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EVALUATION OF ANISOTROPIC NON-COINCIDENT g AND A TENSORS FROM EPR AND ENDOR DATA BY THE METHOD OF LEAST-SQUARES FITTING

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The details of a rigorous least-squares fitting procedure for the evaluation of the principal values of g and A tensors, as well as the direction cosines of their principal axes, are given. Expressions are provided for a quick evaluation of the required energy level differences. In this method all EPR (ENDOR) line positions (frequencies) obtained for several orientation of the external magnetic field in three mutually perpendicular planes are simultaneously fitted to evaluate all the components of the g and A tensors, and to minimize parameter errors. The procedure is illustrated by application to the EPR data analysis of one of the eight inequivalent $(BO_4)^{4-}$ tetrahedral complexes ($S = 1/2$, $I = 3/2$) obtained when $^{11}B^{3+}$ replaces Si^{4+} in $(SiO_4)^{4-}$ complex in danburite single crystal ($CaB_2Si_2O_8$).

1. Introduction

Accurate knowledge of the principal values of the g and A tensors, as well as the direction cosines of their principal axes, is essential for a proper understanding of the interaction of a paramagnetic ion (or complex) with its environment. For example, the g and A values, as observed in a paramagnetic host lattice can be appreciably different from those observed in an isostructural diamagnetic host lattice. This has, indeed, been verified, e.g., by St. John and Myers [1] at liquid helium temperatures for Cu^{2+} ions doping the isostructural crystals paramagnetic α-$NiSO_4 \cdot 6H_2O$ and diamagnetic $ZnSeO_4 \cdot 6H_2O$; the g shift here is related to the Cu^{2+}–Ni^{2+} exchange interaction J. The g values provide information about the chemical structure of a paramagnetic ion (complex) and its interaction with the environment. On the other hand, the principal values of A can be used, among other things, to deduce the orientation of a paramagnetic complex characterized by a non-zero nuclear magnetic moment, e.g. the angle of liaison O–B–O in BO_2 molecule in calcite [2].

Recently, the least-squares procedure, fitting simultaneously a large number of resonant EPR line positions, obtained for several orientations of the external magnetic field, has been rigorously applied to evaluate the spin Hamiltonian parameters of purely electronic systems [3], and further extended to include the electronic–nuclear spin-coupled systems [4]. However, in both these cases, the principal axes of the g and A tensors have been implicitly assumed to be parallel to those of the crystal-field tensors B_q^k. Thus, one only had to take into account the principal values of the g and A tensors using a system of coordinates in which the crystal-field tensors are diagonal [5].

However, when the principal axes of the g and A tensors are non-coincident and have arbitrary directions, complications arise in the determination of the principal values and principal axes of the g and A tensors. The problem is *not* simply expanding the electronic Zeeman term $\mu_B \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S}$ in terms of the g-tensor components $g_{\alpha\beta}$ as spin Hamiltonian parameters like B_q^k in the least-squares fitting procedure. For, the eigenvalues here do not depend upon $g_{\alpha\beta}$ and $A_{\alpha\beta}$, but rather upon their special bilinear combinations, which are, in fact, the elements of the g^2 and A^2 tensors (see section 3 below for more details).

It is the purpose of this paper to present the details of a general least-squares fitting (LSF) procedure for a rigorous evaluation of the principal values of the g and A tensors, as well as the direction cosines of their principal axes, fitting simultaneously all EPR line positions (or

ENDOR frequencies) obtained for several orientations of the external magnetic field in three mutually perpendicular planes. A brief outline of the LSF procedure as applied to the analysis of EPR (ENDOR) data is given in section 2. Section 3 deals with the general problem of the dependence of eigenvalues upon the components of $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors, whose principal axes are assumed to be non-coincident. These results are readily applicable to the proposed LSF procedure, the step-wise details of which are given in section 4. The illustrative example is presented in section 5. The concluding remarks are made in section 6.

