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A Simple Method for the Calculation of the Polycrystalline ESR Lineshape

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Synopsis. A simple interpolation method is developed for calculating the magnetic resonance lineshapes of the polycrystalline samples. The method uses the *spline* function with the optional number of calculated points, at which the spin Hamiltonian is solved most accurately. The calculation procedure and some examples will be given.

The polycrystalline lineshapes of the ESR spectra are generally calculated by integrating the transition fields and probabilities, which are themselves obtained by solving the spin Hamiltonian (1), over the orientational distribution of the spin system:

$$\boldsymbol{H} = \boldsymbol{B}\tilde{\boldsymbol{g}}\boldsymbol{S} + \boldsymbol{S}\tilde{\boldsymbol{D}}\boldsymbol{S} + \sum_i(\boldsymbol{I}_i\tilde{\boldsymbol{A}}_i\boldsymbol{S}+\boldsymbol{I}_i\tilde{\boldsymbol{P}}_i\boldsymbol{I}_i-g_n\beta_n\boldsymbol{B}\boldsymbol{I}_i). \quad (1)$$

Most organic and inorganic free radicals have magnetic nuclei, whose hyperfine tensors do not, in general, have common axes. When these non-coaxial tensors are involved in the Hamiltonian, it takes much time to compute the transition fields accurately, even for a single orientation of the applied field. However, since the resonance field is generally a smoothly varying function of the polar and azimuthal angles (θ, ϕ), the lineshape can be calculated by the use of a suitable interpolation function with a minimum number of data points obtained by the best solution of the Hamiltonian (1). Herring *et al.*[1] have used Newton's divided-difference polynominal as such an interpolation function. In the present note the application of the *spline* function to the calculation of the polycrystalline ESR lineshapes will be described.

From the transition field $(\boldsymbol{H}_i)$ and the probability $(\boldsymbol{q}_i)$ obtained by the solution of Eq. 1 for a specified transition (i), the monocrystalline component with a given width, λ, can be given as follows:

$$F_i(H, \theta, \phi) = (1/\lambda)(2/\pi)^{1/2}\exp\{-[H-\boldsymbol{H}_i(\theta, \phi)]^2/\lambda^2\}, \quad (2)$$

for the Gaussian, and

$$F_i(H, \theta, \phi) = (2/\lambda)/\{1+(2\pi/\lambda)^2[H-\boldsymbol{H}_i(\theta, \phi)]^2\}, \quad (3)$$

for the Lorentzian. The polycrystalline spectrum is, then, given by

$$S_i(H) = 1/4\pi\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\sin\theta F_i(H, \theta, \phi)\boldsymbol{q}_i(\theta, \phi). \quad (4)$$

This integration 4 is, thereby not generally possible by analytical means. Lefebvre and Maruani[2] have applied the Gaussian quadrature to the numerical integration with an optional number of the data points. However, if one has a sufficient number of functional values in the θ-ϕ space, the integration can be approximated by the corresponding summation (Eq. 5):

$$S_i(H) = \sum_{\theta}\sum_{\phi}F_i(H, \theta, \phi)\boldsymbol{q}_i(\theta, \phi). \quad (5)$$

In order to obtain a sufficient number of F_i and $\boldsymbol{q}_i$ values as functions of θ and ϕ from the least number of calculated grid points, the *spline* function[3] was used as an example of the interpolation function with a better quality.

The *spline* method for the interpolation divides the interval into N consecutive subintervals. In each, the function is approximated by a different polynominal with a certain degree, M. At points between two such intervals, the polynominals of the two sides are connected so as to have the same values and derivatives (up to the M-1th derivative). In the present work, the simplest one with $M=3$ was used. The *spline* function, $f(x)$, with the data points of $x^{(j)}$ and $y^{(j)}$ and with equally spaced variables, $x^{(j)}$ $(j=0,1,2,\ldots,n)$, can be defined as follows:

$$f(x) = \sum_{j=0}^{n}C(j, j'; x)y^{(j)};\ (x^{(j'-1)}\leq x\leq x^{(j')}), \quad (6)$$

