Chemical Shift and Quadrupolar Interactions in Solids

Jineun Kim

Department of Chemistry and Research Institute of Natural Sciences
Gyeongsang National University, Chinju 660-701, S. Korea.
Received January 10, 2006

Abstract : General expressions for solid state NMR lines are described for transitions under static, magic angle spinning, and variable angle spinning conditions in the case where the principal axis system for the anisotropic chemical shift tensor is noncoincident with that of the quadrupole coupling tensor. It is demonstrated that solid state NMR powder pattern simulation program VMAS based on the conventional grid point method of integrating over the Euler angle space is fast enough in comparison with the POWDER simulation package and Gauss-point method.
Keywords: single-crystal, solid state NMR, chemical shift, quadrupole, magic angle, variable angle

INTRODUCTION

In solid state NMR, information about the electronic environment and bonding of the nuclei can be obtained from the analysis of powder line shapes. The observed spectrum depends on the interactions present in the sample that add to the Zeeman splitting caused by the static magnetic field. Such interactions are dipolar, quadrupolar (Q), chemical shift (CS) and scalar couplings. Small interactions such as scalar couplings are usually negligible compared to the CS and/or Q interactions. When a suitably sized single crystal is available, it is fairly straightforward process to determine Q^{1-3} or $CS^{4,5}$ tensor. There is no reason to believe that the principal axis system (PAS) for the anisotropic CS tensor will be coincident with that of the Q tensor. The case where the principal axis system (PAS) for the anisotropic

To whom correspondence should be addressed. E-mail : jekim@gnu.ac.kr

CS tensor is noncoincident with that of the Q tensor was described by Power et al. more than a decade ago.[6] Nevertheless, one of the Q principle axes is still coincident with one of the CS principle axes.

On the other hand, NMR peak in polycrystalline solids is remarkably broader than narrower lines in solution. This line broadening is primarily due to an orientation dependence of the magnetic field at the nucleus generated by the anisotropic interactions. In order to obtain these anisotropic parameters, the lineshape analysis of static, magic angle spinning (MAS)[7] or variable angle spinning (VAS)[8] NMR spectra at different magnetic fields are required. Analysis of NMR powder patterns arising from quadrupolar nuclei by spectral simulation is complicated because, in general, the lineshape will depend on both the magnitude and orientation of the Q and CS interactions. The dipolar interaction and the lifetime broadening will broaden and smooth out the theoretical powder pattern. Numerically, the line broadenings can be treated by convolution with a normalized Gaussian or Lorentzian function. Analysis of NMR powder patterns arising from quadrupolar nuclei by spectral simulation is complicated because, in general, the line shape will depend on both the magnitudes and relative orientation of the Q and CS interactions.

Considerable literature is available on the nature of the NMR spectra of powdered samples in the presence of quadrupolar interactions only[9] or chemical shift effects only.[10] There have been earlier studies on the effects of both Q and CS interactions on the NMR line shapes of powder sample, where the interactions were axially symmetric and had the same orientation dependence; i.e., the principal components of the Q and CS tensors could be defined in the same system.[11] Such situations occur for nuclei at trigonal or higher symmetry point group sites in the crystal, as these sites possess an n-fold axis of rotation where $n > 2$. Baugher et al. described the NMR powder pattern for systems involving both nonaxially symmetric Q and CS interactions.[12] For a more general case, one has to consider the second rank tensor properties of both the Q and CS tensors. There is no reason to believe that the principal axis system (PAS) for the anisotropic CS tensor will be coincident with that of the Q tensor. This case was independently described by Cheng et al. and Power et al. at the same time.[13,14] In spite of this achievement, no attempts have been reported accounting for the completely general case where the magnitudes and orientations of the principal axes of the two interactions in a single crystal are allowed to be completely indep-

endent. This paper reports general expressions for NMR lines for transitions under static, MAS, and VAS conditions in the case where the principal axis system (PAS) for the anisotropic CS tensor is noncoincident with that of the Q tensor.

