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Computer Analysis of Electron Paramagnetic Resonance Spectra

Abstract: Algebraic methods that are useful in the reduction of EPR spectra to the magnetic parameters in the phenomenological Hamiltonian are summarized and programs presently available to accomplish the necessary computations are described. Among the topics discussed are (i) the calculation of the spectrum of the complete spin Hamiltonian for single-crystal experiments, with the principal axis system; (ii) the transformation of the Hamiltonian to the magnetic quantization axes, which is convenient for perturbation theory; (iii) the use of iteration methods to determine the parameters by a least-squares technique; (iv) the detailed fitting of EPR spectra of polycrystalline or glassy-state magnetic sites; (v) the correlation methods in the analysis of solution spectra; (vi) a novel integral transformation to improve the resolution; and (vii) the calculation of the dipolar sum for line width studies.

Introduction

Electron paramagnetic resonance is a powerful technique for the study of magnetic properties of solids and has seen extensive use. Some of the systems studied are insulating or semiconducting single crystals doped with transition metal ions, defects and color centers in crystals, triplet states, and free radicals. In general, one is interested in learning the symmetry of the magnetic species, something about its wave function, exchange interactions with neighboring magnetic sites, chemical bonding, nuclear hyperfine interactions and nuclear quadrupole interactions, and, for maser application and low temperature application, the energy levels themselves and the relaxation rates.

In the past most of the analyses have been confined to simple systems; or the analysis was done at the unique crystal directions for which closed expressions were possible; or first- and second-order perturbation theory was used. Currently computers have become available to the point that most physicists and chemists have access to one. Hence more complicated problems can be solved and a more exact answer is readily available. Many times complicated algebraic expressions can be avoided and perturbation theory need not be used. They can, however, conveniently serve to obtain an approximate answer as input for computation. Finally the computer, besides merely being faster than a desk calculator, can be programmed to direct one toward the proper solution.

Many computer programs have been written and used for the determination of spin energy levels, and frequently these are briefly referred to in papers on paramagnetic resonance. The purpose of this paper is (1) to summarize some of the mathematical techniques useful in the calculation of spin energy levels, (2) to list some programs available for the analysis of EPR spectra, and (3) to encourage more complete and accurate spectral analysis in order to extract as much information as possible.

We shall first discuss the spin Hamiltonian and its application to the analysis of single crystals. The simple spin cases will be discussed and then followed by the more complicated cases. The use of the least-squares technique to arrive at the "best fit" for the magnetic parameters will be outlined. The line shape calculation for powder and frozen solution (glassy state) will also be discussed.

The analysis of solution spectra is fairly straightforward but can nevertheless be quite difficult if the number of lines is very large. Here the use of the correlation functions and a simple integral transformation will be illustrated. Finally, lattice sums and exchange effects will be discussed in connection with line shapes.

Spin Hamiltonian

The spin Hamiltonian, derived by Abragam and Pryce,[1,2] has the form

$$\begin{aligned}\mathcal{H} = {}& \beta\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H} + D[S_z^2 - S(S+1)/3] \\ & + E(S_x^2 - S_y^2) + [(a/180) + b][35S_z^4 \\ & - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) \\ & + 3S^2(S+1)^2] + (a/48)(S_+^4 + S_-^4) + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} \\ & + Q[I_z^2 - I(I+1)/3]. \qquad (1)\end{aligned}$$

Here the first term is the Zeeman term, with **g** the gyromagnetic tensor which may contain an orbital contribution to the magnetism. The spin operator S may be the true spin operator or an effective spin operator defined for the lowest level resulting from the splitting of an orbitally degenerate ground state. Only when one relates the results to the physics of the problem will the difference between effective and true spins be apparent. The next terms are the fine structure terms and are present only when the spin $S > 1/2$; the terms in a and b appear only for $S \geq 2$, such as the S-state ions. The last two terms represent the hyperfine interaction and the nuclear quadrupole interaction, respectively. We have neglected the nuclear Zeeman terms, which give only very small contributions, and the exchange terms, which will be briefly discussed later.

According to Koster and Statz[3a] and Bleaney[3b] further terms linear in the Zeeman operator with odd powers of the spin operators are allowed by symmetry when $S \geq 3/2$; these have only rarely been required and will not be included below. In addition, Griffith[4] shows that for an even number of electrons, a ground doublet state may require a zero-field splitting term of the operator form GS_x. Such a term may be derived from (1) for $S = 1$ or 2, if $D < 0$ and if only the lowest pair of states is observed. We shall therefore not discuss this further. Finally, in the rare earth ions J is usually a good quantum number and the spin Hamiltonian is written in terms of J.

In order to determine the eigenvalues of the Hamiltonian (Eq. (1)) it is necessary to evaluate the matrix elements and then diagonalize the matrix. Two convenient directions of quantization are usually used: one is the principal axis system of the g-tensor and the other is closely related to magnetic field direction. Naturally these are constrained to give the same spectra by a unitary transformation, the rotational matrices[5] $D^j(R)$. We give both formulations, which are based on the familiar properties of angular momentum:[6]

$$\begin{aligned} S^2\,|S, M> &= S(S+1)\,|S, M> \\ S_z\,|S, M> &= M\,|S, M> \qquad (2) \\ S_\pm\,|S, M> &= \sqrt{S(S+1) - M(M\pm 1)}\,|S, M\pm 1> \\ S_\pm &= S_x \pm iS_y \end{aligned}$$

The matrix elements of the Hamiltonian (1) in the g-tensor axis system can readily be written. All the elements follow directly from Eq. (2), except those involving the magnetic field. The Hamiltonian for these terms is

$$\begin{aligned}\mathcal{H} = {}& \beta g_{zz}S_zH\cos\theta + \beta g_{xx}S_xH\sin\theta\cos\phi \\ & + \beta g_{yy}S_yH\sin\theta\sin\phi, \qquad (3)\end{aligned}$$

where θ and ϕ are the conventional polar angles between the g-tensor axes and the magnetic field direction. It has been assumed that the principal axes of the fine structure, hyperfine structure, quadrupole moment, and g-tensor are all the same. In general, of course, these axis systems may differ from each other and from the crystallographic axes.

Bleaney[7] transformed the Hamiltonian for the axial case to the magnetic axis and then applied second-order perturbation theory to determine the eigenvalues. The advantage of this technique is that the angular dependences of the various terms are given in a fairly simple way and only a few small second-order corrections need be applied in many cases. This technique is quite useful and has been utilized in the analyses of most reported EPR spectra of single crystals. Low[8] has indicated a derivation of Bleaney's results and Weger and Low[8] have extended the perturbation result to include the $(S_x^2 - S_y^2)$ term. The perturbation theory is accurate when the Zeeman energy dominates the fine structure or when the magnetic field is close to one of the principal axes. The largest errors occur for $\theta \approx 45°$ and are of the order of $(D/8g\beta H)^3$. Much of the data in the literature, however, was derived from measurements along the principal axes only. Also, if the Hamiltonian consists of the Zeeman energy alone, the procedures outlined below are unnecessary, since the principal values and directions of the g-tensor may be derived from rotation data about any three mutually orthogonal axes.[9]

Since only the perturbation results are given we shall show the transformed Hamiltonian from which these perturbations can be readily verified. When a computer is used it is naturally convenient to enter all the elements and obtain an exact solution. We shall treat the various terms successively.