2. Brief outline of the LSF method

In this method, one first starts with a set of initially chosen values of the spin Hamiltonian parameters (represented by the vectors $\boldsymbol{a}_1$); $\boldsymbol{a}_1$ is then iteratively changed to a new vector $\boldsymbol{a}$, as follows, until convergence is achieved:

$$\boldsymbol{a} = \boldsymbol{a}_1 - (D'')^{-1}D' . \tag{2.1}$$

In (2.1), D' and D'' are the matrices whose elements are respectively the first and second derivatives of χ^2 with respect to the spin Hamiltonian parameters, evaluated with a_1,

$$(D')_j = \left(\frac{\partial\chi^2}{\partial a_j}\right)_{a_1}, \tag{2.2}$$

$$(D'')_{jk} = \left(\frac{\partial\chi^2}{\partial a_j \partial a_k}\right)_{a_1}, \tag{2.3}$$

where

$$\chi^2 \equiv \sum_i (|\Delta E_i| - h\nu_i)^2/\sigma_i^2 , \tag{2.4}$$

In eq. (2.4) the summation over i covers all the EPR line position, or ENDOR frequencies, used in the fitting, ΔE_i $(=E_i' - E_i'')$ is the calculated energy difference between the levels E_i' and E_i'' participating in resonance, ν_i are the corresponding klystron (or ENDOR radio) frequencies, h is Planck's constant, and σ_i is the effective weight factor for the ith line position.

From (2.4), one has explicitly for the elements of D' and D''

$$(D')_j = 2\sum_i \frac{|(\Delta E_i - h\nu_i)|}{\sigma_i^2}\frac{\partial|\Delta E_i|}{\partial a_j}, \tag{2.5}$$

and

$$(D'')_{jk} = 2\sum_i \left[\frac{1}{\sigma_i^2}\frac{\partial|\Delta E_i|}{\partial a_j}\frac{\partial|\Delta E_i|}{\partial a_k} + (|\Delta E_i| - h\nu_i)\frac{\partial^2|\Delta E_i|}{\partial a_j \partial a_k}\right]. \tag{2.6}$$

As for the error Δa_j of the parameter a_j, it is [6]:

$$\Delta a_j = \sqrt{\varepsilon_{jj}} \tag{2.7}$$

where ε_{jj} is the jth diagonal element of the matrix E which is the inverse of one-half times the second-derivative matrix of χ^2:

$$E = A^{-1}; \qquad A_{kl} = \frac{1}{2}\frac{\partial^2\chi^2}{\partial a_k \partial a_l} . \tag{2.8}$$

3. Solution of the general problem

The object of this section is to calculate the eigenvalues of the general spin Hamiltonian, $\mathcal{H}$, as required in the application of the LSF method (non-coincident $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors):

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{hf} ,$$

where

$$\mathcal{H}_s = \mu_B \boldsymbol{S}\cdot\boldsymbol{g}\cdot\boldsymbol{H} \qquad \text{and} \qquad \mathcal{H}_{hf} = \boldsymbol{S}\cdot\boldsymbol{A}\cdot\boldsymbol{I}. \tag{3.1}$$

In eqs. (3.1) μ_B is the Bohr magneton, S is the electronic spin, I is the nuclear spin, H is the external magnetic field, and $\boldsymbol{g}$ and $\boldsymbol{A}$ are respectively the electronic-g and hyperfine tensors.

3.1. Eigenvalues of $\mathcal{H}_s$

$\mathcal{H}_s$ can be exactly diagonalized as follows. Expanding it in terms of the components $\boldsymbol{g}_{\alpha\beta}$ ($\alpha, \beta = x, y, z$):

$$\mathcal{H}_s = \mu_B H(S_x a_x + S_y a_y + S_z a_z),$$

where

$$\begin{aligned} a_x &= \boldsymbol{g}_{xx} l + \boldsymbol{g}_{xy} m + \boldsymbol{g}_{xz} n, \\ a_y &= \boldsymbol{g}_{yx} l + \boldsymbol{g}_{yy} m + \boldsymbol{g}_{yz} n, \\ a_z &= \boldsymbol{g}_{zx} l + \boldsymbol{g}_{zy} m + \boldsymbol{g}_{zz} n. \end{aligned} \tag{3.2}$$

In eq. (3.2) l, m, n are the direction cosines of $\boldsymbol{H}$ with respect to the coordinate axes (x, y, z). If now transformation is made to the system of axes (x', y', z') where z' has the direction cosines $(a_x/g_{\text{eff}}, a_y/g_{\text{eff}}, a_z/g_{\text{eff}})$ with respect to (x, y, z) where $g_{\text{eff}} = (a_x^2 + a_y^2 + a_z^2)^{1/2}$, then eq. (3.2) can be expressed as

$$\mathcal{H}_s = \mu_B g_{\text{eff}} H S_{z'}, \tag{3.3}$$

Explicitly,

$$\begin{aligned} g_{\text{eff}} = (&\boldsymbol{g}_{xx}^2 l^2 + 2\boldsymbol{g}_{xy}^2 lm + \boldsymbol{g}_{yy}^2 m^2 + 2\boldsymbol{g}_{xz}^2 ln + \boldsymbol{g}_{zz}^2 n^2 \\ &+ 2\boldsymbol{g}_{yz}^2 mn)^{1/2}, \end{aligned} \tag{3.4}$$

where $\boldsymbol{g}_{\alpha\beta}^2$ are the $\alpha\beta$ components of the $\boldsymbol{g}^2$ matrix ($=\boldsymbol{g}^{\mathrm{T}} \cdot \boldsymbol{g}$ where $\boldsymbol{g}^{\mathrm{T}}$ is the matrix transpose to $\boldsymbol{g}$), i.e.

