delta m_n^{j'} = 0$, $j \neq j'$) take in this approximation the form

$$\nu_{M,m_n}^j = |M\Delta_M{}^j + \bar{Q}^j(2m_n{}^j - 1)| \quad (14)$$

[2)] For an integer spin S, the case M = 0 differs in that the solution depends on the relation of $|\nu_n|$ to $|Q'|$ and $|Q''|$. The formulas presented below remain valid when $|\nu_n| \gg |Q'|, |Q''|$.

[3)] The influence of the deviation of the quantization axis from the direction of H was considered theoretically in a diploma paper by A. A. Voĭtovskaya in 1965 (Kiev Polytechnic Institute). We assume that the principal axes of the tensors of the quadrupole and magnetic hyperfine interaction coincide. If this is not the case, then (13) will contain in lieu of δ_1 and δ_3 the quantities δ_1' and δ_3' which are the direction cosines of n in the system of the principal axes of the quadropole tensor.

and break up into quadrupole multiplets ($2I^j$ lines in the multiplet). In many cases $|b| \ll |a|$, so that for comparison with experiment it is sufficient to use the expansion[4] of the expressions (6) and (7):

$$\Delta_M \approx a - \frac{\nu_n}{M} + b_1(3\cos^2\theta - 1) + b_2(3\cos^2\theta_1 - 1) + \frac{9}{8}\frac{b_1^2}{a}\sin^2 2\theta + \frac{9}{8}\frac{b_2^2}{a}\sin^2 2\theta_1 - 9\frac{b_1 b_2}{a}(3\cos^2\theta - 1)(3\cos^2\theta_1 - 1); \quad (15)$$

$$\frac{\delta_p}{\alpha_p} \approx 1 - \left[\frac{A_1 - a}{a}\alpha_1^2 + \frac{A_2 - a}{a}\alpha_2^2 + \frac{A_3 - a}{a}\alpha_3^2 - \frac{A_p - a}{a}\right]; \quad (16)$$

$$\delta^2_3 \approx \cos^2\theta + \frac{3}{2}\frac{b_1}{a}\sin^2 2\theta - 6\frac{b_2}{a}\cos^2\theta\cos^2\theta_1,$$

$$\delta_1^2 \approx \cos^2\theta_1 - 6\frac{b_1}{a}\cos^2\theta\cos\theta_1 + \frac{3}{2}\frac{b_2}{a}\sin^2 2\theta_1. \quad (17)$$

Here $\alpha_2 = \cos\theta$ and $\alpha_1 = \cos\theta_1$. We note that the direction of the effective field does not depend on M in the first approximation in b/2 and ν_n/a; it is easy to verify that the angle between H and n does not depend on M, accurate to $\sim b^2/a^2$.

Permutation degeneracy holds for the group of nuclei σ, so that the corresponding k_σ frequencies $\nu^j_{M,\,m_n}$ coincide. This degeneracy can be lifted[2,3] by taking into account $\hat{\mathcal{H}}^\sigma_{2ef}$ from (8) and (9). We shall examine the manner in which such a degeneracy is lifted for certain sufficiently general cases, and also how the ENDOR frequencies change and split. It is meaningful to take $\hat{\mathcal{H}}^\sigma_{2ef}$ into account if splittings or shifts of the ENDOR frequencies of order $A_p^2/4\nu_0$ can still be discerned experimentally (for F centers in alkali-halide crystals it is necessary that $A_p^2/4\nu_0$ be larger than or on the order of several kHz).

3. Arbitrary number of nuclei in group. $|a| \gg |b|$, $|\nu_n|$. If $|a| \gg |b|, |\nu_n|$, then it is sufficient to put $A_p^j \approx a$ in $\hat{\Gamma}_{\pm\mp}$. We then obtain from (9)

$$\Gamma_{\pm\mp} = \frac{a^2}{4}\sum_{j,j'}\hat{I}_\mp^j\hat{I}_\pm^{j'} \equiv \frac{a^2}{4}(\hat{F}^2 \div \hat{F}_z^2) \mp \frac{a^2}{4}\hat{F}_z, \quad (18)$$

where $\hat{I}_\pm = \hat{I}_x \pm i\hat{I}_y$, and F^2 is the square of the total angular momentum of k_σ nuclei. By rotating the system of axes in (18) towards the quantization axis n and substituting in (8), we obtain, with the same accuracy with which A_p is replaced by a in (8),

$$\hat{\mathcal{H}}^\sigma_{2ef} = M\frac{a^2}{2\nu_0}(\hat{F}^2 - \hat{F}_n^2) - [S^2 - M^2]\frac{a^2}{2\nu_0}\hat{F}_n. \quad (19)$$

Let us consider the eigenvalues and eigenfunctions of the Hamiltonian (5) when the quadrupole interaction is negligibly small. In this case, as seen from (5) and (19), the conserved quantities will be $F_n = m_\sigma$ and $F^2 = F(F+1)$; $\chi^\sigma = |F m_\sigma\rangle$. If $k_\sigma > 2$, then the energy level E^σ_{M,F,m_σ} is degenerate in the so-called coupling scheme[6] (in the intermediate moments). The energy E^σ_{M,F,m_σ} is obtained from (5) and (19) by replacing $\hat{F}_n$ by m_σ and F^2 by $F(F+1)$. ENDOR magnetic-dipole transitions are possible between the states of one coupling scheme when $\Delta M = 0$, $\Delta F = 0$, and $\Delta m_\sigma = \pm 1$.