where $y^{(j)}$ is the data value at $x=x^{(j)}$ and where j' specifies the interval at which the variable (x) is found. From the definition of the *spline* function, the coefficient, $C(j,j'; x)$, in Eq. 6 is given as follows:

$$\begin{aligned}C(j, j'; x) &= b_{j'}(x)a_{j'-1,j} + b_{j'-1}(x)a_{j',j}\\ &\quad + (x^{(j')}-x)\delta_{j'-1,j}/h + (x-x^{(j'-1)})\delta_{j',j}/h, \quad (7)\end{aligned}$$

where $h=x^{(j)}-x^{(j-1)}$ (=constant), $\delta_{j',j}$ is the usual Kronecker delta, and the b's and a's are given by

$$b_{j'}(x) = (x^{(j')}-x)^3/(6h)-(x^{(j')}-x)h/6$$

$$a_{j',j} = h^2[(\boldsymbol{A}^{-1})_{j',j+1}-2(\boldsymbol{A}^{-1})_{j',j} + (\boldsymbol{A}^{-1})_{j',j+1}]/3.$$

The elements of the inverse matrix $(\boldsymbol{A}^{-1})$ are

$$(\boldsymbol{A}^{-1})_{j',j} = (-1)^{j'+j}D_{j'-1}D_{n-1-j}/(2^{j-j'}D_{n-1}), \qquad (1\leq j'\leq j\leq n)$$

$$(\boldsymbol{A}^{-1})_{j',j} = (-1)^{j'+j}D_{j-1}D_{n-1-j'}/(2^{j'-j}D_{n-1}), \qquad (1\leq j\leq j'\leq n)$$

and

$$(\boldsymbol{A}^{-1})_{j',-1} = (\boldsymbol{A}^{-1})_{j',0} = (\boldsymbol{A}^{-1})_{j',n} = (\boldsymbol{A}^{-1})_{j',n+1} = 0,$$

where D_n is given by $D_n=[(1+\sqrt{3}/2)^{n+1}-(1-\sqrt{3}/2)^{n+1}]\sqrt{3}$. For the present purposes, the interpolation should generally be extended to the case with two variables (θ, ϕ). This can be done by simply multiplying the coefficients for each variable,[3] as is shown in Eq. 8.

$$f(x_1, x_2) = \sum_{i_1}\sum_{i_2}C_1(i_1, i_1'; x_1)C_2(i_2, i_2'; x_2)y^{(i_1,i_2)}, \quad (8)$$

where ${x_1}^{(i'_1-1)}\leq x_1\leq {x_1}^{(i_1')}$ and ${x_2}^{(i_2'-1)}\leq x_2\leq {x_2}^{(i_2')}$. The expanded transition fields and probabilities can be calculated from the original data points $(\boldsymbol{H}_i^0, \boldsymbol{q}_i^0)$ by using the *spline* coefficients as follows:

$$\boldsymbol{H}_i(\theta, \phi) = \sum_{j=0}^{n_\theta}\sum_{k=0}^{n_\phi}C_1(j, j'; \theta)C_2(k, k'; \phi)\boldsymbol{H}_i^0(j, k),$$

$$\boldsymbol{q}_i(\theta, \phi) = \sum_{j=0}^{n_\theta}\sum_{k=0}^{n_\phi}C_1(j, j'; \theta)C_2(k, k'; \phi)\boldsymbol{q}_i^0(j, k), \quad (9)$$

where n_θ and n_ϕ are the number of the original data points minus one in each direction. By putting Eq. 9 into Eqs. 2 or 3, and using Eq. 5, the lineshape due to the i transition can be obtained. When the system contains many transitions, the total lineshape will be given by the summation of $S_i(H)$ (Eq. 10):

$$S(H) = \sum_i S_i(H). \tag{10}$$

In the calculation of Eq. 9, we need only the tabulated data and the spline coefficients, $C(j,j';x)$. The coefficients can be determined without the values of the variable (x) if the original data are calculated for equally spaced variables. For calculation on a computer, therefore, the *spline* coefficients can be calculated independently and stored for common use in a file specified with the total number of the data points and the desired number of the interpolated points in each interval. Using these tabulated *spline* coefficients and the processes described above, the computation of the polycrystalline spectrum can be much simplified. Thus, we believe the spline interpolation is easier to handle and more convenient than the polynominal interpolation in Ref. 1.