$$\boldsymbol{g}_{\alpha\beta}^2 = \sum_{\alpha'=x,y,z} \boldsymbol{g}_{\alpha'\alpha} \boldsymbol{g}_{\alpha'\beta}. \tag{3.5}$$

[From eq. (3.5) it is seen that $\boldsymbol{g}^2$ is a symmetric tensor ($\boldsymbol{g}_{\alpha\beta}^2 = \boldsymbol{g}_{\beta\alpha}^2$), while $\boldsymbol{g}$, in general, is not [5].]

From eq. (3.3) it is seen that the eigenvalues of $\mathcal{H}_s$ are

$$E_s(M) = \mu_B g_{\text{eff}} H M, \tag{3.6}$$

where M is the electronic quantum number,

$$S_{z'}|M\rangle = M|M\rangle. \tag{3.7}$$

From eqs. (3.6) and (3.4) it is clear that $E_s(M)$ depends only upon the (six linearly independent) components of the $\boldsymbol{g}^2$ tensor, as given by (3.5), rather than upon the components of the $\boldsymbol{g}$ tensor. Thus from the EPR line positions, or ENDOR frequencies, which depend upon eigenvalue differences one can only determine the components of the $\boldsymbol{g}^2$ tensor. Further, from eq. (3.4) it is seen that measurements in three mutually perpendicular planes are necessary to determine all the elements of $\boldsymbol{g}^2$ tensor. In order to find the principal values of the $\boldsymbol{g}$ tensor it is sufficient to note that if the unitary matrix U ($U^\dagger = U^{-1}$) diagonalizes it to the diagonal matrix g_d, i.e.

$$g_d = U\boldsymbol{g}U^\dagger, \tag{3.8}$$

then U also diagonalizes the $\boldsymbol{g}^2$ matrix as shown in Appendix A, i.e.

$$g_d^2 = U\boldsymbol{g}^2U^\dagger = U(\boldsymbol{g}^{\mathrm{T}} \cdot \boldsymbol{g})U^\dagger. \tag{3.9}$$

Conversely, then, if one finds the unitary matrix that diagonalizes the $\boldsymbol{g}^2$ matrix, then its elements are the direction cosines of the principal axes of the $\boldsymbol{g}$ tensor, while the eigenvalues of the $\boldsymbol{g}^2$ matrix are the squares of the principal values of the $\boldsymbol{g}$ tensor.

3.2. Eigenvalues of $\mathcal{H}_{\text{hf}}$

In general, in its fully-expanded form

$$\begin{aligned} \mathcal{H}_{\text{hf}} = &A_{xx}S_xI_x + A_{yy}S_yI_y + A_{zz}S_zI_z + A_{xy}S_xI_y \\ &+ A_{yx}S_yI_x + A_{yz}S_yI_z + A_{zy}S_zI_y + A_{zx}S_zI_x \\ &+ A_{xz}S_xI_z. \end{aligned} \tag{3.10}$$

If one now transforms to the new axes (x', y', z') where the z'-axis has the direction cosines $(a_x/g_{\text{eff}}, a_y/g_{\text{eff}}, a_z/g_{\text{eff}})$, as given by eq. (3.2), then in eq. (3.10), S_x gives a component $S_{z'}$ with the coefficient a_x/g_{eff}, while S_y and S_z give the components $S_{z'}$ with coefficients a_y/g_{eff} and a_z/g_{eff}, respectively. Thus in the coordinate system (x', y', z'),

$$\mathcal{H}_{hf} = S_{z'}(I_x b_x + I_y b_y + I_z b_z) + \text{terms in } S_{x'} \text{ and } S_{y'}, \tag{3.11}$$

where

$$\begin{aligned} b_x &= (A_{xx}a_x + A_{yx}a_y + A_{zx}a_z)/g_{eff}, \\ b_y &= (A_{xy}a_x + A_{yy}a_y + A_{zy}a_z)/g_{eff}, \\ b_z &= (A_{xz}a_x + A_{yz}a_y + A_{zz}a_z)/g_{eff}. \end{aligned} \tag{3.12}$$

