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Abstract. Expressions in the form of operators that enable one to calculate the intensity of allowed ($\Delta M = 1$, $\Delta m = 0$) and 'forbidden' ($\Delta M = 1$, $\Delta m = \pm 1$) hyperfine EPR lines have been derived (M and m denote, respectively, the electron and nuclear magnetic quantum numbers). The spin Hamiltonian considered consists of the electron Zeeman, zero-field and hyperfine terms. The axis of quantization for the nuclear spin is assumed to be along the direction of the effective magnetic field at the nucleus. The various spin Hamiltonian 'tensors' are considered to be anisotropic, having non-coincident principal axes. These operators depend only on the components of the spin operators S and I along their respective axes of quantization. To calculate the intensity, it is sufficient to determine the square of the matrix elements of these operators between the zero-order states that take part in resonance. The present results are compared with those published previously. The angular variation in the intensity calculated using the present expressions compares favourably with experimental values.

1. Introduction

The angular variation in the electron paramagnetic resonance (EPR) intensities has been interpreted using three different methods depending on the relative strengths of the Zeeman, crystal-field and hyperfine terms. If the crystal field is comparable with the Zeeman field, then only exact diagonalization of the spin Hamiltonian (SH) will lead to correct results. If the crystal field and hyperfine (HF) interactions are small compared with the Zeeman term, the correct intensity of the EPR transitions can be obtained using perturbation theory and assuming that the axis of quantization for the nuclear spin I remains the same for all the electronic levels involved in the transitions (Abragam and Bleaney 1970). In the case of a strong crystal field (but still smaller than the Zeeman term) and weak HF interaction compared with the crystal field, Bir (1964) has obtained intensity expressions that reproduce experimental results satisfactorily. In this method the axis of quantization for the nuclear spin is taken to be along the direction of the effective magnetic field associated with the HF interaction and is different for different electronic states. The electronic wavefunctions are obtained by applying the perturbation theory to the electronic part of the Hamiltonian and, for each of the electronic states thus obtained, the nuclear states are defined. If the crystal field and HF interactions are of comparable magnitude, the axis of quantization for the nuclear spin must still be

taken along the direction of the effective magnetic field, but the separation of the eigenstates into electronic and nuclear parts cannot then be justified and therefore the complete SH of the paramagnetic ion must be considered in calculating the EPR line intensities (Mialhe and Erbeia 1972). Mialhe (1979) has given a detailed discussion of the various approximate methods used in obtaining analytical expressions for the EPR line intensities as well as a comparison of these expressions with the experimental results on the Mn^{2+} ion in some crystal fields.

'Forbidden' HF transitions ($\Delta M = 1$, $\Delta m \neq 0$; $\Delta M \neq 1$, $\Delta m \neq 0$) arise as a result of the admixing of various nuclear states corresponding to different m-values (here, M and m denote the electron and nuclear magnetic quantum numbers, respectively). Comprehensive reviews on the subject of forbidden HF transitions have been recently given by Weil (1987) and Misra and Upreti (1987). Expressions in the form of operators that permit one to calculate the intensity of allowed ($\Delta M = 1$, $\Delta m = 0$) and forbidden ($\Delta M = 1$, $\Delta m = -1$) HF transitions have been reported by Mialhe and Erbeia (1973a, b) who used them to determine the SH parameters of the Mn^{2+} ion. It was found that their expression for the allowed transition does not simplify to that of Bir (1964) in the absence of HF interaction and that considerable differences exist between their expression for the forbidden HF transition ($\Delta M = 1$, $\Delta m = -1$) and that of Subramanian and Misra (1989) and Golding *et al* (1972). It was therefore decided to re-examine the operator expressions derived by Mialhe and Erbeia (1973a, b).

The intensity of a magnetic resonance transition is proportional to the squared absolute value of the matrix element of the Hamiltonian describing the interaction of the excitation field with the magnetic moment of the electron between the states participating in resonance. The wavefunctions involved in the evaluation of the matrix elements are the perturbed wavefunctions. The task of calculating the intensity would be greatly simplified if one could express the required matrix elements in such a way that only the unperturbed wavefunctions are involved.