• *Zeeman terms*

The Zeeman part of the Hamiltonian in matrix notation can be written as

$$\mathcal{H} = \beta\mathbf{S}^\dagger\mathbf{g}\mathbf{H}, \qquad (4)$$

where $\mathbf{S}^\dagger$ is the adjoint of S and the principal directions of

g define the axes. It is now convenient to write S and H as

$$\mathrm{S} = \begin{bmatrix} S_{+1} \\ S_0 \\ S_{-1} \end{bmatrix} \quad \text{and} \quad \mathrm{H} = \begin{bmatrix} H_{+1} \\ H_0 \\ H_{-1} \end{bmatrix} \tag{5}$$

in order to conform to the rotation matrices

$$S_{\pm 1} = \mp S_{\pm}/\sqrt{2} \tag{6a}$$

$$H_{\pm 1} = \mp H_{\pm}/\sqrt{2}. \tag{6b}$$

The **g**-tensor in Eq. (4) has the form

$$\mathbf{g} = \begin{bmatrix} g_{\perp} & 0 & -g' \\ 0 & g_{\parallel} & 0 \\ -g' & 0 & g_{\perp} \end{bmatrix}, \tag{7}$$

where

$$g_{\perp} = \tfrac{1}{2}(g_{xx} + g_{yy})$$

$$g' = \tfrac{1}{2}(g_{xx} - g_{yy})$$

$$g_{\parallel} = g_{zz}.$$

Now an irreducible tensor transforms according to the relation[5]

$$T_{\nu}^{\prime(i)} = \sum D_{\mu\nu}^{i}(\alpha\beta\gamma)T_{\mu}^{(i)} \tag{8}$$

which is conveniently written in terms of the **M** matrix defined by Rose[6]

$$\begin{aligned} \mathbf{M} &= \tilde{\mathbf{D}} \\ \mathbf{T}' &= \mathbf{MT}, \end{aligned} \tag{9}$$

where

$$\mathbf{M}(\rho, \sigma) = \begin{bmatrix} e^{-i\rho}(1+\cos\sigma)/2 & \sin\sigma/\sqrt{2} & e^{i\rho}(1-\cos\sigma)/2 \\ -e^{-i\rho}\sin\sigma/\sqrt{2} & \cos\sigma & e^{i\rho}\sin\sigma/\sqrt{2} \\ e^{-i\rho}(1-\cos\sigma)/2 & -\sin\sigma/\sqrt{2} & e^{i\rho}(1+\cos\sigma)/2 \end{bmatrix}. \tag{10}$$

Then we have the transformation

$$\mathcal{H} = \beta \mathbf{S}^{\dagger}\mathbf{g}\mathbf{H} = \beta \mathbf{S}^{\dagger}\mathbf{M}^{\dagger}(\rho, \sigma)\mathbf{M}(\rho, \sigma)\mathbf{g}\mathbf{M}^{\dagger}(\theta, \phi)\mathbf{M}(\theta, \phi)\mathbf{H}, \tag{11}$$

$$\mathrm{H}' = \mathbf{M}(\theta, \phi)\mathrm{H} = \begin{bmatrix} 0 \\ H_0 \\ 0 \end{bmatrix} \quad \text{and,} \quad \mathrm{S}' = \mathbf{M}(\rho, \sigma)\mathrm{S}. \tag{12}$$

Here θ and ϕ are Euler angles between the principal directions of **g** and the magnetic field; ρ and σ are chosen to set the coefficients of $S'_{\pm 1}$ in (11) to zero and define the convenient spin quantization direction.

$$\begin{aligned} g_{\perp} &= (g_{xx}^2 \cos^2\phi + g_{yy}^2 \sin^2\phi)^{1/2} \\ g &= (g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2} \\ \cos\rho &= g_{xx}\cos\phi/g_{\perp} \qquad \sin\rho = g_{yy}\sin\phi/g_{\perp} \\ \cos\sigma &= g_{\parallel}\cos\theta/g \qquad \sin\sigma = g_{\perp}\sin\theta/g \end{aligned} \tag{13}$$

and

$$\mathcal{H} = g\beta S'_z H_0. \tag{14}$$

- *Fine structure terms*

The fine structure terms are given in matrix notation as

$$\mathcal{H}_{FS} = \mathbf{S}^{\dagger}\mathbf{D}\mathbf{S}, \tag{15}$$

where the tensor **D** is

$$\begin{bmatrix} -D/3 & 0 & -E \\ 0 & 2D/3 & 0 \\ -E & 0 & -D/3 \end{bmatrix}. \tag{16}$$

Using the same transformation, $\mathbf{M}(\rho, \sigma)$, we obtain the following Hamiltonian:

$$\begin{aligned} \mathcal{H}_{FS} = \{ & D[3g_{\parallel}^2 \cos^2\theta/g^2 - 1]/2 \\ & + 3E[(g_{xx}^2 \cos^2\phi - g_{yy}^2 \sin^2\phi) \\ & \cdot(\sin^2\theta/g^2)]/2\}\{S_z'^2 - S(S+1)/3\} \\ & + \{-D + E(g_{xx}^2 \cos^2\phi - g_{yy}^2 \sin^2\phi)/g_{\perp}^2\} \\ & \cdot(g_{\parallel}g_{\perp}\cos\theta\sin\theta/2g^2) \\ & \cdot\{S'_-S'_z + S'_zS'_- + S'_+S'_z + S'_zS'_+\} \\ & + iEg_{xx}g_{yy}\sin\phi\cos\phi\sin\theta\{S'_+S'_z + S'_zS'_+ \\ & - S'_-S'_z - S'_zS'_-\}/gg_{\perp} + \{(Dg_{\perp}^2 \sin^2\theta/4g^2) \\ & + E(g_{xx}^2 \cos^2\phi - g_{yy}^2 \sin^2\phi) \\ & \cdot(1 + g_{\parallel}^2\cos^2\theta/g^2)/4g_{\perp}^2\}\{S_-'^2 + S_+'^2\} \\ & + iEg_{xx}g_{yy}\cos\phi\sin\phi g_{\parallel}\cos\theta/g_{\perp}^2 g\{S_+'^2 - S_-'^2\} \end{aligned} \tag{17}$$