THEORY

The first step in the analysis of single-crystal NMR data is to place the tensors in a common reference frame in a right-handed fashion. It is convenient to express the CS tensor in the frame of the Q tensor since the more dominant Q interaction is considered up to second order. The Euler angles (φ, θ, ψ) relate the magnetic field $\mathbf{B}_0$ (X, Y, Z) to the goniometer frame (x_g, y_g, z_g). The Euler angles (α, β, γ) relate the goniometer frame to the PAS of the Q tensor of the nucleus (x, y, z). The orientation of the CS tensor in the Q frame of reference is defined by the three Euler angles (α', β', γ'). The sign conventions and the Eulerian angle definitions of Rose are adopted.[15] To express the resonance frequency in the laboratory frame, we have utilized the standard method of employing Wigner rotation matrices. Up to the second order in the shift, the single crystal NMR frequency υ_m that corresponds to the spin transition $m \rightarrow m - 1$ is given by

$$
\begin{aligned}
\upsilon_m = {}& \upsilon_L(1 + \delta_{iso} + \delta f_{20CS}) - \upsilon_Q(m - {}^1\!/_2) f_{20Q} \\
& + (\upsilon_Q{}^2/12\upsilon_L)[\{24\, m(m-1) - 4\, I(I+1) + 9\}\, |\, f_{2\pm 1Q}|^2 \\
& - \{6\, m(m-1) - 2\, I(I+1) + 3\}\, |\, f_{2\pm 2Q}|^2,
\end{aligned} \tag{1}
$$

where *I* and *m* are the nuclear spin and the magnetic quantum number, respectively, and

$$
\begin{aligned}
f_{20CS} = {}& 0.5\, (3\cos^2\theta - 1) f_{20CS}' + ({}^3\!/_2)^{1/2} \sin\theta \cos\theta\, (e^{i\varphi} f_{2\text{-}1CS}' - e^{-i\varphi} f_{21CS}') \\
& + ({}^3\!/_8)^{1/2} \sin^2\theta\, (e^{i2\varphi} f_{2\text{-}2CS}' + e^{-i2\varphi} f_{22CS}'),
\end{aligned} \tag{2}
$$

$$
\begin{aligned}
f_{20CS}' = {}& 0.5\, (3\cos^2\beta - 1) f_{20CS}'' + ({}^3\!/_2)^{1/2} \sin\beta \cos\beta\, (e^{i\alpha} f_{2\text{-}1CS}'' - e^{-i\alpha} f_{21CS}'') \\
& + ({}^3\!/_8)^{1/2} \sin^2\beta\, (e^{i2\alpha} f_{2\text{-}2CS}'' + e^{-i2\alpha} f_{22CS}''),
\end{aligned} \tag{3}
$$

$$f_{21CS}' = (^3/_2)^{1/2} \sin\beta \cos\beta \, e^{-i\gamma} f_{20CS}'' + 0.5 \, (2\cos\beta + 1)(1 - \cos\beta) \, e^{-i\gamma} \, e^{i\alpha} f_{2\text{-}1CS}''$$
$$+ 0.5 \, (2\cos\beta - 1)(\cos\beta + 1) \, e^{-i\gamma} \, e^{i\alpha} f_{21CS}'' - 0.5 \sin\beta (\cos\beta - 1) \, e^{-i\gamma} \, e^{i2\alpha} f_{2\text{-}2\,CS}''$$
$$- 0.5 \sin\beta (1 + \cos\beta) \, e^{-i\gamma} \, e^{-i2\alpha} f_{22CS}'',$$

(4)

$$f_{2\text{-}1CS}' = -(^3/_2)^{1/2} \sin\beta \cos\beta \, e^{i\gamma} f_{20CS}'' + 0.5 \, (2\cos\beta - 1)(\cos\beta + 1) \, e^{i\gamma} \, e^{i\alpha} f_{2\text{-}1CS}''$$
$$+ 0.5 \, (2\cos\beta + 1)(1 - \cos\beta) \, e^{i\gamma} \, e^{-i\alpha} f_{21CS}'' + 0.5 \sin\beta (1 + \cos\beta) \, e^{i\gamma} \, e^{i2\alpha} f_{2\text{-}2\,CS}''$$
$$+ 0.5 \sin\beta (\cos\beta - 1) \, e^{i\gamma} \, e^{-i2\alpha} f_{22CS}'',$$