It is the purpose of the present paper to derive such 'operators' that simplify the calculation of the EPR line intensities. These operators take into account the full admixture of the eigenstates up to second order in perturbation. Following Bir (1964), the axis of quantization for the nuclear spin is taken to be along the direction of the effective magnetic field at the site of the nucleus, an assumption more realistic than that used earlier (Subramanian and Misra 1989). The spin Hamiltonian considered consists of the electronic Zeeman, zero-field and HF terms. The intensity can easily be calculated by evaluating the matrix elements of these operators, which depend on the components of the spin operators S and I, between the zero-order eigenvectors of the components of S and I along their respective axes of quantization.

In section 2 we consider the general case where the various SH 'tensors' are assumed to be anisotropic and have non-coincident principal axes and we obtain the second-order perturbed eigenfunctions required for the derivation of the intensity operators. The operators for the intensity of the allowed and forbidden HF transitions are obtained in section 3 for the case of axial symmetry and coincident SH tensors. Comparison with previously published results is made in section 4. An illustrative example is given in section 5. The results are summarized in section 6.

2. Spin Hamiltonian

Consider the following Hamiltonian consisting of the Zeeman, zero-field and HF terms:

$$\mathcal{H} = \mu_B S^T \cdot \tilde{\mathbf{g}} \cdot B_0 + S^T \cdot \tilde{\mathbf{D}} \cdot S + S^T \cdot \tilde{\mathbf{A}} \cdot I. \tag{1}$$

In equation (1), T represents the transpose, μ_B is the Bohr magneton and B_0 is the external Zeeman field; $\tilde{\mathbf{g}}$, $\tilde{\mathbf{D}}$ and $\tilde{\mathbf{A}}$ are the electronic g, zero-field and HF 'tensors', respectively, and are assumed to be anisotropic and non-coincident, i.e. their principal axes are non-collinear. The axis of quantization for the nuclear spin I is taken to be in the direction of the effective magnetic field B_{eff}, which is defined for a given electronic state $|M\rangle$ as (Bir 1964)

$$\langle M | S^T \cdot \tilde{\mathbf{A}} \cdot I | M \rangle = g_n \mu_n (B_{\text{eff}} \cdot I) \tag{2}$$

where g_n and μ_n are the nuclear g-value and nuclear magneton, respectively. The eigenstates $|M\rangle$ are functions that diagonalize the purely electronic part $\mathcal{H}_e$ of the Hamiltonian (1), i.e.

$$\mathcal{H}_e = \mu_B S^T \cdot \tilde{\mathbf{g}} \cdot B_0 + S^T \cdot \tilde{\mathbf{D}} \cdot S. \tag{3}$$

To find the eigenfunctions $|M\rangle$ from perturbation theory, one transforms equation (3) from the laboratory coordinate system (x, y, z) to a new coordinate system (x_1, y_1, z_1) in which the electron spin S is quantized along the z_1 axis, the unit vector for which is defined by

$$\hat{z}_1 = B_0^T \cdot \tilde{\mathbf{g}} / B_0 g \tag{4}$$

where

$$g^2 B_0^2 = B_0^T \cdot \tilde{\mathbf{g}}^T \cdot \tilde{\mathbf{g}} \cdot B_0. \tag{5}$$