- *Hyperfine structure terms*

The hyperfine terms follow in a similar manner, except that we must define a new transformation $\mathrm{M}(\psi, \chi)$ which relates to the hyperfine interaction axis:

$$\mathcal{H}_{hfs} = \mathbf{S}^{\dagger}\mathbf{A}\mathbf{I} = A_{zz}S_zI_z + A_{xx}S_xI_x + A_{yy}S_yI_y \tag{18}$$

and

$$\mathbf{A} = \begin{bmatrix} A_{\perp} & 0 & -A' \\ 0 & A_{\parallel} & 0 \\ -A' & 0 & A_{\perp} \end{bmatrix} \qquad \begin{aligned} A_{\parallel} &= A_{zz} \\ A_{\perp} &= \tfrac{1}{2}(A_{xx} + A_{yy}) \\ A' &= \tfrac{1}{2}(A_{xx} - A_{yy}). \end{aligned} \tag{19}$$

By setting the A'_{01} (and A'_{0-1}) element to zero we arrive at the well-known first-order perturbation energy

$$\mathrm{E}_{\mathrm{hfs}} = KMm, \tag{20}$$

where

$$K = (A_{\parallel}^2 g_{\parallel}^2 \cos^2\theta + B^2 g_{\perp}^2 \sin^2\theta)^{1/2}/g \tag{21a}$$

$$B = (A_{xx}^2 g_{xx}^2 \cos^2\phi + A_{yy}^2 g_{yy}^2 \sin^2\phi)^{1/2}/g_{\perp}, \tag{21b}$$

$$\cos\psi = A_{\parallel} g_{\parallel} \cos\theta/Kg \qquad \sin\psi = Bg_{\perp}\sin\theta/Kg$$

$$\cos\chi = A_{xx}g_{xx}\cos\phi/Bg_{\perp} \quad \sin\chi = A_{yy}g_{yy}\sin\phi/Bg_{\perp}.$$

The transformed Hamiltonian is then

$$\begin{aligned}\mathcal{H}_{hfs} = {} & KS'_zI'_z + p(S'_-I'_+ + S'_+I'_-)/2 \\ & + ir(S'_-I'_+ - S'_+I'_-)/2 - q(S'_-I'_- + S'_+I'_+)/2 \\ & + ir(S'_-I'_- - S'_+I'_+)/2 - tI'_z(S'_+ + S'_-)/\sqrt{2},\end{aligned} \tag{22}$$

where

$$p = (A_{xx}A_{yy}/2B) + (A_{zz}A_{xx}/2K)$$

$$\begin{aligned} r = {} & A_{zz}g_{xx}g_{yy}g_{zz}\cos\phi\sin\phi\cos\theta \\ & \cdot(A_{yy}^2 - A_{xx}^2)/(2BKg_{\perp}^2 g)\end{aligned}$$

$$q = (A_{xx}A_{yy}/2B) - (A_{zz}A_{xx}/2K)$$

$$t = g_{\parallel}g_{\perp}\cos\theta\sin\theta(A_{zz}^2 - B^2)/(\sqrt{2}Kg^2).$$

• *Quadrupole terms*

And finally the quadrupole terms of the Hamiltonian are

$$\mathcal{H}_{eqQ} = \mathbf{I}^{\dagger}\mathbf{Q}\mathbf{I}, \tag{23}$$

where

$$\mathbf{Q} = \begin{bmatrix} -Q/3 & 0 & 0 \\ 0 & 2Q/3 & 0 \\ 0 & 0 & -Q/3 \end{bmatrix}, \tag{24}$$

and the transformed Hamiltonian is

$$\begin{aligned}\mathcal{H}_{eqQ} = {} & \tfrac{1}{2}Q[3A_{\parallel}^2 g_{\parallel}^2\cos^2\theta/(K^2g^2) - 1] \\ & \cdot[I_z'^2 - I(I+1)/3] \\ & - Q[A_{zz}Bg_{\parallel}g_{\perp}\cos\theta\sin\theta/(2K^2g^2)] \\ & \cdot(I'_+I'_z + I'_zI'_+ + I'_-I'_z + I'_zI'_-) \\ & + Q[B^2g_{\perp}^2\sin^2\theta/(4K^2g^2)](I_-'^2 + I_+'^2).\end{aligned} \tag{25}$$

• *Calculations for single crystals*

Where these various terms of the Hamiltonian are combined and perturbation theory is applied we arrive at Bleaney's result[7,8] and Weger and Low's result[9] for the axial and rhombic cases, respectively. In some instances, perturbation theory is inadequate; an extreme example, for which the perturbation theory would not be used, is provided by the much-studied resonance spectrum of ruby, for which the zero-field splitting between the levels $S_z = \pm 3/2$ and $S_z = \pm 1/2$ (0.76 cm^{-1}) corresponds to K-band microwave radiation. Schulz - du Bois[10] illustrates how for irradiation at 9.3 kMc/sec, the transition $1/2 \leftrightarrow -1/2$ occurs twice, once for low magnetic field and once for high magnetic field. The perturbation result, however, has the transition frequency linear in the magnetic field and provides for only a single resonance. With a computer, it is easy to include all the terms of the Hamiltonian and the formulation in terms of the principal axes (Eqs. (1), (2), and (3)) or in terms of the magnetic axes (Eqs. (2), (13), (14), (17), (22), and (25)) can be used.

A number of calculations for ruby (Cr^{+++}:$\mathrm{Al_2O_3}$) have been done for maser application. Schulz - du Bois[10] used the magnetic axis representation for the axial case with no hyperfine terms. The effect of the anisotropy in the **g**-tensor on the fine structure terms was, however, neglected. Stahl-Brada and Low[11] used the principal axis representation for the $S = 3/2$ case and present tables of eigenvalues and matrix elements of S_z^2 and S_z^2 for intensity calculations at various selected values of the fine structure terms. Chang and Siegmann[12] have an extensive set of tables for ruby. Fox and Swalen[13] have written a program to solve for the eigenvalues, eigenvectors, and transition moments for the $S = 3/2$ case with the magnetic field representation. In addition a provision is provided for a "best fit" to experimental data. This point will be discussed below. Gladney[14] has written a general program for the cases from $S = 1/2$ to $S = 5/2$ with no hfs terms. He used the principal axis representation and treated the rhombic case. Gerritsen and Sabisky[15] report a program for the $S = 2$ case in which the energy levels are calculated.

From, Dorain, and Kikuchi[16] recently report the use of computer programs for $S = 3/2$ which adjust the values of g, D, E, A, and the parameters for the hfs from ligand atoms to fit the observed magnetic fields measured at unique crystal directions. They then calculated the various resonances as a function of the angles.