From the obtained energy we get for the ENDOR frequencies due to the group σ (we omit the index σ for simplicity)

$$\nu_{M,m_\sigma} = \left| M\Delta_M - \frac{(S^2 - M^2)a^2}{2\nu_0} - M\frac{a^2}{2\nu_0}(2m_\sigma - 1)\right|; \quad (20)$$

Δ_M must be taken from (6) or (15), $m_\sigma = k_\sigma I,\ k_\sigma I - 1,\ \ldots,\ -k_\sigma I + 1$.

Thus, when account is taken of $\hat{\mathcal{H}}_{2ef}$, each energy level (M, m_σ) splits into $(k_\sigma I + 1 - m_\sigma)$ sublevels corresponding to $F = k_\sigma I,\ k_\sigma I - 1,\ \ldots,\ m_\sigma$. The ENDOR frequencies $|M\Delta^\sigma_M|$ split into $2k_\sigma I$ components, which are separated from one another in our approximation by $\Delta\nu_M = |Ma^2/\nu_0|$. It follows from (15) that the frequencies will contain, in lieu of the Larmor frequency ν_n, the effective Larmor frequency $\nu_n - [S^2 - M^2]a^2/2\nu_0$. The intensities of lines with different m_σ will be proportional to the number of transitions with a given frequency ν^σ_{M,m_σ}. Disregarding the "oscillator strengths" for the transition $(F, m_\sigma \longleftrightarrow F, m_\sigma \pm 1)$, let us obtain the relative intensity J'_{m_σ} of the frequencies ν^σ_{M,m_σ}. Omitting the proof of formulas (21) and (22), we write

$$J'_{m_\sigma} = \sum_{F=m_\sigma}^{F=k_\sigma I} N_F, \quad N_F = f(F) - f(F-1), \quad (21)$$

where N_F is the number of states in the group of k_σ nuclei with given value of total angular momentum F, and f(F) is the number of states with projection m_σ = F, where

$$f(F) = \sum{}' (k_\sigma)! \Big/ \prod_{m=I}^{-I}(k_m)! \quad (22)$$

Here k_m is the number of nuclei in the group σ with projections of the nuclear spin m ($|m| \le I$); the prime next to the sum denotes that it is taken over all possible decompositions of the number k_σ into terms k_m, under the condition that

$$\sum_{m=-I}^{m=I} k_m = k_\sigma, \quad \sum_{m=-I}^{m=I} m k_m = F. \quad (23)$$

Taking into account the "oscillator strength," which is proportional to $[F(F+1) - m_\sigma(m_\sigma - 1)]$, the relative intensities $J''_{m\sigma}$ are equal to

$$J''_{m_\sigma} = \sum_{F=m_\sigma}^{k_\sigma I} N_F[F(F+1) - m_\sigma(m_\sigma - 1)]. \quad (24)$$

It can be verified that the ratio of the numbers J'_{m_σ} and J''_{m_σ} differ little from each other, since in (24) N_F is a factor that varies strongly with F, and $[F(F+1) - m_\sigma(m_\sigma - 1)]$ is a factor that varies relatively weakly. For $k_\sigma = 2$ we get from (24)

$$J''_{m_\sigma}(k_\sigma = 2) = (2I - m_\sigma + 1)\left[\frac{(2I - m_\sigma)(4I + 4m_\sigma + 1)}{6} + \frac{3}{2}m_\sigma + I\right], \quad (25)$$

where the first factor is J'_{m_σ}.

Bearing in mind a comparison with experiment, we present the ratio of the intensities, in accord with (21) and (24), for $k_\sigma = 2$ and $k_\sigma = 4$ ($I = {}^3/_2$):[5]

[4] A different expansion of Δ_M, which is more convenient in the case when $|b_1|, |b_2| \sim |a|$, is given in [4].

[5] For $k_\sigma = 4$ and I = 3/2, it is easy to obtain the value of N_F directly, bypassing (22), by considering the addition of the momenta of two pairs of particles.

$$k_\sigma = 2,\begin{cases} J_3':J_2':J_1':J_0':J_{-1}':J_{-2}' = 1:2:3:3:2:1 \\ J_3''J_2'':J_1'':J_0'':J_{-1}'':J_{-2}'' = 1:2{,}3:3{,}3:3{,}3:2{,}3:1, \end{cases}$$

$$k_\sigma = 4,\begin{cases} J'_{6,-5}:J'_{5,-4}:J'_{4,-3}:J'_{3,-2}:J'_{2,-1}:J_1':J_0'' = 1:4:10:20:31:40:40 \\ J''_{6,-5}:J''_{5,-4}:J''_{4,-3}:J''_{3,-2}:J''_{2,-1}:J_1'':J_0'' = 1:4{,}3:11:21:31:38:38. \end{cases} \quad (26)$$

If $Q', Q'' \neq 0$, then to obtain the energy levels and the frequencies it is necessary to solve a secular equation of order $(2I+1)^{k_\sigma}$. The problem simplifies greatly when $|Q'| \gg a^2/4\nu_0$. The difficulty of the problem greatly increases if $b \sim a$, $k_\sigma > 2$, and $I > 1/2$.