Eq. (3.11) can be reexpressed as

$$\mathcal{H}_{hf} = A_{eff}S_{z'}I_{z''} + \text{terms in } S_{x'} \text{ and } S_{y'}, \tag{3.13}$$

where

$$\begin{aligned} A_{eff} &= (b_x^2 + b_y^2 + b_z^2)^{1/2} \\ &= (\boldsymbol{A}_{xx}^2 a_x^2 + 2\boldsymbol{A}_{xy}^2 a_x a_y + \boldsymbol{A}_{yy}^2 a_y^2 + 2\boldsymbol{A}_{xz}^2 a_x a_z \\ &\quad + \boldsymbol{A}_{zz}^2 a_z^2 + 2\boldsymbol{A}_{yz}^2 a_y a_z)^{1/2} \end{aligned} \tag{3.14}$$

In (3.14), explicitly, in the coordinate system (x', y', z') in which the $\boldsymbol{g}$ tensor is diagonal $a_x = l'g'_x/g_{eff}$, $a_y = m'g'_y/g_{eff}$ and $a_z = n'g'_z/g_{eff}$, where g'_x, g'_y and g'_z are the principal values of the $\boldsymbol{g}$ tensor, and l', m', n' are the direction cosines of the external magnetic field with respect to the coordinate system (x', y', z'). Explicitly,

$$\begin{aligned} l' &= l\cos(x, x') + m\cos(y, x') + n\cos(z, x'), \\ m' &= l\cos(x, y') + m\cos(y, y') + n\cos(z, y), \\ n' &= l\cos(x, z') + m\cos(y, z') + n\cos(z, z'). \end{aligned} \tag{3.15}$$

In eq. (3.15), (x, x') is the angle between the axes x and x', etc., $\cos(x, x')$, etc. have already been determined in section 3.1, being the direction cosines of the principal values of the $\boldsymbol{g}$ tensor in the (x, y, z) coordinate system.

In eq. (3.13), $I_{z''}$ represents the component of $\boldsymbol{I}$ along the direction z'' whose direction cosines with respect to (x', y', z') are b_x/A_{eff}, b_y/A_{eff}, b_z/A_{eff}. From (3.13), then, in zero order, neglecting the terms in $S_{x'}$ and $S_{y'}$, the eigenvalues of $\mathcal{H}_{hf}$ can be expressed as

$$E_{hf}(M, m) = A_{eff}Mm, \tag{3.16}$$

where m is the nuclear quantum number, i.e.

$$I_{z''}|m\rangle = m|m\rangle. \tag{3.17}$$

Further, in eq. (3.14) for A_{eff}, the $\boldsymbol{A}_{\alpha\beta}^2$ are the $\alpha\beta$ $(\alpha, \beta = x, y, z)$ components of the $\boldsymbol{A}^2$ $(= \boldsymbol{A}^T\boldsymbol{A}$; $\boldsymbol{A}^T$ is transposed to matrix $\boldsymbol{A}$) matrix, i.e.

$$\boldsymbol{A}_{\alpha\beta}^2 = \sum_{\alpha'=x,y,z} \boldsymbol{A}_{\alpha'\alpha}\boldsymbol{A}_{\alpha'\beta}. \tag{3.18}$$

[From (3.18) it is noted that $\boldsymbol{A}^2$ is a symmetric tensor $(\boldsymbol{A}_{\alpha\beta}^2 = \boldsymbol{A}_{\beta\alpha}^2)$ while $\boldsymbol{A}$, in general, is not [5].]

It is now clear from eqs. (3.16) and (3.14) that the eigenvalues $E_{hf}(M, m)$ depend only upon the six linearly independent components of the $\boldsymbol{A}^2$ tensor, as given by (3.18), rather than upon the components of the $\boldsymbol{A}^2$ tensor. Thus from the EPR line positions, or ENDOR frequencies, which depend only upon the eigenvalue differences, one can only determine the six components of the symmetrical $\boldsymbol{A}^2$ tensor. Moreover, from (3.14), it is obvious that measurements in three mutually perpendicular planes are necessary to determine *all* the elements of the $\boldsymbol{A}^2$ tensor. Similar to the considerations for the $\boldsymbol{g}^2$ tensor, as given in section 3.1, the eigenvalues of the $\boldsymbol{A}^2$ tensor are the squares of the principal values of the $\boldsymbol{A}$ tensor, while the eigenvectors of the unitary matrix, that diagonalizes the $\boldsymbol{A}^2$ matrix, are the direction cosines of the principal axes of the $\boldsymbol{A}$ tensor with respect to the principal axes of the $\boldsymbol{g}$ tensor.