No doubt there are many more programs written to determine the eigenvalues and eigenvectors. There are four additional points worth mentioning:

1) In the usual EPR experiment one varies the magnetic field strength and keeps the frequency constant. Hence the difference in eigenvalues as a function of magnetic field must be formed which corresponds to the microwave frequency. In the programs of Fox and Swalen[13] and of Gladney[14], a technique involving Newton's method is used. The derivative $d\nu/dH$ is calculated by differentials for small displacements.

$$H^{(n+1)} = H^{(n)} + (\nu_0 - \nu^{(n)})/(d\nu/dH)^{(n)}. \tag{26}$$

The $n + 1^{\text{st}}$ value of magnetic field can be calculated from the n^{th} value, the microwave frequency (ν_0), the eigenvalue difference ($\nu^{(n)}$), and the derivative of the eigenvalue difference with respect to magnetic field. This process is iterated until convergence, which is very fast for pairs of energy levels that are almost linear. Because of crossing situations or large curvature various magnetic fields should be used as starting points for the iteration in order to ensure that all the resonance conditions between a pair of levels are calculated. Occasionally an oscillation occurs where two levels approach a resonance condition and then are deflected away by some interaction. In our experience convergence occurs within ten iterations or not at all. A closer investigation of the eigenvalues can show if oscillation is occurring.

2) A "best fit" of experimental values can be found very conveniently by the computer and has been incorporated. The magnetic field for resonance depends on the frequency, crystal angles, and the various magnetic parameters to be determined. By calculating the derivatives of the magnetic field with respect to each magnetic parameter, a set of linear equations can be written—one for each transition observed at each different set of angles. By a least-squares technique, a set of corrections to the magnetic parameters can be determined and this process repeated until the sum of residuals squared is a minimum.

$$\frac{\partial H^i}{\partial x_1}\,\Delta x_1 + \frac{\partial H^i}{\partial x_2}\,\Delta x_2 \cdots \frac{\partial H^i}{\partial x_n}\,\Delta x_n = (H^i_{\text{obs}} - H^i_{\text{calc}}), \tag{27}$$

$i = 1$ to m, where m is the number of transitions observed.

3) In the case of rhombic symmetry in either representation the terms are complex. The complex eigenvector problem,

$$\mathbf{C}\mathbf{x} = \lambda\mathbf{x},$$

$$\text{where}\quad \mathbf{C} = \mathbf{A} + i\mathbf{B} \qquad\qquad (28)$$
$$\text{and}\quad \mathbf{x} = \boldsymbol{\mu} + i\boldsymbol{\nu},$$

is equivalent to the simultaneous real eigenvector problems,

$$\mathbf{A}\boldsymbol{\mu} - \mathbf{B}\boldsymbol{\nu} = \lambda\boldsymbol{\mu} \quad \text{and} \tag{29}$$

$$\mathbf{B}\boldsymbol{\mu} + \mathbf{A}\boldsymbol{\nu} = \lambda\boldsymbol{\nu}, \tag{30}$$

whose solutions occur in degenerate pairs, $\begin{pmatrix}\boldsymbol{\mu}\\ \boldsymbol{\nu}\end{pmatrix}$ and $\begin{pmatrix}\boldsymbol{\nu}\\ -\boldsymbol{\mu}\end{pmatrix}$, so that the diagonalization of a Hermitian $n \times n$ matrix may be accomplished by selecting half the eigenvalues and vectors of a related $2n \times 2n$ real symmetric matrix.

4) The intensities of the transitions are given by:

$$W_{ij} = |\langle i|\mathcal{H}'|j\rangle|^2 f(\nu)/h^2, \tag{31}$$

where $\langle i|\mathcal{H}'|j\rangle$ is the matrix element of the perturbation from the microwave field, H_1, inducing the transition from i to j. The term $f(\nu)$ is the line shape function normalized so the integral is equal to unity. Equation (31) can be written more conveniently:

$$W_{ij} = \left(\frac{g\beta H_1}{2h}\right)^2 f(\nu)|\langle i|S_k|j\rangle|^2, \tag{32}$$

where S_k is the component of spin along the space-fixed axis of the microwave field and is a linear combination of the components along the principal axes:

$$S_k = aS_x + bS_y + cS_z; \tag{33}$$

here a, b, and c are the direction cosines. The actual value depends on the crystal orientation and the direction of H_1. Frequently the matrix elements of $|\langle j|S_x'|i\rangle|^2$ are calculated and assumed to be equivalent to $|\langle j|S_y'|i\rangle|^2$. This could be incorrect and Eq. (33) should be used. In the principal axis system, the perturbation $\mathcal{H}'$ in the Zeeman coordinate system must be transformed to the principal axis system by the inverse of **M** (Eq. (10)). In either case, however, for orthorhombic symmetry an additional angle is necessary to denote the rotation about the new z axis, i.e., the magnetic field axis, giving the orientation of the x' and y' axes. For example, if H_1 is perpendicular to z', then

$$S_k^2 = \cos^2\gamma S_x'^2 + \sin^2\gamma S_y'^2. \tag{34}$$

Polycrystalline samples

The EPR spectrum of a polycrystalline or glassy-state sample involves a spatial average over different magnetic site orientations. The determination of magnetic parameters has been discussed by a number of authors, whose usual method requires some assumption about the line shape of a single magnetic site. Considerable information is available from these spectra; detailed computation, to plot estimates of the spectrum from assumed parameters, has been useful, particularly in the more complex cases. However, Weil and Hecht[17] point out that if the line width of a single site is small compared to differences in $H_\parallel$ and $H_\perp$, most of the desired information, including line shape, is available near $\cos^2\theta = 1$ in the form of absorption envelopes in the normal first derivative trace.

The simplest case is that of axial anisotropy in **g** without fine structure or hyperfine structure terms. Bleaney[18] and Sands[19] considered this situation and assumed a delta function for the line shape of each crystallite; the absorption is

$$I(H) \propto \int f(H - H')\sin\theta\, d\theta, \tag{35}$$

where H', the line center, depends on the orientation of the magnetic site. For f as a delta function

$$I(H) \propto \left.\frac{d(\cos\theta)}{dH'}\right|_{H=H'}, \tag{36}$$

where H lies between $H_\parallel$ and $H_\perp$.
Since

$$h\nu = (g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}\beta H, \tag{37}$$

then

$$I(H) \propto H^{-2}(H_\perp^2 - H^2)^{-1/2}, \tag{38}$$

where $H_\perp = h\nu/g_\perp\beta$. This crude procedure gives only an approximate relation to the expected line shape and can be improved. Searl, Smith, and Wyard[20]; Chirkhov and Kokin[21]; and Ibers and Swalen[22] have included a Lorentzian line shape for $f(H - H')$ and a variation in the transition probability according to Bleaney.[23] The absorption curves for various Lorentzian line widths was given in Ref. 22 and is shown in Fig. 1. Equation (36) represents the limiting case. If one combines the algorithm for the expected absorption spectrum as a function of a number of parameters with the "best fit" procedure described for single-crystal spectra, an iterative program has been devised to improve the estimated parameterization.[22,24] The only change from the previous procedure is that the fit is to a large number of observed intensities at discrete intervals of field rather than to a set of resonance fields at specified angles. As examples there are shown, in Figs. 2 and 3, results for powder samples of K_3CrO_8 and CuF_2.