It is then possible to rewrite equation (3) as the sum of two terms: a zero-order term

$$\mathcal{H}_{e0} = \mu_B g B_0 S_{z1} + \tfrac{1}{2}(\hat{z}_1^T \cdot \tilde{\mathbf{D}} \cdot \hat{z}_1)[3S_{z1}^2 - S(S+1)] \tag{6}$$

and a perturbation

$$\mathcal{H}_e' = \tfrac{1}{2}[(r_1^T \cdot \tilde{\mathbf{D}} \cdot \hat{z}_1)(S_+ S_{z1} + S_{z1} S_+) + (l_1^T \cdot \tilde{\mathbf{D}} \cdot \hat{z}_1)(S_- S_{z1} + S_{z1} S_-)]$$
$$+ \tfrac{1}{4}[(r_1^T \cdot \tilde{\mathbf{D}} \cdot r_1)S_+^2 + (l_1^T \cdot \mathbf{D} \cdot l_1)S_-^2] \tag{7}$$

where

$$r_1 = \hat{x}_1 - i\hat{y}_1$$
$$l_1 = \hat{x}_1 + i\hat{y}_1 \tag{8}$$
$$S_{\pm} = S_{x1} \pm iS_{y1}.$$

The second-order perturbed wavefunctions $|M\rangle$ of the Hamiltonian (3) can then be written as (Golding 1969)

$$|M\rangle = \sum_{N=0}^{4} a_{M \pm N} |M \pm N\rangle^0 \tag{9}$$

where $a_{M \pm N}$ are the admixture coefficients and $|M \pm N\rangle^0$ are the zero-order eigenfunctions of equation (6).

The effective magnetic field B_{eff} defined by equation (2) and which determines the direction of the nuclear axis of quantization in the electronic state $|M\rangle$ can now be expressed as

$$g_n \mu_n B_{\text{eff},\alpha} = (\hat{x}_1^T \cdot \tilde{\mathbf{A}} \cdot \bar{\alpha})\langle M|S_{x1}|M\rangle$$

$$+ (\hat{y}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{\alpha})\langle M|S_{y1}|M\rangle$$

$$+ (\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{\alpha})\langle M|S_{z1}|M\rangle \qquad \alpha = x, y, z. \tag{10}$$

This direction, defined by the polar angle φ' measured from the z axis, for the case of axial symmetry in which the principal axes of $\tilde{\mathbf{D}}$ and $\tilde{\mathbf{A}}$ are coincident with the x, y, z axes, is given by (Bir *et al* 1965)

$$\cos \varphi' = (A/KM)[M \cos \varphi + (\lambda/G)\{3M^2 - S(S+1)\} \sin \varphi]$$

$$\sin \varphi' = (B/KM)[M \sin \varphi - (\lambda/G)\{3M^2 - S(S+1)\} \cos \varphi] \tag{11}$$

where φ is the polar angle of the z_1 axis. The remaining constants in equation (11) are defined in equation (19). The non-parallelism of the axes of quantization of the electron and nuclear spins is most significant for $M = \pm\frac{1}{2}$ (Mialhe and Erbeia 1972)

Having determined the orientation of B_{eff} relative to the laboratory coordinate system (x, y, z), the HF interaction can be written as

$$S^T \cdot \tilde{\mathbf{A}} \cdot I = [S_{x1}(\hat{x}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{x}_2) + S_{y1}(\hat{y}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{x}_2) + S_{z1}(\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{x}_2)]I_{x2}$$

$$+ [S_{x1}(\hat{x}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{y}_2) + S_{y1}(\hat{y}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{y}_2) + S_{z1}(\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{y}_2)]I_{y2}$$

$$+ [S_{x1}(\hat{x}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{z}_2) + S_{y1}(\hat{y}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{z}_2) + S_{z1}(\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{z}_2)]I_{z2}. \tag{12}$$

In equation (12), the unit vector $\hat{z}_2$ is defined by

$$\hat{z}_2 = B_{\text{eff}}/|B_{\text{eff}}| \tag{13}$$

and determines the axis of quantization for the nuclear spin I; the axes x_2, y_2 are unspecified.