For the case $k_\sigma = 4$ and $I = 1/2$, the secular problem was solved by Kravitz and Piper,[3] who obtained an expression for $\hat{\mathcal{H}}_{2ef}$ in the case of an octahedral arrangement of the nuclei and for H oriented along the [001] direction. Naturally, the spin Hamiltonian of their paper[3] can be obtained as a particular case from (8) and (9).

4. Case of two nuclei. If the paramagnetic center is an inversion center, then the most general case of the group is $k_\sigma = 2$.[2] The axes ξ, η, and ζ have the same orientations for both nuclei of the group, A_p does not depend on the index j, so that we obtain from (9) (F is the total angular momentum of the pair)

$$\Gamma_{\pm\mp} = \frac{1}{4}\sum_{p,q} A_pA_q\hat{F}_p\hat{F}_q(\beta_p \mp i\gamma_p)(\beta_q \pm i\gamma_q). \quad (27)$$

Separating the parts of this operator that are symmetrical and antisymmetrical with respect to $(\hat{F}_p\hat{F}_q)$, and retaining only the operators diagonal in $\hat{F}_n$, we obtain for $\hat{\mathcal{H}}_{2ef}$ from (9)

$$\hat{\mathcal{H}}_{2ef}^{diag} = 2MB[\hat{F}^2 - \hat{F}_n^2] + 2MC\hat{F}_n^2 - 2(S^2 - M^2)B'\hat{F}_n, \quad (28)$$

where

$$B = \frac{1}{4\nu_0}\frac{\Gamma_0 - \Gamma_1}{2}, \quad C = \frac{1}{4\nu_0}\Gamma_1, \quad B' = \frac{1}{4\nu_0}\Gamma_2, \quad (29)$$

$$1/2\,\Gamma_0 = 1/2\sum_p A_p^2(1-\alpha_p^2) = a^2 - ab_1(3\cos^2\theta - 1) - ab_2(3\cos^2\theta_1 - 1)$$

$$- 1/2\,b_1^2(3\cos^2\theta - 5) - 1/2\,b_2^2(3\cos^2\theta_1 - 5) + b_1b_2(3\cos^2\theta + 3\cos^2\theta_1 - 4), \quad (30)$$

$$\Gamma_1 = \sum_p (A_p\delta_p)^2 - \Big(\sum_p A_p\alpha_p\delta_p\Big)^2 \approx 9(b_1^2\sin^2 2\theta + b_2^2\sin^2 2\theta_1$$

$$- 8b_1b_2\cos^2\theta\cos^2\theta_1) + O\Big(\sim\frac{b_p^3}{a}, \frac{b^2\nu_n}{a}\Big), \quad (31)$$

$$\Gamma_2 = A_1A_2\alpha_3\delta_3 + A_1A_3\alpha_2\delta_2 + A_2A_3\alpha_1\delta_1 \approx a^2 - ab_1(3\cos^2\theta - 1)$$
$$- ab_2(3\cos^2\theta_1 - 1) + b_1^2[3\cos^2\theta - 2 - {}^{27}/_8\sin^2 2\theta] + b_2^2]3\cos^2\theta_1 - 2$$
$$- {}^{27}/_8\sin^2 2\theta_1] + b_1b_2[5 - 6\cos^2\theta - 6\cos^2\theta_1 + 27\cos^2\theta\cos^2\theta_1]$$
$$+ O(\sim b^3/a,\ b^2\nu_n/a). \quad (32)$$

The expression for Γ_0 is determined only by the orientation of H and does not depend on the orientation of the effective field; $\Gamma_1 = 0$ if H is directed along any principal axis. In the case of axial symmetry $\Gamma_1 = 0$ also if $\theta = \pi/2$. The approximate equalities in (31) and (32) are obtained with the aid of the expansion (16). All the terms in the approximate equality, with the exception of those explicitly written out, vanish in (32) if $\mathbf{n} \| \mathbf{H}$. In the case of axial symmetry and $\theta = 0$ we have $B' = B = (a-b)^2/4\nu_0$. If $|b| \ll |a|$, then $B' \approx B$ if we neglect terms proportional to b^2 in Γ_0 and Γ_2.