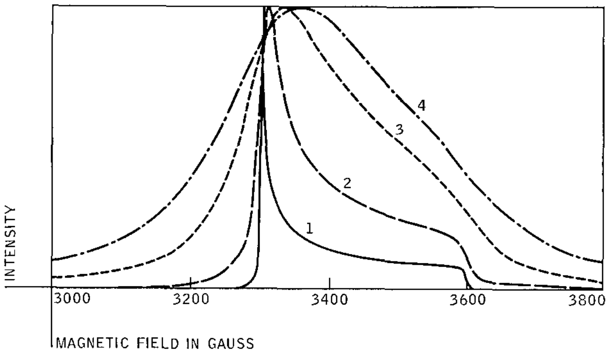
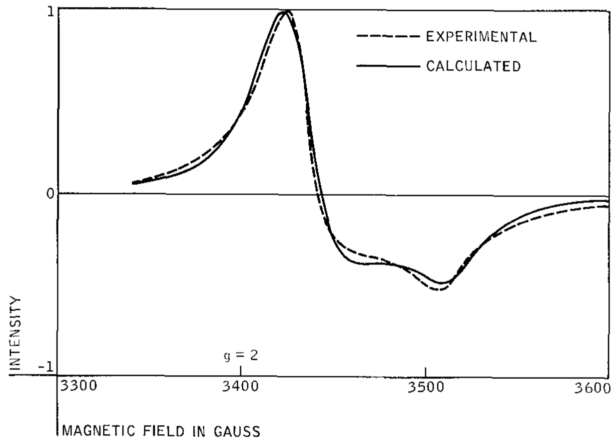


Figure 1 **Calculated EPR line shapes for polycrystalline samples.** *Lorentzian linewidths: (1) 1 G, (2) 10 G, (3) 50 G, (4) 100 G; $H_\parallel$ = 3600 G, $H_\perp$ = 3300 G. (From Ref. 22, Fig. 1).*

Figure 2 **EPR signal from K_3CrO_8 at 20°C.** *$H_\parallel$ = 3512.1 G, $H_\perp$ = 3429.8 G, b = 23.5. (From Ref. 22, Fig. 3).*



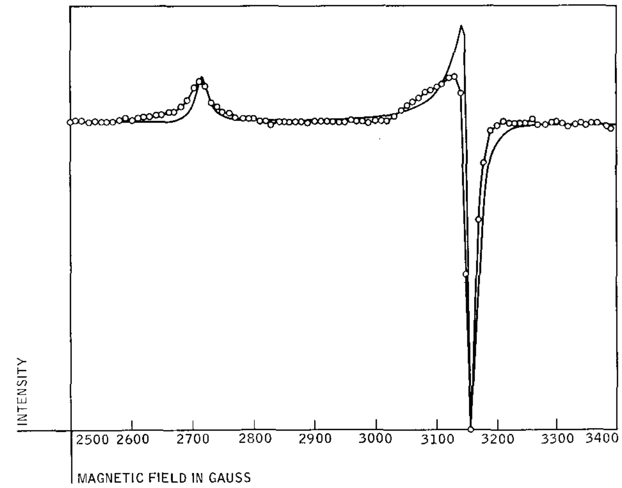


Figure 3 **Powder EPR Spectrum of CuF_2:**
o—o—o—o—o *Experimental spectrum*
———— *Calculated spectrum.*
$H_\parallel$ = 2710 G; $H_\perp$ = 3154 G; W = 13.0 G.

The extension to complete anisotropy ($g_x \neq g_y \neq g_z$) is possible, but a numerical integration would no doubt be necessary. Kneubühl[25] has treated this problem using the delta-function approximation. As far as we know no computer program has been written for this situation; however, it would be straightforward by computing H for various values of θ and ϕ and then numerically integrating Eq. (35) converted to a double integral by adding the ϕ dependence.

$$I(H) \propto \int_0^{2\pi} d\phi \int_0^{\pi} K(\theta, \phi, \psi) f(H - H'(\theta, \phi)) \cdot \sin\theta \, d\theta \tag{39}$$

Here K is the transition probability which depends on θ and ϕ and ψ, the angle between the molecular axis and the oscillating magnetic field H_1. Essentially one generates a set of values of magnetic field for each value of θ and ϕ and the envelope gives the line shape.

The inclusion of hyperfine structure terms was done by

Sands,[19] Blinder,[26] Neiman and Kivelson,[27] and Gersmann and Swalen.[28] A delta-function line shape was used in each case. In addition, Blinder used a Gaussian function but restricted the problem to an isotropic g value. For the work in Ref. 28 a simple computer program was written and used, with the Hamiltonian for an axial case with hfs

$$\mathcal{H} = g_{\|}\beta S_z H_z + g_{\perp}\beta(S_x H_x + S_y H_y) + A_{\|} S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (40)$$

or transformed to the magnetic field direction, in first order,

$$E = g\beta H_0 M + KMm. \quad (41)$$

Since g and K depend on the polar angle, θ, it is relatively straightforward to calculate the magnetic field as a function of θ. With the delta-function approximation, Eq. (36) will lead to an intensity calculation.

The current interest and research in triplet state molecules started with the single-crystal work on naphthalene by Hutchison and Mangum.[31] Van der Waals and de Groot[30] then observed the $\Delta m = \pm 2$ transitions in the glassy (random orientation) state and Kottis and Lefebvre[31] wrote a computer program which evaluated the line shape by simulating the delta function by a Gaussian function. Although the $\Delta m = \pm 1$ transitions are hard to detect because they are spread over a large magnetic field, the $\Delta m = \pm 2$ are much less angle-dependent. Also, because the Zeeman terms and the fine structure terms are of the same order of magnitude there is sufficient intensity to be observed. Yager, Wasserman and Cramer[32] have, however, observed also the $\Delta m = \pm 1$ transitions with the triplet state molecules randomly oriented and have pointed out that the edges of the line will be observable in a derivative recording. Kottis and Lefebvre[33] have recently extended their earlier work on triplet state molecules to include the $\Delta m = \pm 1$ transitions and discuss the analysis of these spectra in extensive qualitative and quantitative detail. The computer program by Kottis and Lefebvre[31,33] to calculate the line shape diagonalizes the 3×3 matrix, including the Zeeman terms and the fine structure terms in the crystal axis system by expanding the secular determinant into a cubic equation. The eigenvalues are then the roots of this equation which is solved by conventional methods. Although the reduction to a cubic equation is a good method, here it suffers from the disadvantage that it is difficult to extend to larger cases, e.g., the inclusion of hfs. We, therefore, recommend the calculation of magnetic fields and the transition probabilities for various angles—the grid being set by the desired accuracy—and then a numerical integration of Eq. (39) with a Lorentzian or Gaussian line shape fit to reproduce the whole line shape. Snyder and Kornegay[32] have recently described a program performing this calculation. By this method, all the determinable interaction terms can be included and matrix techniques can be used.