4. Details of the LSF procedure

The results of section 3 will now be used to describe the LSF procedure as applied to the specific evaluation of the principal values of non-coincident $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors, and the direction cosines of their principal axes from EPR data. (The details of application to the analysis of ENDOR data can be similarly worked out.) It is first noted that for the spin Hamiltonian, as described by eq. (3.1), there will be 2S sets of fine lines corresponding to "allowed" transitions $(\Delta M = \pm 1)$, each set consisting of $(2I + 1)$ hyperfine lines $(\Delta m = 0)$. From section 3, it is

clear that corresponding to the eigenvalues

$$E(M, m) = \mu_B g_{eff} HM + A_{eff} Mm$$

the "allowed" EPR transitions will occur at the magnetic field values ($M \leftrightarrow M - 1$, $m \leftrightarrow m$):

$$H(M, m) = (h\nu - A_{eff} m)/\mu_B g_{eff} . \quad (4.1)$$

The centre of a hyperfine set, consisting of $(2I + 1)$ lines for $m = -I, -(I-1), \ldots, (I-1), I$ then gives the corresponding fine line position

$$H(M) = h\nu/\mu_B g_{eff} , \quad (4.2)$$

i.e. $H(M)$ will be the EPR line position had the hyperfine interaction been turned to zero. These centres of the hyperfine sets can thus be used in a simultaneous fitting in the least-squares procedure as given in section 2 to evaluate rigorously the six independent components of the $\boldsymbol{g}^2$ tensor. The $\boldsymbol{g}^2$ matrix so obtained can then be diagonalized to find the principal values and direction cosines of the $\boldsymbol{g}$ tensor.

In another LSF procedure, using the principal values and direction cosines of the principal axes of the $\boldsymbol{g}$ tensor, already determined above, all the hyperfine line positions in three mutually perpendicular planes can be fitted simultaneously in the LSF procedure and the six independent elements of the $\boldsymbol{A}^2$ tensor can be evaluated rigorously. From the eigenvalues and eigenvectors of the resulting $\boldsymbol{A}^2$ matrix, the principal values of the $\boldsymbol{A}$ tensor, and the direction cosines of its principal axes can be determined.

The recommended steps for the proposed LSF procedure can be summarized as follows:

(i) Fitting simultaneously the centres of the hyperfine sets, for magnetic field orientations in three mutually perpendicular planes, evaluate using the LSF procedure, as described in section 2, the six linearly independent components of the $\boldsymbol{g}^2$ tensor. The required energy-level differences, and their derivatives are to be calculated using the results of section 3.1. The specific expressions are given in Appendix B.

(ii) Diagonalize, on the computer, using a standard subroutine for the diagonalization of real symmetric matrices, the 3×3 $\boldsymbol{g}^2$ matrix as obtained in (i) above. The resulting eigenvalues are the squares of the principal values of the $\boldsymbol{g}$ tensor and the (normalized) eigenvectors are the direction cosines of the principal axes of the $\boldsymbol{g}$ tensor with respect to the coordinate axes (x, y, z) chosen.

(iii) Now fit simultaneously all the hyperfine line positions, as obtained in three mutually perpendicular planes, using the LSF procedure as described in section 2, and evaluate rigorously the six linearly independent components of the $\boldsymbol{A}^2$ matrix, using the required principal values and directions of the $\boldsymbol{g}$ tensor as evaluated in (ii) above. The required energy level differences, and their derivatives, are explicitly given in appendix B. [Note that the magnetic field orientations are to be given with respect to the principal directions of the $\boldsymbol{g}$ tensor, as given by eq. (3.15).]

(iv) Evaluate the eigenvalues and the (normalized) eigenvectors of the 3×3 $\boldsymbol{A}^2$ matrix on the computer in a manner similar to that given in (ii) above. The resulting eigenvalues are the squares of the principal values of the $\boldsymbol{A}$ tensor, while the eigenvectors are the direction cosines of the principal axes of the $\boldsymbol{A}$ tensor (with respect to the principal axes of the $\boldsymbol{g}$ tensor).

Similar steps can be worked out for the analysis of ENDOR data, taking into account the fact that for ENDOR it is the external magnetic field whose intensity is kept fixed, while the radio frequency is varied. However, the expressions of section 2 are completely general, in that they admit of the possibility of varying both the external magnetic field intensity, as well as the frequency.