Using equations (6), (7) and (12) the spin Hamiltonian (1) can be written as

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}'$$

where

$$\mathscr{H}_0 = \mu_B g B_0 S_{z1} + \tfrac{1}{2}(\hat{z}_1^T \cdot \tilde{\mathbf{D}} \cdot \hat{z}_1)[3S_{z1}^2 - S(S+1)] + (\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{z}_2)S_{z1}I_{z2} \tag{14}$$

and

$$\mathscr{H}' = \tfrac{1}{2}[(r_1^T \cdot \tilde{\mathbf{D}} \cdot \hat{z}_1)(S_+ S_{z1} + S_{z1}S_+) + (l_1^T \cdot \tilde{\mathbf{D}} \cdot \hat{z}_1)(S_- S_{z1} + S_{z1}S_-)]$$

$$+ \tfrac{1}{4}[(r_1^T \cdot \tilde{\mathbf{D}} \cdot r_1)S_+^2 + (l_1^T \cdot \tilde{\mathbf{D}} \cdot l_1)S_-^2 + S_+ I_+(r_1^T \cdot \tilde{\mathbf{A}} \cdot r_2)$$

$$+ S_+ I_-(r_1^T \cdot \tilde{\mathbf{A}} \cdot l_2) + S_- I_+(l_1^T \cdot \mathbf{A} \cdot r_2) + S_- I_-(l_1^T \cdot \tilde{\mathbf{A}} \cdot l_2)]$$

$$+ \tfrac{1}{2}\{S_{z1}[(\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot l_2)I_- + (\hat{z}_1^T \cdot \tilde{\mathbf{A}} \cdot r_2)I_+]$$

$$+ I_{z2}[(r_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{z}_2)S_+ + (l_1^T \cdot \tilde{\mathbf{A}} \cdot \hat{z}_2)S_-]\} \tag{15}$$

where

$$r_2 = \hat{x}_2 - i\hat{y}_2$$
$$l_2 = \hat{x}_2 + i\hat{y}_2 \tag{16}$$
$$I_{\pm} = I_{x2} \pm iI_{y2}.$$

3. Intensity operator

Operator expressions that enable one to evaluate the intensities of the EPR HF transitions $\Delta M = 1$, $\Delta m = 0$, ± 1 will now be derived for the case where the excitation field B_1 is perpendicular to the Zeeman field B_0. In order to compare the present results with those of Mialhe and Erbeia (1973a, b), it will be assumed that the $\tilde{g}$, $\tilde{D}$ and $\tilde{A}$ tensors are axial and that their principal axes coincide with the laboratory axes x, y, z. The spin Hamiltonian (equations (14) and (15)) then simplifies to

$$\mathcal{H}_0 = \mu_B g B_0 S_{z1} + \sigma[3S_{z1}^2 - S(S+1)] + K_0 S_{z1} I_{z2} \tag{17}$$

$$\mathcal{H}' = -(\lambda/2)(S_+ S_{z1} + S_{z1} S_+ + S_- S_{z1} + S_{z1} S_-) + \rho(S_+^2 + S_-^2)$$
$$+ S_1(I_+ + I_-) - P(S_+ + S_-)I_{z2}$$
$$+ Q(S_+ I_+ + S_- I_-) + R(S_+ I_- + S_- I_+) \tag{18}$$

with

$$\sigma = (D/6)(3\cos^2\varphi - 1)$$
$$\lambda = D\sin\varphi\cos\varphi$$
$$\rho = (D/4)\sin^2\varphi$$
$$P = [(A^2 - B^2)/2K]\sin\varphi\cos\varphi$$
$$\qquad + (\lambda/2GKM)(A^2\sin^2\varphi + B^2\cos^2\varphi)[3M^2 - S(S+1)]$$
$$S_1 = (\lambda AB/2GK)[3M^2 - S(S+1)]$$
$$Q = (B/4)(A/K - 1)$$
$$R = (B/4)(A/K + 1)$$
$$K_0 = K + [(A^2 - B^2)/KM](D/G)\sin^2\varphi\cos^2\varphi[3M^2 - S(S+1)]$$
$$g^2 K^2 = g_\parallel^2 A^2 \cos^2\theta + g_\perp^2 B^2 \sin^2\theta$$
$$D = \tfrac{3}{2}D_{zz}$$
$$A = A_{zz}$$
$$B = A_{xx} = A_{yy}$$
$$\tan\varphi = (g_\perp/g_\parallel)\tan\theta$$
$$G = \mu_B g B_0$$

(19)

θ is the angle between the Zeeman field B_0 and the z principal axis.