(5)

$$f_{22CS}' = (^3/_8)^{1/2} \sin^2\beta \, e^{-i2\gamma} f_{20CS}'' - 0.5 \sin\beta (\cos\beta - 1) \, e^{-i2\gamma} \, e^{i\alpha} f_{2\text{-}1CS}''$$
$$+ 0.5 \sin\beta (1 + \cos\beta) \, e^{-i2\gamma} \, e^{-i\alpha} f_{21CS}'' + \sin^4(\beta/2) \, e^{-i2\gamma} \, e^{i2\alpha} f_{2\text{-}2\,CS}''$$
$$+ \cos^4(\beta/2) \, e^{-i2\gamma} \, e^{-i2\alpha} f_{22CS}'',$$

(6)

$$f_{2\text{-}2CS}' = (^3/_8)^{1/2} \sin^2\beta \, e^{i2\gamma} f_{20CS}'' - 0.5 \sin\beta (1 + \cos\beta) \, e^{i2\gamma} \, e^{i\alpha} f_{2\text{-}1CS}''$$
$$+ 0.5 \sin\beta (\cos\beta - 1) \, e^{i2\gamma} \, e^{-i\alpha} f_{21CS}'' + \cos^4(\beta/2) \, e^{i2\gamma} \, e^{i2\alpha} f_{2\text{-}2\,CS}''$$
$$+ \sin^4(\beta/2) \, e^{i2\gamma} \, e^{-i2\alpha} f_{22CS}'',$$

(7)

$$f_{20CS}'' = 0.5 \, (3\cos^2\beta' - 1 + \eta^{CS} \sin^2\beta' \cos 2\alpha'),$$

(8)

$$f_{2\pm1CS}'' = \pm\{(^3/_2)^{1/2} \sin\beta' \cos\beta' - (\eta^{CS}/6^{1/2})(\sin\beta' \cos\beta' \cos 2\alpha' \mp i \sin\beta' \sin 2\alpha')\} \, e^{\mp i\gamma'},$$

(9)

$$f_{2\pm2CS}'' = 0.5 \, \{(^3/_2)^{1/2} \sin^2\beta' + (\eta^{CS}/6^{1/2})[(1 + \cos^2\beta') \cos 2\alpha' \mp i \cos\beta' \sin 2\alpha']\} \, e^{\mp i2\gamma'},$$

(10)

$$f_{20Q} = 0.5 \, (3\cos^2\theta - 1) f_{20Q}' + (^3/_2)^{1/2} \sin\theta \cos\theta \, (e^{i\varphi} f_{2\text{-}1Q}' - e^{-i\varphi} f_{21Q}')$$
$$+ (^3/_8)^{1/2} \sin^2\theta \, (e^{i2\varphi} f_{2\text{-}2Q}' + e^{-i2\varphi} f_{22Q}'),$$

(11)

$$f_{21Q} = (^3/_2)^{1/2} \sin\theta \cos\theta \, e^{-i\psi} f_{20Q}' + 0.5 \, (2\cos\theta + 1)(1 - \cos\theta) \, e^{-i\psi} \, e^{i\varphi} f_{2\text{-}1Q}'$$
$$+ 0.5 \, (2\cos\theta - 1)(\cos\theta + 1) \, e^{-i\psi} \, e^{i\varphi} f_{21Q}' - 0.5 \sin\theta (\cos\theta - 1) \, e^{-i\psi} \, e^{i2\varphi} f_{2\text{-}2Q}'$$
$$- 0.5 \sin\theta (1 + \cos\theta) \, e^{-i\psi} \, e^{-i2\varphi} f_{22Q}',$$

(12)

$$f_{2\text{-}1Q} = -(^3/_2)^{1/2} \sin\theta \cos\theta \, e^{i\psi} f_{20Q}' + 0.5 \, (2\cos\theta - 1)(\cos\theta + 1) \, e^{i\psi} \, e^{i\varphi} f_{2\text{-}1Q}'$$
$$+ 0.5 \, (2\cos\theta + 1)(1 - \cos\theta) \, e^{i\psi} \, e^{-i\varphi} f_{21Q}' + 0.5 \sin\theta (1 + \cos\theta) \, e^{i\psi} \, e^{i2\varphi} f_{2\text{-}2Q}'$$

$$+ 0.5 \sin \theta \, (\cos \theta - 1) \, e^{i\psi} \, e^{-i2\varphi} \, f_{22Q}',$$