The energies, the ENDOR frequencies, and the wave functions χ^σ can be obtained by diagonalizing the matrix of the operator

$$\hat{\mathcal{H}}_{ef} - \nu_0 M = [M\Delta_M - 2(S^2 - M^2)B']\hat{F}_n + 2MB(\hat{F}^2 - \hat{F}_n^2)$$
$$+ 2MC\hat{F}_n^2 + \sum_{j=1}^{2}\hat{\mathcal{H}}_{Q_1}^j + \sum_{j=1}^{2}\hat{\mathcal{H}}_{Q_2}^j. \quad (33)$$

If the first term on the right is regarded as the zero-order Hamiltonian, then the second, third, and fourth terms give the contribution made to the energy in first order of perturbation theory, and the last term gives the contribution in second order of perturbation theory, with $\hat{\mathcal{H}}_{Q_2}^j = \hat{\mathcal{H}}_Q^j - \hat{\mathcal{H}}_{Q_1}^j$, where $\hat{\mathcal{H}}_{Q_1}^j$ is taken from (12).

If $Q' = Q'' = 0$, then the ENDOR frequencies are determined by formulas (20), except that $a^2/4\nu_0$ in the quasi-Larmor term is replaced by B', and the frequency splitting is $\Delta\nu_M = |4M(B-C)|$.[6] For the case $S = 1/2$, $I = 3/2$, in which we are now interested, we can use the correct zeroth-approximation formulas and the tables of the ENDOR frequencies and energies as obtained by Feuchtwang.[2] However, although the effective spin Hamiltonian of the paired particles was obtained correctly in [2],[7] its diagonalization has been inaccurately performed. Therefore the quantities B, C, and $\tilde{Q}_0$ of Tables II and III of [2] should be replaced by the values given here and obtained from formulas (29)–(32) and (13). In addition, the quantity $(A_- + D_-)$ in [2][8] should be replaced by $(1/2\,\Delta_{-1/2} + B')$. In [2], the states are determined by the quantum number M_F—the total projection of the spins of the two nuclei on the magnetic field. This number should be replaced by m_σ, the total projection on the quantization axis n(M), so that the functions of the nuclear spins become, generally speaking, dependent on M.

The diagonalization in [2] is inaccurate because incorrect account was taken of the deviation of the nuclear-spin quantization axis from H. This is manifest in the fact that the coefficients B and C in the energies of [2] contain the incorrect terms $\sim b^2/\nu_0$, and the constant $\tilde{Q}_0$ contains not the direction cosines δ_p but α_p. When $|b| \ll |a|$, the inaccuracies connected with the terms $\sim b^2/\nu_0$ are insignificant. As regards $\tilde{Q}_0$, its relative change as a result of the deviation of the quantization axis is $\sim b/a$. Even when $b/a \sim 1/20$ (sphere 1 of the F center in KCl), the change of $\tilde{Q}_0$ due to the deviation of n from H is of the order of or larger than B (when $\theta = \pi/4$). In the case of axial symmetry and $\theta = 0, \pi/2$, the value of $\tilde{Q}_0$ from [2] coincides with our data.

The correct zeroth-approximation functions are characterized by a total spin projection of the two nuclei m_σ and parity with respect to their permutation.[2] In the first approximation of perturbation theory, the degeneracy is completely lifted. Magnetic-dipole transitions are possible between states of like parity, and the ENDOR frequencies are given by the condition $\Delta M = 0$, $\Delta m_\sigma = \pm 1$. The characteristic feature of such a spectrum is its symmetry relative to the frequency $\nu_m = |M\Delta_M - 2MB'|$.

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[6] The wave functions $|Fm_\sigma\rangle$ are in this case even or odd relative to the permutation of the nuclei, and their parity is equal to $(-1)^{2I-F}$ [6].

[7] In the effective spin-Hamiltonian of [2] it is assumed that $B' = B$, which in general is incorrect.

[8] In tables II and III of [3] it is necessary to reverse the sign of C, and in the 14th line of Table III it is necessary to reverse the sign of the term 5B.

Experiment shows, however, that in the case of axial symmetry and $\theta \neq 0$ the spectrum is asymmetrical. This may be caused by the quadrupole interaction, or more accurately by its nondiagonal part, the contribution of which was not taken into account in [2].

Taking into account the quadrupole interaction in second order of perturbation theory, we have calculated, starting from the known correct zeroth-approximation functions, the corrections to the ENDOR frequencies and energies of a pair of nuclei with $I = {}^3/_2$ (see the table) in the case of axial symmetry. The following notation is used in the table:

$$I = -\frac{3Q'^2}{\Delta_{-1/2}}\left(\sin^2 2\varphi - \frac{1}{2}\sin^4\varphi\right),$$

$$II = -\frac{3Q'^2}{\Delta_{-1/2}}\left(\frac{1-\alpha^2}{1+\alpha^2}\sin^2 2\varphi - \frac{1}{2(1+\alpha^2)}\sin^4\varphi\right),$$

$$III = \frac{3Q'^2}{\Delta_{-1/2}}\left(\frac{1-\alpha^2}{1+\alpha^2}\sin^2 2\varphi + \frac{1}{2}\frac{\alpha^2}{1+\alpha^2}\sin^4\varphi\right),$$