The spin Hamiltonian given by equations (17) and (18) differs from that of Mialhe and Erbeia (1972) in two essential respects.

(i) The coefficients Q and R defined by equation (19) of the present paper are different from the coefficients derived by Mialhe and Erbeia.

(ii) The sign of the coefficient S_1 of the present paper is opposite to the coefficient given by them.

The second-order normalized perturbed eigenfunctions of the spin Hamiltonian (equations (17) and (18)) can be written as (Golding 1969):

$$|M, m\rangle = (1 + a_{M,m}^{M,m})|M, m\rangle^0 + \sum_{N,n}{}' c_{M \pm N, m \pm n}^{M,m}|M \pm N, m \pm n\rangle^0 \tag{20}$$

where N, n are positive integers and $|M, m\rangle^0$ are the zero-order wavefunctions of $\mathcal{H}_0$ (equation (17)); a is required for normalization and the c are admixture coefficients. The prime on the summation sign indicates that the term with $N = n = 0$ is to be omitted.

The intensity $I_{M,m;M',m'}$ of the magnetic resonance transitions between the perturbed states $|M', m'\rangle$ and $|M, m\rangle$ is given by (Orton 1968)

$$I_{M,m;M'm'} = \mathcal{H}|\langle M', m'|\mathcal{H}_{\text{ex}}|M, m\rangle|^2 \tag{21}$$

where $\mathcal{H}$ is a constant and

$$\begin{aligned}
\mathcal{H}_{\text{ex}} &= \mu_{\text{B}}S^{\text{T}} \cdot \tilde{\mathbf{g}} \cdot \boldsymbol{B}_1 \\
&= \mu_{\text{B}}[\tfrac{1}{2}(r_1^{\text{T}} \cdot \tilde{\mathbf{g}} \cdot \boldsymbol{B}_1)S_+ + \tfrac{1}{2}(l_1^{\text{T}} \cdot \tilde{\mathbf{g}} \cdot \boldsymbol{B}_1)S_- + (\hat{z}_1^{\text{T}} \cdot \tilde{\mathbf{g}} \cdot \boldsymbol{B}_1)S_{z1}]
\end{aligned} \tag{22}$$

In equation (22), $\boldsymbol{B}_1$ is the amplitude of the excitation microwave field.

The basic idea behind the formulation of an operator to evaluate the intensity of EPR transitions is that it is possible to express equation (21) in the form

$$I_{M,m;M'm'} = \mathcal{H}|^0\langle M', m'|J|M, m\rangle^0|^2 \tag{23}$$

where J is the required operator.

The derivation of the intensity operator J is illustrated below with the help of one specific example. To facilitate comparison with previously published results (Mialhe and Erbeia 1973a, b, Golding *et al* 1972, Subramanian and Misra 1989), it will be assumed that $\tilde{\mathbf{g}}$, $\tilde{\mathbf{D}}$ and $\tilde{\mathbf{A}}$ have axial symmetry and that the principal axes of $\tilde{\mathbf{D}}$ and $\tilde{\mathbf{A}}$ coincide with the x, y, z axes. One of the terms appearing in the intensity expression (21) for the allowed HF transition $M - 1, m \leftrightarrow M, m$ is proportional to

$$^0\langle (c_{M+1,m}^{M-1,m})M + 1, m|S_+|(1 + a_{M,m}^{M,m})M, m\rangle^0. \tag{24}$$

Keeping only terms in $1/G^2$, this becomes

$$S_{0,1}c_{M+1,m}^{M-1,m} \tag{25}$$

where

$$S_{0,1} = {}^0\langle M + 1, m|S_+|M, m\rangle^0 = {}^0\langle M, m|S_-|M + 1, m\rangle^0. \tag{26}$$