(13)

$$f_{22Q} = (^3/_8)^{1/2} \sin^2 \theta \, e^{-i2\psi} f_{20Q}' - 0.5 \sin \theta \, (\cos \theta - 1) \, e^{-i2\psi} \, e^{i\varphi} f_{2\text{-}1Q}'$$
$$+ 0.5 \sin \theta \, (1 + \cos \theta) \, e^{-i2\psi} \, e^{-i\varphi} f_{21Q}' + \sin^4 (\theta/2) \, e^{-i2\psi} \, e^{i2\varphi} f_{2\text{-}2Q}'$$
$$+ \cos^4 (\theta/2) \, e^{-i2\psi} \, e^{-i2\varphi} f_{22Q}',$$

(14)

$$f_{2\text{-}2Q} = (^3/_8)^{1/2} \sin^2 \theta \, e^{i2\psi} f_{20Q}' - 0.5 \sin \theta \, (1 + \cos \theta) \, e^{i2\psi} \, e^{i\varphi} f_{2\text{-}1Q}'$$
$$+ 0.5 \sin \theta \, (\cos \theta - 1) \, e^{i2\psi} \, e^{-i\varphi} f_{21Q}' + \cos^4 (\theta/2) \, e^{i2\psi} \, e^{i2\varphi} f_{2\text{-}2Q}'$$
$$+ \sin^4 (\theta/2) \, e^{i2\psi} \, e^{-i2\varphi} f_{22Q}',$$

(15)

$$f_{20Q}' = 0.5 \, (3 \cos^2 \beta - 1 + \eta^{Q} \sin^2 \beta \cos 2\alpha)$$
$$= A,$$

(16)

$$f_{2\pm1Q}' = \pm\{(^3/_2)^{1/2} \sin \beta \cos \beta - (\eta^{Q}/6^{1/2}) (\sin\beta \cos \beta \cos 2\alpha \mp i \sin \beta \sin 2\alpha)\} \, e^{\mp i\gamma}$$
$$= \{\mp B + iC\} \, e^{\mp i\gamma},$$

(17)

$$f_{2\pm2Q}' = 0.5 \, \{(^3/_2)^{1/2} \sin^2 \beta + (\eta^{Q}/6^{1/2})[(1 + \cos^2 \beta) \cos 2\alpha \mp i \cos \beta \sin 2\alpha]\} \, e^{\mp i2\gamma}$$
$$= \{D \pm iE\} \, e^{\mp i2\gamma}.$$

(18)

The terms υ_L and υ_Q are the Larmor and the quadrupolar frequencies, respectively. The chemical shift tensor elements, δ_{11}, δ_{22}, and δ_{33}, are chosen such that

$$|\delta_{33} - \delta_{\text{iso}}| \geq |\delta_{22} - \delta_{\text{iso}}| \geq |\delta_{11} - \delta_{\text{iso}}| \qquad (19)$$

$$\delta_{\text{iso}} = (\delta_{33} + \delta_{22} + \delta_{11})/3 \qquad (20)$$

$$\delta = \delta_{33} - \delta_{\text{iso}} \qquad (21)$$

$$\eta^{CS} = (\delta_{11} - \delta_{22})/ (\delta_{33} - \delta_{\text{iso}}). \qquad (22)$$

The electric field gradient tensor elements, V_{11}, V_{22}, and V_{33}, are chosen in a similar way to those of the chemical shift tensor.

$$|V_{33}| \geq |V_{22}| \geq |V_{11}| \qquad (23)$$

$$\eta^Q = (V_{11} - V_{22})/V_{33} \qquad (24)$$

When a single crystal is mounted on a goniometer in a well defined fashion, i.e. the crystal axes have a known relation to the goniometer axes. The goniometer rotates clockwise the crystal by an angle φ about its rotation axis z_g from the starting position ($X \parallel y_g$, $X \parallel z_g$, $X \parallel x_g$) which usually has an angle $\theta = \pi/2$ with respect to the magnetic field. The Euler angles (α, β, γ) are calculated from the matrix, which is composed of the eigenvectors, using $\mathbf{R}(\alpha \beta \gamma)$.

$$\mathbf{R}(\alpha\,\beta\,\gamma) = \begin{bmatrix} \cos\alpha\,\cos\beta\,\cos\gamma - \sin\alpha\,\sin\gamma & \sin\alpha\,\cos\beta\,\cos\gamma + \cos\alpha & \sin\gamma - \sin\beta\,\cos\gamma \\ -\cos\alpha\,\cos\beta\,\sin\gamma - \sin\alpha\,\cos\gamma & -\sin\alpha\,\cos\beta\,\sin\gamma + \cos\alpha & \cos\gamma\,\sin\beta\,\sin\gamma \\ \cos\alpha & \sin\beta\sin\alpha\,\sin\beta & \cos\beta \end{bmatrix} \qquad (25)$$