$$IV = \frac{3Q'^2}{\Delta_{-1/2}}\sin^2 2\varphi;$$

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

$$\alpha = \frac{\tilde{Q}_0 + B - \varepsilon}{2B\sqrt{6}}.$$

The states j and j′ are numbered in accordance with Table II of the paper of Feuchtwang:[2] g and u are states that are even and odd, respectively, relative to permutation of two nuclei; the letter c denotes that the transition is forbidden if $\tilde{Q}_0 = 0$; f denotes a forbidden transition. For transitions indicated in the parentheses, the frequencies $\nu^{(2)}_{jj'}$ must be taken with the opposite sign, and the frequencies $\nu^{(2)}_{Qjj'}$ should be taken the same as for transitions without the parentheses; m is the larger of the two numbers m or m − 1; $\nu^{(2)}_{jj'}$ is the addition due to $\hat{\mathcal{H}}_{Q1} + \hat{\mathcal{H}}_{2ef}$; $\nu^{(2)}_{jj'}$ and ε, η, ζ, and α are given in [2], while B, C, and $\tilde{Q}_0$ are taken from the formulas of our paper. $\nu^{(2)}_{Qjj'}$ is the addition due to $\hat{\mathcal{H}}_{Q2}$. The frequencies $\nu^{(2)}_{Qjj'}$ are given for the case of axial symmetry. For $M = {}^1/_2$, the frequency $\nu_{-1/2}$ should be replaced by $\nu_{1/2} = {}^1/_2\Delta_{1/2} - B'$, and the quantity $\tilde{Q}_0$ in $\nu^{(2)}_{jj'}$, should be replaced by $-\tilde{Q}_0$, $\Delta_{-1/2}$ in $\nu^{(2)}_{Qjj'}$, should be replaced by $\Delta_{1/2}$, and the sign of B should be reversed in the expression for α.

ENDOR frequencies of a pair of nuclei with $I = {}^3/_2$ ($M = -{}^1/_2$). $\nu_{-1/2, m, (jj')} = \nu_{-1/2} + C(2m-1) + \nu^{(2)}_{jj'} + \nu^{(2)}_{Qjj'}$; $\nu_{-1/2} = {}^1/_2\Delta_{-1/2} + B'$

$j \to j'$, parity	m	$\nu^{(2)}_{jj'}$	$\nu^{(2)}_{Qjj'}$
12 → 11 (16 → 15) u	−1 (2)	3B	I
9 → 8 (3 → 2) g, c	(−1)	$-\tilde{Q}_0 + 2B + \varepsilon$	II
6 → 4 (7 → 6) g	0 (1)	$-\tilde{Q}_0 + B - \varepsilon + \eta$	II
2 → 1 (10 → 9) g	−2 (3)	$2\tilde{Q}_0 + 5B$	IV
4 → 2 (9 → 7) g	−1 (2)	$\tilde{Q}_0 - 2B + \varepsilon$	III
6 → 3 (8 → 6) g, c	0 (1)	$-\tilde{Q}_0 + B + \varepsilon + \eta$	III
14 → 12 (15 → 14) u	0 (1)	$-2B + \zeta$	IV
15 → 13 (13 → 12) u, c	1 (0)	$2B + \zeta$	IV
8 → 5 (5 → 3) g	1 (0)	$\tilde{Q}_0 - B - \varepsilon + \eta$	III
7 → 5 (5 → 4) g, f	1 (0)	$\tilde{Q}_0 - B + \varepsilon + \eta$	II

The asymmetry effect can be separated by calculating the centers of gravity of the three groups consisting of six lines each (see the table). Then the difference $\Delta\nu_1 - \Delta\nu_2$ (see Fig. 1) has the following form ($M = -{}^1/_2$):

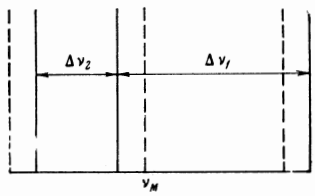

FIG. 1. Asymmetry of ENDOR spectrum of a pair of nuclei with I = 3/2. The solid lines characterize the shift of the centers of gravity of three groups of lines when account is taken of the quadrupole interaction in second order of perturbation theory while the dashed lines represent their previous symmetrical projection.

$$\Delta\nu_1 - \Delta\nu_2 = \frac{12Q'^2}{\Delta_{-1/2}}\left[\frac{1}{12}\left(5 + 7\frac{1-\alpha^2}{1+\alpha^2}\right)\sin^2 2\varphi - \frac{1}{12}\left(1 + \frac{2}{1+\alpha^2} - \frac{3}{2}\frac{\alpha^2}{1+\alpha^2}\right)\sin^4\varphi\right]. \quad (34)$$

Here $\cos\varphi = \delta_3$ from (7). For $|a| \gg |b|$ it is necessary to use the expansions (15) and (17). For $M = {}^1/_2$, the quantity $\Delta_{-1/2}$ in (34) should be replaced by $\Delta_{1/2}$. If $\alpha \ll 1$, then (34) goes over into the analogous formula for a single nucleus with $I = {}^3/_2$ [7] (the values of α are given in the table).