The admixture coefficient of the state $|M - 1, m\rangle$ with the state $|M + 1, m\rangle$, $c_{M+1,m}^{M-1,m}$, is given in the second-order perturbation approximation as (Golding 1969)

$$\begin{aligned}
c_{M+1,m}^{M-1,m} = \Bigg[&\frac{{}^0\langle M + 1, m|\mathcal{H}'|M - 1, m\rangle^0}{E_0^{M-1,m} - E_0^{M+1,m}} + \frac{1}{E_0^{M-1,m} - E_0^{M+1,m}} \\
&\times \Bigg(\sum{}' \frac{{}^0\langle M + 1, m|\mathcal{H}'|M', m'\rangle^0 {}^0\langle M', m'|\mathcal{H}'|M - 1, m\rangle^0}{E_0^{M-1,m} - E_0^{M',m'}}
\end{aligned}$$

$$- \frac{{}^0\langle M+1, m|\mathcal{H}'|M-1, m\rangle^0 \, {}^0\langle M-1, m|\mathcal{H}'|M-1, m\rangle^0}{E_0^{M-1,m} - E_0^{M+1,m}}\Bigg)\Bigg]$$

$$= -\Bigg(\frac{{}^0\langle M+1, m|\rho S_+^2|M-1, m\rangle^0}{2G} - \frac{\lambda^2}{8G^2}$$

$$\times \big[{}^0\langle M+1, m|(2S_z - 1)S_+|M, m\rangle^0$$

$$\times {}^0\langle M, m|(2S_z - 1)S_+|M-1, m\rangle^0\big]\Bigg). \tag{27}$$

Using equations (27) and (26), equation (25) can be written as

$$-(\rho/2G){}^0\langle M, m|S_-|M+1, m\rangle^0 \, {}^0\langle M+1, m|S_+^2|M-1, m\rangle^0 + (\lambda^2/8G^2)$$

$$\times {}^0\langle M, m|S_-|M+1, m\rangle^0 \, {}^0\langle M+1, m|(2S_z - 1)S_+|M, m\rangle^0$$

$$\times {}^0\langle M, m|(2S_z - 1)S_+|M-1, m\rangle^0$$

$$= {}^0\langle M-1, m|[-(\rho/2G)S_-^2 S_+ + (\lambda^2/8G^2)$$

$$\times S_-(2S_z - 1)S_-(2S_z - 1)S_+]|M, m\rangle^0. \tag{28}$$

Let us define an operator $C_{M+1,m}^{M-1,m}$ by

$$S_{0,1}c_{M+1,m}^{M-1,m} = {}^0\langle M-1, m|C_{M+1,m}^{M-1,m}|M, m\rangle^0. \tag{29}$$

The required operator is then given by

$$C_{M+1,m}^{M-1,m} = -(\rho/2G)S_-^2 S_+ + (\lambda^2/8G^2)S_-(2S_z - 1)S_-(2S_z - 1)S_+. \tag{30}$$

Operator expressions thus obtained for the allowed ($\Delta M = 1$, $\Delta m = 0$) and forbidden ($\Delta M = 1$, $\Delta m = \pm 1$) HF transitions are given below.

For the transition $M - 1, m \leftrightarrow M, m$ ($\Delta M = 1$, $\Delta m = 0$),

$$J = \{1 + (\rho/G)(2S_z - 1) + (\lambda^2 A^2 B^2/2G^2 K^4)[S_z^{-1}(S_z - 1)^{-1}(3S_z^2 - S^2)$$

$$\times (3S_z^2 - 6S_z - S^2 + 3)](I^2 - I_{z'}^2) - (\lambda^2 A^2 B^2/4G^2 K^4)$$

$$\times [S_z^{-2}(3S_z^2 - S^2)^2 + (S_z - 1)^{-2}(3S_z^2 - 6S_z - S^2 + 3)^2](I^2 - I_{z'}^2)$$