Then, the transformation from the goniometer frame to the laboratory frame is described by $\mathbf{R}(\varphi\ 90°\ 90°)$. The crystal is rotated in small steps from 0° to 180° about mutually orthogonal directions. From fitting of the rotation plots, eigenvalues such as $\delta_{11}, \delta_{22}, \delta_{33}, V_{11}, V_{22}$, and V_{33}, and eigenvectors are obtained. In the case of off-axis rotation experiment ($\theta \neq 90°$), one rotation from 0° to 360° is necessary for the determination of the tensors.

In the case of static experiment, the Euler angles (φ, θ, ψ) are zero. Therefore, $f_{20Q} = f_{20Q}'$, $f_{2\pm1Q} = f_{2\pm1Q}'$, $f_{2\pm2Q} = f_{2\pm2Q}'$, $f_{20CS} = f_{20CS}'$, $f_{2\pm1CS} = f_{2\pm1CS}'$, $f_{2\pm2CS} = f_{2\pm2CS}'$. Then, the frequency υ_m becomes as follows;

$$\upsilon_m = \upsilon_L[1 + \delta_{iso} + \delta\{0.5\,(3\cos^2\beta - 1)\,f_{20CS}'' + (^3/_2)^{1/2}\sin\beta\cos\beta\,(e^{i\alpha}f_{2\text{-}1CS}'' - e^{-i\alpha}f_{21CS}'')$$
$$+ (^3/_8)^{1/2}\sin^2\beta\,(e^{i2\alpha}f_{2\text{-}2CS}'' + e^{-i2\alpha}f_{22CS}'')\}] - \upsilon_Q(m - ^1/_2)\,0.5(3\cos^2\beta - 1 + \eta^Q\sin^2\beta\cos 2\alpha)$$
$$+ (\upsilon_Q^2/_{12}\upsilon_L)[\{24\,m(m-1) - 4\,I(I+1) + 9\}\{(-\eta^{Q2}/6\cos^2 2\alpha + \eta^Q\cos 2\alpha - 3/2)\cos^4\beta$$
$$+ (\eta^{Q2}/3\cos^2 2\alpha - \eta^Q\cos 2\alpha - \eta^{Q2}/6 + 3/2)\cos^2\beta + \eta^{Q2}/6\,(1 - \cos^2 2\alpha)\}$$
$$- \{6\,m(m-1) - 2\,I(I+1) + 3\}\{(\eta^{Q2}/24\cos^2 2\alpha - 1/4\,\eta^Q\cos 2\alpha + 3/8)\cos^4\beta$$
$$+ (-\eta^{Q2}/12\cos^2 2\alpha + \eta^{Q2}/6 - 3/4)\cos^2\beta + (\eta^{Q2}/24\cos^2 2\alpha + 1/4\,\eta^Q\cos 2\alpha + 3/8)\}].$$

(26)

Eq (26) reduced to equations in the literature by Cheng et al. for m=1/2.[13]

In the case where the principal axes of the CS and Q tensors be coincident ($\alpha' = \beta' = \gamma' = 0°$), the frequency υ_m is simplified to

$$\upsilon_m = \upsilon_L[1 + \delta_{iso} + \delta\{0.5\,(3\cos^2\beta - 1\,\eta^Q\sin^2\beta\cos 2\alpha)\}]$$
$$- \upsilon_Q(m - \tfrac{1}{2})\,\{0.5\,(3\cos^2\beta - 1 + \eta^Q\sin^2\beta\cos 2\alpha)\}$$
$$+ (\upsilon_Q^2/12\upsilon_L)[\{24\,m(m-1) - 4\,I(I+1) + 9\}\{(-\eta^{Q2}/6\cos^2 2\alpha + \eta^Q\cos 2\alpha - 3/2)\cos^4\beta$$
$$+ (\eta^{Q2}/3\cos^2 2\alpha - \eta^Q\cos 2\alpha - \eta^{Q2}/6 + 3/2)\cos^2\beta + \eta^{Q2}/6\,(1 - \cos^2 2\alpha)\}$$
$$- \{6\,m(m-1) - 2\,I(I+1) + 3\}\{(\eta^{Q2}/24\cos^2 2\alpha - \eta^Q/4 \quad \cos 2\alpha + 3/8)\cos^4\beta$$
$$+ (-\eta^{Q2}/12\cos^2 2\alpha + \eta^{Q2}/6 - 3/4)\cos^2\beta + (\eta^{Q2}/24\cos^2 2\alpha + \eta^Q/4\cos 2\alpha + 3/8)\}].$$