5. Single nucleus. If $k_\sigma = 1$, then $\hat{\mathcal{H}}_{2ef}$ is given by (28), but the momentum operator $\hat{F}$ of the pair of nuclei should be replaced by the operator $\hat{I}$, so that

$$\hat{\mathcal{H}}_{ef} = (\nu_0 + 2B\hat{I}^2)M + (M\Delta_M - 2[\hat{S}^2 - M^2]B')\hat{I}_n + [\tilde{Q}_0 - 2M(B-C)]\hat{I}^2{}_n + \hat{\mathcal{H}}_{Q2}. \quad (35)$$

We have left out the insignificant term $(-{}^1/_3\tilde{Q}_0 I^2)$. A detailed analysis of the single-nucleus case is given in [7].

In concluding this section, let us clarify when the indirect interaction between nuclei of different groups σ can be neglected. Let a_{max} be the maximum constant of hyperfine interaction with the nuclei, and a^σ the constant of interaction with nuclei of group σ. It follows from the foregoing that the energy of the nuclei σ changes by an amount $\sim (a^\sigma)^2/\nu_0$. On the other hand, it can be verified that the nondiagonal operators (relative to F^σ_n) introduce into the energy of the nuclei σ a correction of the order of $a^\sigma(a_{max}/\nu_0)^2$. It can be neglected if $a^\sigma/a_{max} \gg a_{max}/\nu_0$.

EXPERIMENT

We used for the measurements single crystals of KCl, KBr, and LiF grown by the Kyropoulos method in

air. The F centers in KCl and KBr were obtained by electrolytic coloring, and in LiF by γ irradiation. The F-center concentration as given by optical measurements was $\sim 10^{18}$ cm^{-3}.

The investigations were made with a superheterodyne ENDOR spectrometer operating in the 3-cm band ($\nu_{\text{microwave}}$ = 9290 MHz).[8]

1. **LiF.** A detailed study was made of the spectra of coordination sphere 1 of the F centers. Figure 2 illustrates the ENDOR line from a pair of Li^7 nuclei at $\theta = 0°$

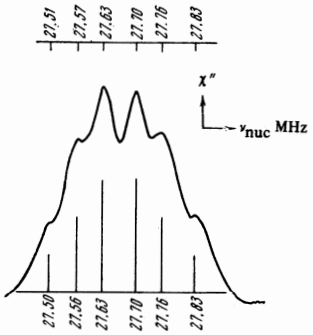

FIG. 2. ENDOR spectrum of a pair of Li^7 nuclei of sphere 1 of the F center in LiF, $\theta = 0°$, T = 20°K. The vertical segments correspond to the theoretical frequencies (lower scale), calculated from formula (20), and their heights are calculated in accordance with (25). The upper scale represents the experimental values of the frequencies. a = 38.15 MHz, b = 3.06 MHz, χ'' is the imaginary part of the paramagnetic susceptibility, ν_{nuc} is the frequency of the applied radio-frequency beam.

and $M = -1/2$. The line structure is due to second-order effects, as is confirmed by the good agreement between the theoretical values of the frequencies calculated from formulas (15) and (20) with the experimental values ($a^2/4\nu_0$ for $k_\sigma = 2$ must be replaced in (20) by the exact value of (B − C) from (29); for $\theta = 0$ we have $(B - C) = (a - b)^2/4\nu_0$). The relative intensities of the structure lines are also in good agreement with those predicted by formula (26).

Since according to [9] the quadrupole moment of Li^7 differs from zero, we calculated the dependence of the frequencies of the second-order structure for the aforementioned ENDOR line on the possible values of Q′. A comparison with experiment had shown that the possible value is $|Q'| < 10$ kHz.

Since $b/a \sim 3/40$ in our case, we can expect formulas (20) and (25) to describe sufficiently well the line structure for $k_\sigma > 2$. The case $k_\sigma = 4$ is realized in sphere 1 of the F center when $\mathbf{H} \| [100]$. Figure 3 shows the theoretical values of the ENDOR frequencies and the experimental spectrum for the quartet of Li^7 nuclei of sphere 1. Some difference between the intensity ratios of the experimental lines and those calculated by formula (25) is apparently due to the overlap of the rather broad lines in the experimental spectrum.