$$- (\lambda^2/G^2)(S^2 + 3S_z^2 - 3S_z) - (\rho^2/G^2)$$

$$\times (S^2 - 3S_z^2 + 3S_z - \tfrac{3}{2})\}S_+ \tag{31}$$

For the transition $M - 1, m \mp 1 \leftrightarrow M, m$ ($\Delta M = 1$, $\Delta m = \pm 1$),

$$J = \pm(\lambda AB/2GK^2)[\![S_-\{[3S_z^2 - S(S+1)]/S_z\} - \{[3S_z^2 - S(S+1)]/S_z\}S_-]\!]I_\mp$$

$$\pm (\lambda\rho AB/8G^3 K)\{[S(S+1) - S_z^2 - 3S_z - 2]S_-[3(S_z + 1)^2 - S(S+1)]$$

$$+ [3(S_z - 1)^2 - S(S+1)]S_-[S(S+1) - S_z^2 + 3S_z - 2]\}I_\mp$$

$$+(\lambda^3 A^3 B^3/8G^3 K^6)[\![\{[3S_z^2 - S(S+1)]/S_z\}S_-\{[3S_z^2 - S(S+1)]/S_z\}^2$$

$$\times I_\mp[I(I+1) - I_{z'}^2] - \{[3S_z^2 - S(S+1)]/S_z\}^2 S_-\{[3S_z^2 - S(S+1)]/S_z\}$$

$$\times [I(I+1) - I_{z'}^2]I_\mp]\!] - (Q\lambda/G^2)\{S_-(2S_z - 1)$$

$$\times [S(S+1) - S_z^2 + S_z - (3 \pm 2)]\}I_\mp$$

$$- (R\lambda/G^2)\{S_-(2S_z - 1)[S(S+1) - S_z^2 + S_z - (3 \mp 2)]\}I_\mp$$

$$\pm (\lambda \rho A B / 2 G^2 K^2) [S_-(2S_z - 1)\{[3S_z^2 - S(S + 1)]/S_z\}$$
$$- \{[3S_z^2 - S(S + 1)]/S_z\}S_-(2S_z - 1)]I_\mp . \tag{32}$$

In the derivation of equations (31) and (32), terms involving $(A - B)/K$ were neglected as was done by Mialhe and Erbeia (1973a, b).

4. Comparison with previous results

The above results for the intensity operator given by equations (31) and (32) are now compared with those of Mialhe and Erbeia (1973a, b). It is seen that the present results differ from theirs significantly. In the case of the allowed HF transitions ($\Delta M = 1, \Delta m = 0$), it is noticed that the expression (equation (13)) obtained by Mialhe and Erbeia (1973a) does not simplify to that given by Bir (1964) for the case where the HF interaction is absent, wheras the present result (equation (31)) does. The result derived in the present paper (equation (31)) is also in agreement with that of Subramanian and Misra (1989). As regards the forbidden HF transition ($\Delta M = 1, \Delta m = -1$) the expression given by Mialhe and Erbeia (1973b) is quite different from those given by Golding *et al* (1972) and Subramanian and Misra (1989). Remarkably, the term $(\lambda A/2G^2)(2M - 1)$ $[S(S + 1) - M^2 + M - 5]$ found in the above-mentioned references is absent in the work of Mialhe and Erbeia (1973b). The expression derived in the present paper (equation (32)), on the other hand, is in agreement with the results of Golding *et al* (1972) and Subramanian and Misra (1989). However, the sign of the term $(\lambda A/2G^2)(2M - 1) \times [S(S + 1) - M^2 + M - 5]$ in the present paper (equation (32)) is opposite to the signs given by Golding *et al* and by Subramanian and Misra. The reason for this is that these workers used a different direction, namely along the direction of $B_0^T \cdot \tilde{g} \cdot \tilde{A}$, to quantize the nuclear spin; the direction used in the present paper is given by equation (13).

The intensity of the forbidden HF transition $\Delta M = 1, \Delta m = +1$ has been calculated by Subramanian and Misra (1989). The present result (equation (32)) is in agreement with their value.