(27)

Then, the explicit dependence of the central line $\upsilon_{1/2}^{(2)}$ can be obtained as

$$\upsilon_{1/2}^{(2)} = -(\upsilon_Q^2/6\upsilon_L)\{\,I(I+1) - 3/4\}\{(-3/8\,\eta^{Q2}\cos^2 2\alpha + 9/4\,\eta^Q\cos 2\alpha - 27/8)\cos^4\beta$$
$$+ (3/4\,\eta^{Q2}\cos^2 2\alpha - 2\eta^Q\cos 2\alpha - \eta^{Q2}/2 + 15/4)\cos^2\beta$$
$$+ (-3/8\,\eta^{Q2}\cos^2 2\alpha - \eta^Q/4\cos 2\alpha + \eta^{Q2}/3 - 3/8)\}.$$

(28)

Eq (28) is the same as equations in the literatures.[12,16]

The angle φ may be time dependent ($\varphi = \omega_r t$) in a sample spinning experiment. The time dependence is introduced by rotating the sample by an angle $\varphi(t)$ about the spinner axis with $\varphi(t) = \varphi_0 + \omega_r t$. The angle θ is the angle between the static field $\mathbf{B}_0$ and the spinning axis For rapid sample spinning, such that υ_r is greater than the second-order quadrupole linebreadth of the (½, −½) transition, the sidebands are well separated from central line and become vanishingly small with increasing υ_r. Time dependent parts, $e^{\pm i\varphi}$ and $e^{\pm i2\varphi}$ may be averaged over one cycle to give zero (Strictly speaking, they show cyclic behavior which lead to rotational spin echos.[17]), while other time dependent parts, $(e^{\pm i\varphi})^2$ and $(e^{\pm i2\varphi})^2$ become one. In the VAS case where the angle θ can vary from 0° to 90° with respect to the magnetic field, the $\upsilon_m^{(2)}$ can be written as

$$
\begin{aligned}
\upsilon_m = {}& \upsilon_L[1 + \delta_{iso} + \delta \{0.5\,(3\cos^2\theta - 1)\}\{0.5\,(3\cos^2\beta - 1)f_{20CS}'' \\
& + (^3/_2)^{1/2}\sin\beta\cos\beta\,(e^{i\alpha}f_{2\text{-}1CS}'' - e^{-i\alpha}f_{21CS}'') + (^3/_8)^{1/2}\sin^2\beta\,(e^{i2\alpha}f_{2\text{-}2CS}'' + e^{-i2\alpha}f_{22CS}'')\}] \\
& - \upsilon_Q(m - {}^1/_2)\{0.5\,(3\cos^2\theta - 1)\}\{0.5\,(3\cos^2\beta - 1 + \eta^Q\sin^2\beta\cos 2\alpha)\} \\
& + (\upsilon_Q{}^2/12\upsilon_L)[\{24\,m(m - 1) - 4\,I(I + 1) + 9\}[1/2\,(1 - \cos^4\theta)(D^2 + E^2) \\
& + 1/2\,(1 - 3\cos^2\theta + 4\cos^4\theta)(B^2 + C^2) + 3/2\,(1 - \cos^2\theta)\cos^2\theta\,A^2] \\
& - \{6\,m(m - 1) - 2\,I(I + 1) + 3\}\}[1/8\,(1 + 6\cos^2\theta + \cos^4\theta)(D^2 + E^2) \\
& + 1/2\,(1 - 4\cos^4\theta)(B^2 + C^2) + 3/8\,(1 - \cos^2\theta)^2\,A^2],
\end{aligned}
$$

$$(29)$$

where

$$A = 0.5\,(3\cos^2\beta - 1 + \eta^Q\sin^2\beta\cos 2\alpha)$$

$$B = -(^3/_2)^{1/2}\sin\beta\cos\beta + (\eta^Q/6^{1/2})\sin\beta\cos\beta\cos 2\alpha$$