2. **KCl.** The influence of the deviation of the nuclear-spin quantization axis from **H** and of the quadrupole interaction, taken into account in second-order of perturbation theory, was investigated on the F centers in KCl. We studied the spectra from the pair of K^{39} nuclei of sphere 1. The angle θ was varied from zero to 45° in the (001) plane. A detailed comparison of theory with experiment was made for $\theta = 30°$ ($M = -1/2$). At this orientation, a high-frequency forbidden transition was also observed (the low-frequency transition was over-

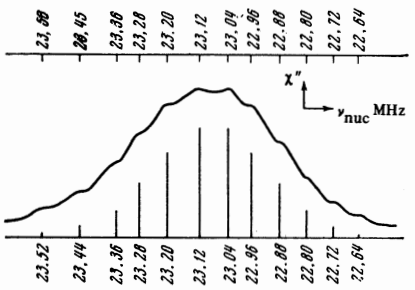

FIG. 3. ENDOR spectrum of a quartet of Li^7 nuclei of sphere 1 of LiF, $\theta = 90°$, T = 77°K. a = 38.16 MHz, B = 3.05 MHz. Vertical segment - theoretically predicted values (in accordance with formulas (20) and (25)).

lapped by lines from other nuclei). The frequencies of the observed transitions are well described, within the limits of the measurement errors, by the formulas given in the table, provided $\tilde{Q}_0$ and B are taken from expressions (13), (17), and (29)–(32). On the other hand, the use of the formulas of [2] for $\tilde{Q}_0$ and B results in a discrepancy on the order of 20 kHz.[9)]

The asymmetry of the spectrum observed at $\theta = 30°$ agrees with the theoretical asymmetry. Thus, according to formula (34), $(\Delta\nu_1 - \Delta\nu_2)_{\text{theor}} = 12$ kHz and $(\Delta\nu_1 - \Delta\nu_2$ also agrees in the indicated interval with the quantity given by expression (34).

3. **KBr.** The second-order effects were taken into account also in the spectra of a pair of K^{39} nuclei of sphere 1 of the F centers in KBr for orientations of **H** with $\theta = 0°$ and $\theta = 90°$ in the (001) plane. For both orientations, the theoretically calculated frequencies were compared with the experimentally observed ones. In analogy with [2], it was found from the comparison that for this case $Q' > 0$. An example of a comparison of the theory with experiment is shown in Fig. 4.

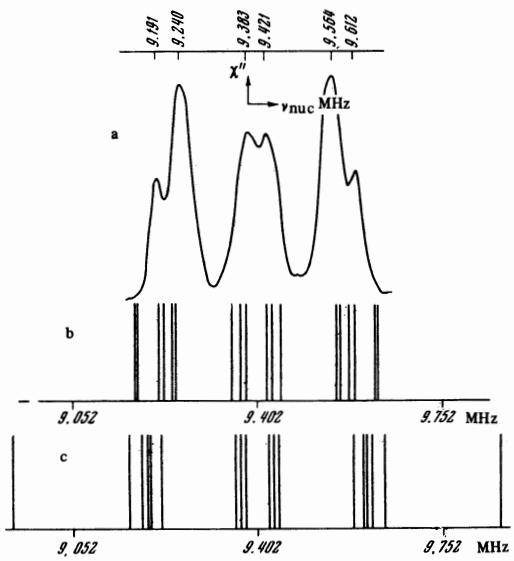

FIG. 4. ENDOR spectrum of a pair of K^{39} nuclei of sphere 1 in KBr, $\theta = 90°$, T = 20°K. a) Experimental spectrum, b) theoretical spectrum, $Q' > 0$; c) theoretical spectrum, $Q' < 0$. a = 18.228 MHz, b = 0.769 MHz, $|Q'| = 0.190$ MHz.

9)In calculating the theoretical values of the ENDOR frequencies in KCl, we used the following values of the hyperfine constans: a = 20.72 MHz, b = 0.930 MHz. The experiment was performed at T = 20°K. The error in the measurement of the ENDOR frequencies did not exceed 3 kHz in KCl and DBr and 5 kHz in LiF.

Thus, it can be assumed that the fine details of the ENDOR spectra of F centers in alkali-halide crystals can be explained on the basis of the foregoing theory, and that the spin-Hamiltonian (1) describes well the interaction between the electron and the nuclei, as is demonstrated by experiments on KCl, KBr, and LiF crystals. Zheru[10] has predicted additional terms of the spin Hamiltonian (1), of higher order in the spins. It can be concluded that the coupling constants for these terms are so small, that they do not appear in the experiment.

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APPENDIX

CONCERNING THE DERIVATION OF THE SECOND-ORDER SPIN HAMILTONIAN

We divide the spin Hamiltonian (1) into three parts:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2,$$

where

$$\hat{\mathcal{H}}_1 = \sum_j [-\nu_n{}^j \hat{I}_z{}^j + \hat{S}_z(A_1{}^j\alpha_1{}^j\hat{I}_1{}^j + A_2{}^j\alpha_2{}^j\hat{I}_2{}^j + A_3{}^j\alpha_3{}^j\hat{I}_3{}^j) + \hat{\mathcal{H}}_Q{}^j],$$

$$\hat{\mathcal{H}}_2 = \hat{S}_x \sum_j (A_1{}^j\beta_1{}^j\hat{I}_1{}^j + A_2{}^j\beta_2{}^j\hat{I}_2{}^j + A_3{}^j\beta_3{}^j\hat{I}_3{}^j)$$

$$+ S_y \sum_j (A_1{}^j\gamma_1{}^j\hat{I}_1{}^j + A_2{}^j\gamma_2{}^j\hat{I}_2{}^j + A_3{}^j\gamma_3{}^j\hat{I}_3{}^j). \qquad (A.1)$$