The extension of these techniques to higher spin cases is reasonably straightforward. Singer[34] considered the line shape for $1/2 \leftarrow -1/2$ transition in the $S = 3/2$ case with $D \gg g\beta H$. Van Reijen and Swalen[35] considered the other approximate case, i.e., $D \ll g\beta H$. Computer techniques with the methods described above, and the matrix techniques described in the section on single-crystal work, however, could be used quite effectively to calculate and fit line shapes in order to determine the magnetic parameters. Van Reijen has very recently discussed the variation of spectra of polycrystalline samples for various values of D.

Lefebvre[36] describes a program for the calculation of the EPR line shapes for glassy-state radicals with an anisotropy in g and hyperfine structure from nuclei with spin 1/2. This program has recently been extended to include hyperfine structure from nuclei of spin 1 and 3/2. Young[37] described two programs which evaluate Gaussian or Lorentzian lines to fit EPR spectra. These programs require the various positions of the lines to be entered.

Free radicals in liquids

A large class of organic free radicals in liquid solution may be described by the spin Hamiltonian of (1), usually with $S = 1/2$ and without zero-field or nuclear electric quadrupolar terms. The effective Hamiltonian is further simplified by rapid molecular tumbling which averages the angular-dependent terms of (22). It may be written as

$$\mathcal{H} = g\beta H S_z + \sum_N A_N S_z I_{Nz} + \tfrac{1}{2} \sum_N A_N(S_+ I_{N-} + S_- I_{N+}), \quad (42)$$

where the summation is over magnetic nuclei. Usually the Zeeman term is dominant and electronic and nuclear spins are separately quantized (Paschen-Back effect). Then the first two terms are diagonal in this representation, and the final term contributes second-order corrections which will be ignored below. In fact, most calculations to date have not included second-order shifts in line positions or alternations in line intensities.[38] Goldsborough and Koehler,[39] however, wrote and used a program which diagonalized for $S = 1/2$ the complete equation (42) augmented by a nuclear Zeeman term; this study does not make the usually valid assumption that the hyperfine interaction is relatively small.

At constant frequency, for $S = 1/2$, there appear lines at fields given by

$$H = H_0 + \sum_N h_N I_{Nz}, \quad (43)$$

where $h_N = A_N/g\beta$.

Even for fairly simple molecules the spectrum (43) can be quite complex, so that a number of numerical techniques to aid the assignment of these spectra have been investigated. Since the line position and intensity relationships implied by (43) are straightforward, such EPR spectra have been used to study general methods for assigning spectra in which there were many more structural components than parameters to be assigned.

For very simple spectra of irradiated organic compounds Marquardt, Bennett, and Burrell[40] have applied a least-squares analysis to fit theoretical spectra of Gaussian lines; to test, using statistical criteria of goodness-of-fit, the significance of extra freedom in the choice of hyperfine parameters; and to refine the parameters for spectra with limited resolution. This technique seems to be limited to cases of relatively few experimental parameters. Programs accomplishing exactly the same type of fit have been described in studies on ultraviolet spectroscopy.[41] The procedure is almost identical to that described for polycrystalline samples.

Two other classes of numerical techniques have been found to aid the decomposition of complex spectra—correlation methods and integral transformation.[42,43] The numerical problem to which these have been addressed is quite different from the problems discussed above for single-crystal and polycrystalline spectra. In the latter cases, generally the assignment of the spectrum is known or can be easily deduced as one of a small number of alternatives. For liquid solutions of free radicals with hyperfine interactions, it is often difficult to choose the parameters h_i to provide a complete assignment of the spectra. The problem studied[42,43] was to find numerical procedures for determining a set of h_i which qualitatively reproduces the spectrum in question, assuming the availability of a model of the spectrum relating the positions and intensities of the lines to the values of the unknown parameters. Of course, such a model is not always available; however, it should be noticed that the techniques studied generally depend only on a few of the features of the model. In (43), absorption lines are spaced at intervals which are algebraic sums of the parameters h_i. The parameters appear as periodic distances along the magnetic field axis. Where $I(H)$ is the observed intensity, the autocorrelation integral

$$A(h) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} I(H-h)I(H)\,dH \tag{44}$$

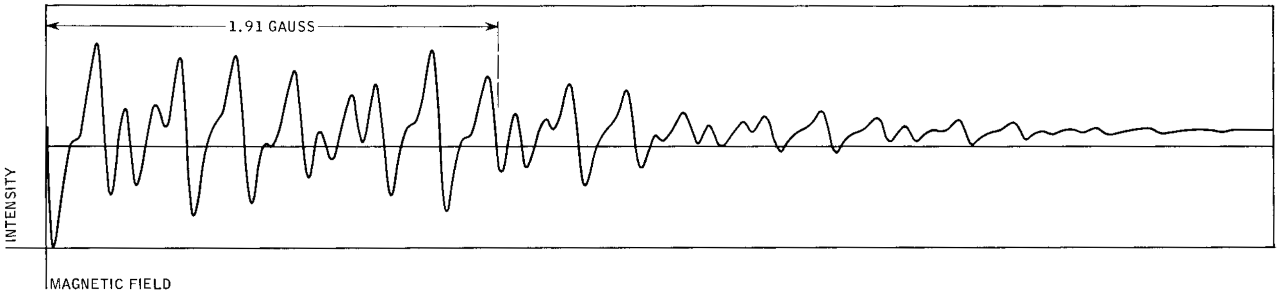
has its local maxima at periodic distances of $I(H)$, so that from a plot of $A(h)$, algebraic sums of the hyperfine parameters may be quickly discovered. The relative intensities of the peaks are a partial guide for removing from further consideration algebraic sums of parameters (e.g., $h_1+h_2-h_3$).

Closely related to autocorrelation is the more powerful technique of crosscorrelation; with whatever current information about a spectrum is available, a partial model $I_t(H;\,h_i')$ with undetermined parameters h_i', may be constructed; when the undetermined h_i' take the values h_i, the cross-correlation

$$C(h_i') = \int_{-\infty}^{\infty} I_{\text{expt}}(H)I_t(H;\,h_i')\,dH \tag{45}$$

has a local maximum. Since the method works when some of the h_i' are set to zero, successive searches with fixed values of previously discovered parameters are possible. Typical results are illustrated by calculations on a sample spectrum that corresponds to a hypothetical radical with interactions from three groups of four equivalent protons each; the spectrum, illustrated in Fig. 4, has parameters $h_1 = 1.91$, $h_2 = 0.67$, $h_3 = 0.27$. The line at $(n_1h_1 + n_2h_2 + n_3h_3)$ has intensity proportional to the coefficient of $h_1^{n_1}h_2^{n_2}h_3^{n_3}$ in $\Pi_i(h_i^{-1} + h_i)^4$. In Fig. 5, the cross-correlation graphs are given: the test function I_t used to calculate 5(a) has five lines, positioned as described in the previous sentence, with $h_2 = h_3 = 0$ and h_1 as the independent variable; that used for the correlation 5(b) has 25 lines, with $h_2 = 1.92$, $h_3 = 0$ and variable h_1; finally, the test function for 5(c) has 125 lines, which follow the prescribed algorithm, with $h_2 = 1.92$, $h_3 = 0.67$ and variable h_1. We find that if the structure of the varying part of the test pattern is qualitatively similar to some part of