3. Illustrative example

The illustrative example of the evaluation of principal values and directions of the (non-coincident) $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors, from liquid nitrogen X-band data, corresponding to one of the eight paramagnetic centres of danburite single crystal is presented in this section. These paramagnetic centres are obtained

when a boron atom replaces a silicon atom in any one of the eight SiO_4 tetrahedra in the unit cell. Here the EPR spectra are mainly due to the more abundant (81.2%) ^{11}B isotope which has a spin $I = 3/2$, while the electronic spin of the paramagnetic centre is $S = 1/2$. Thus, for each orientation of the external magnetic field a total of four hyperfine lines ($2I + 1 = 4$) corresponding to one fine line ($2S = 1$) are expected. (For, further details for a full investigation of a single danburite crystal, see ref. 7; the centre used for the present illustration is denoted as I in ref. 7, the y axis is chosen parallel to the a axis of the crystal, while the x axis is in the bc plane, 45° from c to b).

Although a total of 82 lines in various planes were simultaneously fitted (25 lines in each of the zx and zy planes and 32 lines in the xy plane) ten selected line positions in each of the three planes are listed in table I, which also includes the corresponding klystron frequencies.

The initial values of $\boldsymbol{g}^2_{\alpha\beta}$ chosen were:

$$\boldsymbol{g}^2_{\alpha\alpha} = 5.0 \qquad (\alpha = x, y, z),$$
$$\boldsymbol{g}^2_{\alpha\beta} = 0.1 \qquad (\alpha \neq \beta = x, y, z),$$

corresponding to a χ^2 value ($\sigma_i = 1$) of 16.6 GHz^2. The centres of a total of 82 four-line hyperfine sets in the three planes were then fitted simultaneously in the LSF method. After three iterations $\chi^2 = 6 \times 10^{-3}$ GHz^2 and the resulting values are:

$$\boldsymbol{g}^2_{xx} = 4.0350, \qquad \boldsymbol{g}^2_{xy} = \boldsymbol{g}^2_{yx} = -0.0126,$$
$$\boldsymbol{g}^2_{yy} = 4.0158, \qquad \boldsymbol{g}^2_{yz} = \boldsymbol{g}^2_{zy} = -6.0054,$$
$$\boldsymbol{g}^2_{zz} = 4.1878, \qquad \boldsymbol{g}^2_{zx} = \boldsymbol{g}^2_{xz} = -0.0025.$$

The $\boldsymbol{g}^2$ matrix was then diagonalized using the JACOBI method on the computer, the eigenvalues are (the corresponding direction cosines with respect to x, y, z axes are given in brackets):

$$\boldsymbol{g}^2_{x'} = 4.0094 \qquad (0.8962, 0.0333, 0.4423),$$
$$\boldsymbol{g}^2_{y'} = 4.0413 \qquad (-0.4425, -0.0007, 0.8968),$$
$$\boldsymbol{g}^2_{z'} = 4.1880 \qquad (-0.0302, 0.9994, -0.0142).$$

The 82 sets of four hyperfine lines each, were then fitted, using the LSF procedure, to evaluate the elements of the $\boldsymbol{A}^2$ matrix. The initial values chosen were

$$\boldsymbol{A}^2_{\alpha'\alpha'} = 0.0007 \text{ GHz}^2 \qquad (\alpha' = x', y', z'),$$
$$\boldsymbol{A}^2_{\alpha'\beta'} = 0.0 \quad \text{GHz}^2 \qquad (\alpha' \neq \beta'),$$

corresponding to a χ^2 (all $\sigma_i = 1$) value of 0.0170 GHz^2. After two iterations, $\chi^2 = 0.0036$ GHz^2 and the resulting elements are (in GHz^2):

$$\boldsymbol{A}^2_{x'x'} = 0.73 \times 10^{-3}; \quad \boldsymbol{A}^2_{x'y'} = \boldsymbol{A}^2_{y'x'} = 0.36 \times 10^{-4},$$
$$\boldsymbol{A}^2_{y'y'} = 0.81 \times 10^{-3}; \quad \boldsymbol{A}^2_{y'z'} = \boldsymbol{A}^2_{z'y'} = -0.25 \times 10^{-4},$$
$$\boldsymbol{A}^2_{z'z'} = 0.21 \times 10^{-3}; \quad \boldsymbol{A}^2_{z'x'} = \boldsymbol{A}^2_{x'z} = -0.23 \times 10^{-5}.$$