5. Illustrative example

The present calculated expression (32) will now be used to compare the intensity of the forbidden HF lines with the experimental values. For this, the values of the intensity of Mn^{2+} ion in Al_2O_3 reported by Mialhe and Erbeia (1973b) will be used. In order to calculate the intensity theoretically, one needs to know the values of the SH parameters D, A and B as well as the klystron frequency. The values of D, A and B have been reported by Mialhe and Erbeia (1973b) from measurements of the EPR line positions to be $D = 207.4$ G, $A = -85.1$ G and $B = -83.7$ G. However, the klystron frequency is not reported by Mialhe and Erbeia. It had, therefore, to be estimated using a least-squares procedure (Misra *et al* 1989) and the theoretical (incorrect) expression given by Mialhe and Erbeia. The χ^2-value for the EPR data was defined as $\chi^2 = \Sigma_i (I^i_{calc} - I^i_{rep})^2$ where i denotes the number of data points used in the fitting procedure and I_{calc} and I_{rep}, respectively, represent the intensities calculated using their theoretical expression and the (calculated) values actually reported by them. The best-fit value of the klystron frequency was then determined to be 9.62 GHz. This value of the klystron frequency
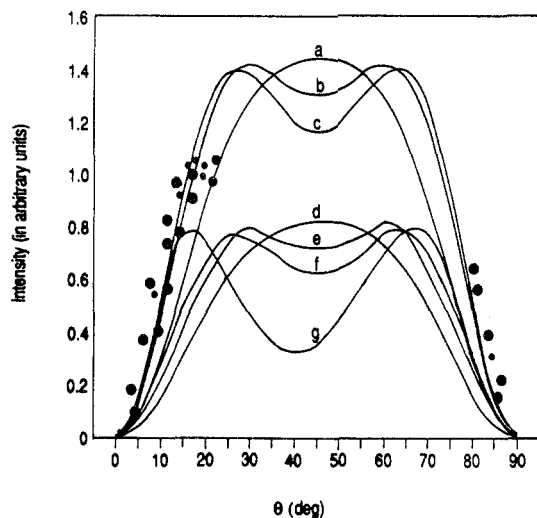
Figure 1. Angular variation in the intensity of the forbidden HF transition $-\frac{1}{2}$, $m + 1 \leftrightarrow \frac{1}{2}$, m for Mn^{2+} ions in Al_2O_3: curves a $(m = \frac{3}{2})$, b $(m = \frac{1}{2})$ and c $(m = -\frac{1}{2})$ are based on equation (32) of the present paper; curves d, e and f are for corresponding m-values according to Mialhe and Erbeia (1973b); curve g is for $m = -\frac{1}{2}$ as predicted by Bir (1964): ●, from Mialhe and Erbeia.

along with the values of D, A and B reported by Mialhe and Erbeia was then used to calculate the intensity theoretically, using equation (32). The angular variation in the intensity so calculated is shown in figure 1 for $M = \frac{1}{2}$.

It is seen that the agreement between the intensities calculated using the present derived expression and the experimental results of Mialhe and Erbeia is quite good. For completeness, the angular variation in the intensity predicted by Mialhe and Erbeia (1973b) and Bir (1964) are also shown in the same figure. It is clear that Bir's expression cannot reproduce the data satisfactorily, which shows that the separation of the wavefunction into electronic and nuclear parts is not valid when the crystal-field and HF energies are of the same magnitude. Bir's expression gives good agreement with experiment only in the case of crystal-field splitting larger than the HF splitting (Bir *et al* 1965, Dickey and Drumheller 1964).

5. Conclusion

A comparison of the theoretically calculated intensities of forbidden HF transitions with the experimental values shows that good agreement is obtained if one considers the exact quantization axes for electronic and nuclear spins. Use of the conventional quantization axis for nuclear spin adopted by Abragam and Bleaney (1970) also gives similar results. The advantage of the present method is that only first-order calculations of the wavefunctions are needed to get results that the conventional method gives in second order. This greatly simplifies the task of evaluating the matrix elements required in the computation of the EPR intensities.

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