Figure 1 shows the spectrum of the randomly oriented NO_2 radical, where both n_θ and n_ϕ are equal to 5. For the sake of simplicity, the second-order perturbation solution of the spin Hamiltonian[4] was used in the calculation of the original data points. The spectrum is comparable to that of NO_2 observed (Fig. 2).[5]

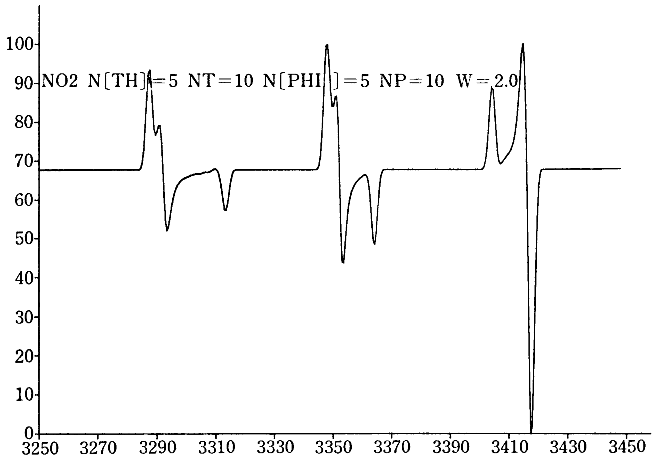

Fig. 1. The X-band spectrum of the randomly oriented NO_2 ($S=1/2$, $I=1$) calculated by the use of the spline function. The number of the data points $n_\theta=n_\phi=5$ ($0\leq\theta$, $\phi\leq\pi/2$) and each interval is further interpolated by 10 points. The magnetic parameters used in the calculation are $g_1=2.0056$, $g_2=1.9956$, $g_3=2.0029$; $A_1=56.0$, $A_2=51.0$, $A_3=65.0$ (G), and component width 2.0 G.

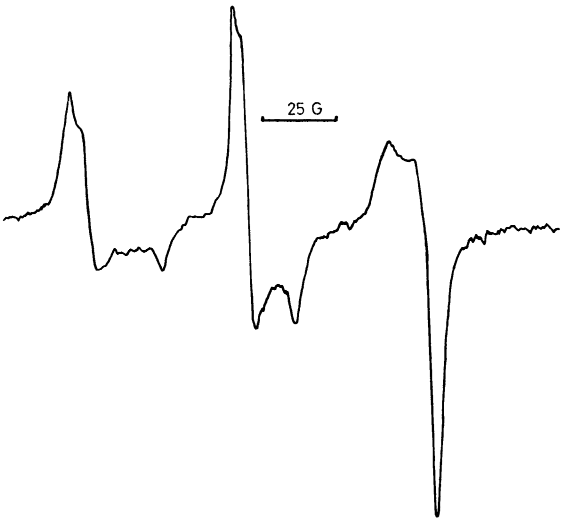

Fig. 2. The X-band spectrum of NO_2 adsorbed on silica gel and measured at 77 K. The resolution of the spectrum is somewhat poor, but the magnetic parameters derived from the spectrum is comparable to those of the spectrum in Fig. 1.

As in the case of the Gaussian integration,[2] the accuracy of of the calculated lineshapes is dependent on the number of the original data points, and also on the smoothness of the angular variation. The smoothness of the variation depends on the anisotropy of the tensors. It is, therefore, necessary to calculate more data points to obtain an accurate lineshape when the anisotropy of the tensors is large. In the case of the spectrum in Fig. 1, the lineshape did not change when the data points were increased from 5 to 10 in each variable if the total interpolated number of the transition field is large enough.

In the above calculations there is no restriction on the source of the transition fields and probabilities. This technique can, therefore, easily be applied to the calculation of the NMR lineshape of the polycrystalline samples by using the nuclear-spin transitions instead of the electron spin's.

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