The $\boldsymbol{A}^2$ matrix so obtained was then diagonalized using the JACOBI method. The resulting

Table I
X-band (liquid nitrogen temperature) EPR line positions (in gauss) for some orientations of external magnetic field and the corresponding klystron frequencies

Angle (°)	Line I	Line II	Line III	Line IV
(a) zx plane (klystron frequency = 9.1404 GHz for all lines, z-axis = 0°, x-axis = 90°)				
0	3183	3188	3192	3198
20	3189	3195	3201	3207
40	3203	3210	3218	3226
60	3220	3230	3240	3249
80	3235	3245	3254	3264
90	3237	3247	3257	3266
100	3235	3245	3255	3264
120	3224	3233	3241	3250
140	3207	3214	3221	3227
160	3191	3196	3202	3207
(b) zy plane (klystron frequency = 9.1394 GHz for all lines, z-axis = 0°, y-axis = 90°)				
0	3245	3254	3264	3273
20	3236	3245	3254	3263
40	3216	3223	3231	3240
60	3196	3202	3209	3215
80	3185	3189	3194	3199
90	3183	3188	3193	3198
100	3185	3190	3195	3201
120	3199	3205	3212	3218
140	3220	3228	3236	3243
160	3238	3246	3255	3263
(c) xy plane (klystron frequency = 9.1444 GHz for all lines, x-axis = 0°, y-axis = 90°)				
−78	3243	3253	3262	3272
−58°	3238	3249	3258	3268
−38°	3235	3246	3255	3265
−18°	3234	3246	3255	3265
− 1°	3237	3247	3257	3267
22°	3242	3252	3261	3272
42°	3247	3256	3266	3276
62°	3249	3258	3268	3278
82°	3248	3257	3267	3276
102°	3244	3254	3263	3273

eigenvalues (GHz^2) are (the direction cosines with respect to x', y', z', the principal directions of the **g** tensor are included in brackets):

$$\mathbf{A}_1^2 = 0.82 \times 10^{-3} \quad (0.368, 0.929, -0.039),$$

$$\mathbf{A}_2^2 = 0.72 \times 10^{-3} \quad (-0.930, 0.368, -0.014),$$

$$\mathbf{A}_3^2 = 0.21 \times 10^{-3} \quad (0.002, 0.041, 0.999).$$

6. Concluding remarks

The present paper deals with the procedure of a rigorous evaluation of the principal values of (non-coincident) $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors, as well as their principal axes direction cosines. The important point to realize is that the individual elements of the $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors cannot be evaluated from EPR data since the eigenvalues of the applicable spin Hamiltonian only depend upon the elements of the squares of matrices i.e. of $\boldsymbol{g}^2$ and $\boldsymbol{A}^2$, rather than upon the elements of $\boldsymbol{g}$ and $\boldsymbol{A}$ themselves. Further, it should be noted that, in this paper, while the electronic Zeeman term has been considered exactly, the hyperfine term has been considered only in the zeroth order of approximation. This approximation is valid in practically all cases. However, should further refinement be necessary, the hyperfine terms depending upon $S_{x'}$ and $S_{y'}$ (section 3.2) can be treated, using the standard perturbation theory.

The results of this paper are applicable equally to the analysis of both EPR and ENDOR data.

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Appendix A

Here it is shown that the unitary matrix $U(U^\dagger = U^{-1})$ that diagonalizes the $\boldsymbol{g}$ tensor to the diagonal matrix $\boldsymbol{g}_d = \boldsymbol{U}\boldsymbol{g}\boldsymbol{U}^\dagger$ also diagonalizes the tensor $\boldsymbol{g}^2$ $(=\boldsymbol{g}^T \cdot \boldsymbol{g})$, to the diagonal matrix $\boldsymbol{g}_d^2$. The following steps lead to the required result:

$$\begin{aligned}\boldsymbol{U}\boldsymbol{g}^2\boldsymbol{U}^\dagger &= \boldsymbol{U}\boldsymbol{g}^T\boldsymbol{g}\boldsymbol{U}^\dagger = \boldsymbol{U}\boldsymbol{g}^T\boldsymbol{U}^\dagger\boldsymbol{U}\boldsymbol{g}\boldsymbol{U}^\dagger \\ &= \boldsymbol{U}\boldsymbol{g}^\dagger\boldsymbol{U}^\dagger\boldsymbol{U}\boldsymbol{g}\boldsymbol{U}^\dagger = (\boldsymbol{U}\boldsymbol{g}\boldsymbol{U}^\dagger)^\dagger\boldsymbol{U}\boldsymbol{g}\boldsymbol{U}^\dagger\end{aligned}$$

(Q.E.D.)