Figure 4 **A synthetic ESR spectrum, used to test correlation schemes.**



the spectrum being analyzed, it is not very important how extensive the test pattern is. The most prominent peaks of Fig. 5 correspond to coupling constants h_i of the spectrum; subsidiary peaks for sums and differences of the h_i's also appear. For more complicated spectra these confuse the issue to the point that more powerful correlation techniques were sought.[42]

Attempts have been made to use the redundancy inherent in the hyperfine spectrum to discriminate against the spurious maxima: the method is related to minimax strategy of game theory. Cross-correlations of individual lines were calculated—in each case the minimum correlation of a set of lines was taken as representative of the whole set. Success has been limited because a method has not yet been found for corrections forced by overlap of lines. For a much extended discussion of these correlation methods, with detailed examples, the reader is referred elsewhere.[43]

Recently, an integral transformation has been described[43,44] with which, in principle, a spectrum $I_{\text{expt}}(H)$ whose lines all have the same shape and width may be replotted as an ideal spectrum, $I_{\text{ideal}}(H)$, in which the line width is reduced to nil. The Fourier transform $K(\omega)$ of the kernel K in the integral transformation

$$I_{\text{ideal}}(H) = \int_{-\infty}^{\infty} K(H - H')I_{\text{expt}}(H')\, dH' \qquad (46)$$

is the reciprocal of the Fourier transform of a single line; i.e., if a single line at the origin is described by $f(H)$, then

$$K(\omega) = \left[\int_{-\infty}^{\infty} dHe^{i\omega H}f(H)\right]^{-1}. \qquad (47)$$

For Gaussian lines, with half-width W, the transformation takes the final form

$$I_{\text{ideal}}(H) = \left\{1 - \frac{W^2}{4 \ln 2}\frac{d^2}{dH^2} + \frac{W^4}{32(\ln 2)^2}\frac{d^4}{dH^4} - \cdots\right\}I_{\text{expt}}(H). \qquad (48)$$

For Lorentzian lines a slightly more complicated formula occurs. Because differentiation introduces inaccuracies, the practical enhancement of resolution is not unlimited, but very significant improvement has been obtained in a number of cases. A very simple example of filtering to the fourth derivative term is illustrated in Fig. 6. The method is quite insensitive to the assumptions of line shape or width; it has been implemented in an analog device as well as digitally. Similar devices, empirically based, have been previously described to deconvolute lines broadened by slit width effects in infrared spectroscopy.[45] The present method, however, does not need to distinguish between instrumental and natural broadening mechanisms.

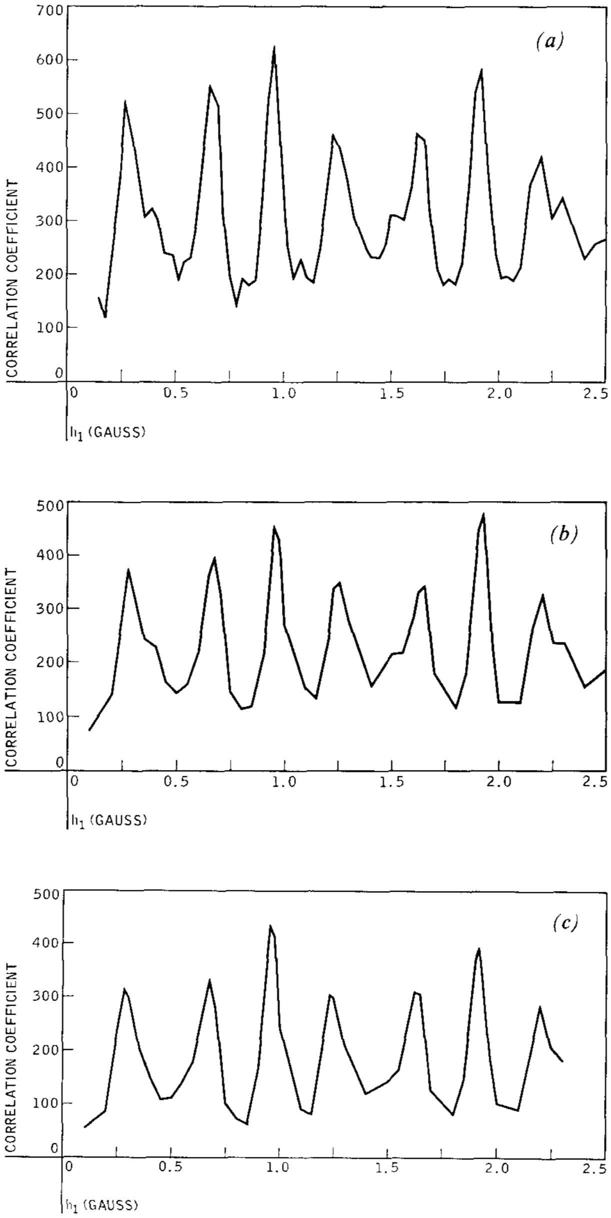


Figure 5 **Cross-correlation for the synthetic spectrum of Fig. 4.**
(a) 5-line test function
(b) 25-line test function. ($h_2 = 1.92$ *G*)
(c) 125-line test function ($h_2 = 1.92$ *G*; $h_3 = 0.62$ *G*).

Computer programs to accomplish each of the functions above have been described.[43] In addition there are a number of programs[43,46,47] to plot hyperfine spectra from a series of assumed hyperfine parameters for comparison with experimental spectra. One by Gladney plots spectra of Lorentzian lines for radicals with up to twelve groups of equivalent nuclei with nuclear spins up to 3/2.

Lattice sums and line shape studies

Lattice sums over spherical harmonics are encountered in studies of EPR line shapes[48] and also in the estimation of crystalline field potentials required for the theory of magnetic and optical properties of paramagnetic centers in crystals. The dipole-dipole interaction contribution to the second moment of magnetic resonance lines is given by

$$\langle \Delta H^2 \rangle_{\text{dipole}} = \tfrac{1}{3} S(S+1) g^2 \beta^2 \sum_k B_k^2$$
$$B_k = -3 r_k^{-3}\left[\tfrac{3}{2}\gamma_k^2 - \tfrac{1}{2}\right], \qquad (49)$$

where (r_k, γ_k) are the distance and direction cosine of the k^{th} magnetic center from the origin. Examples of evaluation of this expression are given by Van Vleck[49] for a simple cubic lattice, by Ibers et al.[50] for a triclinic system and by Shulman and Sugano[51] for the edge center of a simple cubic system (the fluorine site in $KNiF_3$). In the event that the sample is polycrystalline, the angular factors may be averaged and (49) reduces to

$$\langle \Delta H^2 \rangle_{\text{dipolar}} = \tfrac{3}{5} g^2 \beta^2 S(S+1) \sum_k r_k^{-6}. \qquad (50)$$

This final sum has been calculated for a number of simple arrays[52]; the values appear in Table 1.