The notation here is the same as in the article; α_p^j, β_p^j, and γ_p^j are the direction cosines of the axes z, x, and y, connected with the field H, in the coordinate system (ξ, η, ζ) of the j-th nucleus; $\hat{\mathcal{H}}_0$ is the zeroth Hamiltonian which does not depend on the nuclear spins; $\hat{\mathcal{H}}_1$ and $\hat{\mathcal{H}}_2$ are perturbations, with $\hat{\mathcal{H}}_1$ a diagonal operator. As shown in [11], the diagonalization of $\hat{\mathcal{H}}$, accurate to second order of perturbation theory inclusive, is equivalent to diagonalization of the matrix

$$\langle M(m)|\hat{\mathcal{H}}'|M(m')\rangle = \nu_0\delta_{(m)(m')} + \langle M(m)|\hat{\mathcal{H}}_1|M(m')\rangle$$

$$+ \sum_{M''(m'')} \frac{\langle M(m)|\hat{\mathcal{H}}_2|M''(m'')\rangle\langle M''(m'')|\hat{\mathcal{H}}_2|M(m')\rangle}{E_M{}^0 - E_{M''}{}^0}. \qquad (A.2)$$

By m is meant a certain complete system of nuclear spin functions. The matrix $\nu_0\delta_{mm'} + \langle M(m)|\hat{\mathcal{H}}_1|M(m')\rangle$ is obviously equivalent to the operator $\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1$, in which S_Z is replaced by the projection of the electron spin. Upon rotation to the quantization axis n(M),[4] this operator takes the form $\hat{\mathcal{H}}_{1ef} + \hat{\mathcal{H}}_Q$, where $\hat{\mathcal{H}}_{1ef}$ is given by formula (11), and $\hat{\mathcal{H}}_Q = \sum_j \hat{\mathcal{H}}_Q^j$.

After simple transformations, the third matrix in the right side of (A.2) can be represented as the matrix of the operator

$$\hat{\mathcal{H}}_{2ef} = \frac{(S_+)^2_{M,M-1}}{\nu_0}\hat{\Gamma}_{+-} - \frac{(S_+)^2_{M+1,M}}{\nu_0}\hat{\Gamma}_{-+}, \qquad (A.3)$$

where

$$\Gamma_{\pm\mp} = \frac{1}{4}\sum_{p,q}\sum_{j,j'} A_p{}^j A_q{}^{j'}(\beta_p{}^j \mp i\gamma_p{}^j)(\beta_q{}^{j'} \pm i\gamma_q{}^{j'})\hat{I}_p{}^j\hat{I}_q{}^{j'}, \qquad (A.4)$$

and $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. Thus, the problem of solving the Schrödinger equation with Hamiltonian (A.1) has been reduced to the solution of the Schrödinger equation with Hamiltonian $\hat{\mathcal{H}}_{1ef} + \hat{\mathcal{H}}_Q + \hat{\mathcal{H}}_{2ef}$. The operator $\hat{\mathcal{H}}_{2ef}$ is considered in the last expression as a perturbation and should be taken into account in first order of perturbation theory, together with $\hat{\mathcal{H}}_Q$. Since we can write

$$\hat{\mathcal{H}}_{1ef} - \nu_0 M = \sum_\sigma \hat{\mathcal{H}}_{1ef}^\sigma; \quad \hat{\mathcal{H}}_{1ef}^\sigma = M\Delta_M{}^\sigma\hat{F}_n{}^\sigma, \quad \hat{F}_n{}^\sigma = \sum_{j=1}^{k_\sigma}\hat{I}_n{}^j, \qquad (A.5)$$

it is evident that $\hat{\mathcal{H}}_{1ef}^\sigma$ is the sum of k_σ single-particle operators of the nuclei, with respect to the permutation of which the Hamiltonian $\hat{\mathcal{H}}_{1ef} + \hat{\mathcal{H}}_Q$ is invariant. Contributions to the secular perturbation matrix of the group of nuclei σ will be made only by those nuclei in (A.4) belonging to this group. Retaining in (A.4) j, j' = 1, 2, ..., k_σ, we obtain the value of $\hat{\mathcal{H}}_{2ef}$ given in (8) and (9). In other words, the Hamiltonian matrix $\hat{\mathcal{H}}_{1ef}$ consists of diagonal blocks of dimension $(2I+1)^{k_\sigma}$. Account should be taken only of the perturbation operators contributing to the matrix elements of these blocks. Such an operator is $\sum_\sigma \hat{\mathcal{H}}_{2ef}^\sigma$. Since the unperturbed operator of the group of nuclei will be the operator of the total projection of k_σ nuclei $\hat{F}_n^\sigma$, the contributions to the diagonal blocks will be made by those parts of $\hat{\mathcal{H}}_{2ef}$ which have nonzero matrix elements between the states with $m_\sigma = \sum_j m_n^j = \text{const}$.

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