In arriving at the above result, the facts that (i) the elements of $\boldsymbol{g}$ are real (i.e. $\boldsymbol{g}^T = \boldsymbol{g}^\dagger$) and (ii) the elements of $\boldsymbol{g}_d$ are real (i.e. $\boldsymbol{g}_d^\dagger = g_d$) have been used.

Appendix B

The expressions for the eigenvalue differences and their derivatives are provided in this appendix.

For the fitting of the centres of the hyperfine sets the eigenvalues can be expressed as

$$E_s(M) = \mu_B g_{eff} H M,$$

where

$$g_{eff} = (l^2\boldsymbol{g}_{xx}^2 + 2lm\boldsymbol{g}_{xy}^2 + m^2\boldsymbol{g}_{yy}^2 + 2ln\boldsymbol{g}_{xz}^2 + n^2\boldsymbol{g}_{zz}^2 + 2mn\boldsymbol{g}_{yz}^2)^{1/2}$$

Then, for the fine transition $M \leftrightarrow M-1$,

$$|\Delta E| = E_s(M) - E_s(M-1) = \mu_B e_{eff} H. \tag{B.1}$$

From (B.1), the first derivatives can be expressed as follows:

$$\frac{\partial|\Delta E|}{\partial \boldsymbol{g}_{\alpha\beta}^2} = \mu_B H(2-\delta_{\alpha\beta})L_\alpha L_\beta / 2g_{eff}, \tag{B.2}$$

where $L_x = l$, $L_y = m$, and $L_z = n$. In (B.2) $\delta_{\alpha\beta}$ is the Kronecker delta, i.e. $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, zero otherwise. Using (B.2) one can express the second derivatives as

$$\frac{\partial^2|\Delta E|}{\partial \boldsymbol{g}_{\alpha\beta}^2 \partial \boldsymbol{g}_{\alpha'\beta'}^2} = -\frac{\mu_B H(2-\delta_{\alpha\beta})(2-\delta_{\alpha'\beta'})}{4g_{eff}^3} L_\alpha L_\beta L_{\alpha'} L_{\beta'}. \tag{B.3}$$

For the fitting of the hyperfine lines in the LSF procedure the required eigenvalues are (section 3.2): $E(M, m) = E_s(M) + E_{hf}(M, m)$, where E_s

does not depend upon the elements of the $\boldsymbol{A}^2_{\alpha\beta}$ tensor. Explicitly (section 3.2),

$$E_{\rm hf}(M, m) = A_{\rm eff} M m ,$$

where

$$A_{\rm eff} = (a_x^2 \boldsymbol{A}^2_{xx} + 2a_x a_y \boldsymbol{A}^2_{xy} + a_y^2 \boldsymbol{A}^2_{yy} + 2a_x a_z \boldsymbol{A}^2_{xz} + a_z^2 \boldsymbol{A}^2_{zz} + 2a_y a_z \boldsymbol{A}^2_{yz})^{1/2} .$$

Then, for the hyperfine transition $M,\ m \leftrightarrow (M-1),\ m$:

$$|\Delta E| = A_{\rm eff} m . \tag{B.4}$$

From (B.4) the first- and second-derivative expressions are:

$$\frac{\partial |\Delta E|}{\partial \boldsymbol{A}^2_{\alpha\beta}} = m(2 - \delta_{\alpha\beta}) c_\alpha c_\beta / 2A_{\rm eff} , \tag{B.5}$$

$$\frac{\partial^2 |\Delta E|}{\partial \boldsymbol{A}^2_{\alpha\beta} \partial \boldsymbol{A}^2_{\alpha'\beta'}} = -m(2 - \delta_{\alpha\beta})(2 - \delta_{\alpha'\beta'}) c_\alpha c_\beta c_{\alpha'} c_{\beta'} / 4A^3_{\rm eff} . \tag{B.6}$$

In (B.5) and (B.6),

$$c_x = g_{x'} l' / g_{\rm eff} ,$$

$$c_y = g_{y'} m' / g_{\rm eff} ,$$

$$c_z = g_{z'} n' / g_{\rm eff} ,$$

where (l', m', n') are the direction cosines of the external magnetic field with respect to the principal axes of the $\boldsymbol{g}$ tensor [eqs. (3.5)] and $g_{x'}$, $g_{y'}$, $g_{z'}$ are the principal values of the $\boldsymbol{g}$ tensor.

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