The dipole sums are sufficient to estimate line widths if dipolar interactions are dominant. Often it is necessary to include exchange interactions as well. As pointed out by Van Vleck[48] the isotropic exchange operator $J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2$ does not contribute to the second moment of a resonance line but does contribute to the fourth moment. No simple relationship between dipolar interactions and curve shapes therefore exists. Measurements of the second and, in particular, the fourth moments in order to determine the exchange interactions are not very accurate because they depend on the wings of the line where the signal is weak. With the theory of Anderson and Weiss,[53] however, line widths may be combined with the dipole sum calculations to estimate exchange energies, ω_e:

$$\langle \Delta\omega^2 \rangle = 2\omega_{1/2}\omega_e. \qquad (51)$$

Here $\langle \Delta\omega^2 \rangle$ is the second moment calculated with dipole sums and $\omega_{1/2}$ is the measured half-width of resonance. Recently the results of this method have been substantiated with EPR measurements of magnetic ion pairs as crystal impurities. A cautionary note is necessary. Since the convergence properties of dipole sums are not simple, care is necessary in their evaluation and use, particularly for powder samples for which size and shape effects can be large.[54]

Nijboer and de Wette[55] describe methods of performing general types of sums and present a straightforward method with good convergence properties. Adler[56] discusses in detail the Ewald method for a lattice sum sufficiently

Figure 6 **Top: Synthetic ESR spectrum with linewidth 0.10, line positions 0.25 and 0.35. Bottom: Spectrum filtered to fourth derivative term.** *(From Ref. 44, Fig. 4).*

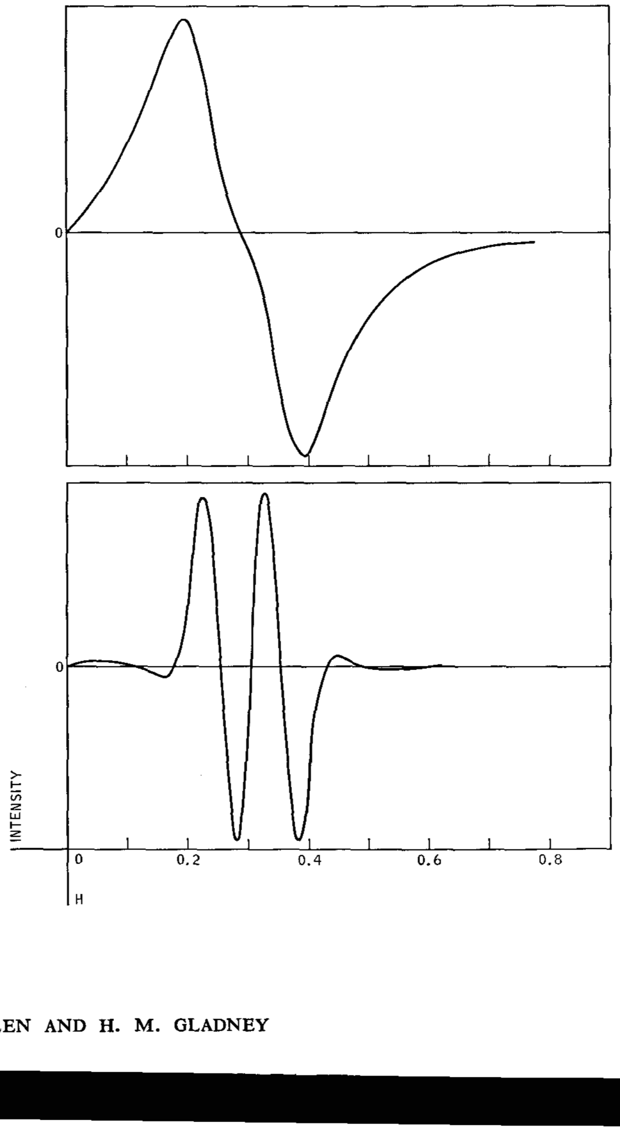


Table 1 **Dipole sums for simple lattices Σr_j^{-6}.**

Lattice	*Same Ions**	*Counter Ions**
Simple cubic	8.402	
Bcc	29.03	
Fcc	115.6	
NaCl type	115.6	422.1
CsCl type	8.402	20.65
hcp	14.45	
CaF_2 type—for Ca	115.6	660.5
for F	537.7	660.5

* In units of a^{-6}, where a is the edge of the unit cell, except for hcp crystals, where it is the side of the hexagon.

general for all the problems encountered in this field. His formulae are in a form very convenient for programming any particular case. Cohen and Keffer[57] tabulate for a series of points in K-space the dipole sums for the simple cubic, face-centered-cubic and body-centered-cubic arrays, and discuss their behavior for small K (the conventional dipole-field sum has $K = 0$) for infinite and finite lattices. Takahasi[58] presents a table of the numerical values of a dipole field for a close mesh of locations in the unit cell of a cubic lattice.

A number of computer programs are available for the evaluation of lattice sums. Weakliem and McClure[59] have used a program specialized to Al_2O_3-type geometry for crystal field estimations. This program has recently been extended to assemblies of point electric and magnetic dipoles by Artman and Murphy.[60] Shulman[61] has available a dipole sum program which computes the elements of the dipole field tensor at an arbitrary point due to an array of parallel dipoles on any primitive lattice; complex lattices may also be treated by combining separate calculations on simple sublattices.

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Note added in proof

A few further related papers have come to our attention. R. L. White, G. F. Herrmann, J. W. Carson, and M. Mandel (*Phys. Rev.* **136**, A231 (1964)) discuss a perturbation approach to the spin Hamiltonian for S-state ions. Subtraction of the fields for transitions with $M_s \leftarrow M_s - 1$ and $-M_s + 1 \leftarrow -M_s$ eliminates the even terms in the perturbation series, so that the observed spectra may be fit to third order. The same procedure may be applied to the $S = 3/2$ Hamiltonian if the Zeeman terms dominate. W. G. Nilsen and S. K. Kurtz (*Phys. Rev.* **136**, A262 (1964)) mention a machine program to fit the parameters of an $S = 5/2$ Hamiltonian to experimental results. They also describe point charge calculations of lattice potentials in zinc tungstate.

Errors in the measurement of moments of Gaussian and Lorentzian lines are estimated by H. S. Judeikis (*J. Appl. Phys.* **35**, 2615 (1964)).

An IBM 1620 program for Eq. (40) with finite single-center linewidth is described by T. Vänngard and R. Aasa, *Proc. 1st Int. Conf. Paramagnetic Resonance*, Academic Press, New York, 1963; pp. 509.

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