$$C = \sin\beta\sin 2\alpha$$

$$D = 0.5\,\{(^3/_2)^{1/2}\sin^2\beta + (\eta^Q/6^{1/2})(1 + \cos^2\beta)\cos 2\alpha]$$

$$E = -0.5\cos\beta\sin 2\alpha.$$

Under MAS condition, the angle θ is 54.74°, i.e. $3\cos^2\theta - 1 = 0$. The central line $\upsilon_{1/2}$ can be expressed as

$$
\begin{aligned}
\upsilon_{1/2} = {}& \upsilon_L[1 + \delta_{iso}] - (\upsilon_Q{}^2/6\upsilon_L)\{\,I(I + 1) - 3/4\}\{(7/48\,\eta^{Q2}\cos^2 2\alpha - 7/8\,\eta^Q\cos 2\alpha \\
& + 21/16)\cos^4\beta + (-7/24\,\eta^{Q2}\cos^2 2\alpha + \eta^Q\cos 2\alpha + \eta^{Q2}/12 - 9/8)\cos^2\beta \\
& + (7/48\,\eta^{Q2}\cos^2 2\alpha - \eta^Q/8\cos 2\alpha + 5/16)\}.
\end{aligned}
$$

$$(30)$$

Eq (30) is the same as Eq (6) by Müller.[18]

A Fortran program 'XTALNMR' is listed at the end of this article, which is based on Eq (1) in order to calculate single-crystal nmr lines at every given rotations with a starting orientation with the Euler angles (α, β, γ) and (α', β', γ'). This program with nonlinear least squares fitting program Kinfit2[19] was used to fit single-crystal ^{133}Cs NMR data of Cs$^+$(15-crown-5)$_2$·I$^-$.[20]

A powder spectrum is computed by summing the spectra from an ensemble of randomly oriented single crystals. A Fortran program 'VMAS' is given at the end of this article, which is based on Eq (26) in order to calculate a powder NMR line under static,

magic angle, or variable angle condition. The efficiency of this program is comparable to the program 'POWDER'[21] (under 10 s on a VAX 8800 computer). This comes from the efficiency in the loop calculation for the polar ($\cos \beta$) and azimuthal angle (α) grid point space. In the VMAS, common factors in the equation are factorized out, calculated outside of the loop and stored in memory sites. Therefore, calculation in the loop summation is minimized. Run time for 360×360 grid point integration was less than 1 s with Pentium III MMX 500MHz computer. Gauss-point integration method was also comparable to the VMAS in run time.[22] The program VMAS with nonlinear least squares fitting program Kinfit2 was used to fit ^{85}Rb, ^{87}Rb and ^{39}K NMR powder patterns.[19]

In summary, general expressions for solid state NMR lines are described for transitions under static, magic angle spinning, and variable angle spinning conditions in the case ($\alpha' \neq 0°$ $\beta' \neq 0°$ $\gamma' \neq 0°$) where the principal axis system for the anisotropic chemical shift tensor is noncoincident with that of the quadrupole coupling tensor.

REFERENCES

1. G. M. Volkoff, H. E. Petch, D. W. L. Smellie, *Canadian J. Phys.* **30**, 270 (1952).

2. G. M. Volkoff, *Canadian J. Phys.* **31**, 820 (1953).

3. H. E. Petch, N. G. Cranna, G. M. Volkoff, *Canadian J. Phys.* **31**, 837 (1953).

4. M. Mehring, "Principles of High Resolution NMR in Solids" Chap. 2, Springer-Verlag, Berlin, Heidelberg, New York, 1983.

5. U. Haeberlen, *Advan. Magn. Res.* Supplement New York, Academic Press, 1976.

6. W. P. Power, S. Mooibroek, R. E. Wasylishen, T. S. Cameron, *J. Phys. Chem.* **98**, 1552 (1994).

7. E. R. Andrew, A. Bradbury, R. G. Eades, *Nature* **182**, 1659 (1958).

8. S. Ganapathy, S. Schramm, E. Oldfield, *J. Chem. Phys.* **77**, 4360 (1982).

9. M. H. Cohen, F. Reif, "Quadrupole Effects in Nuclear Magnetic Resonance Studies of Solids" in "Solid State Physics" V.5 New York, Academic Press, 1957 and references therein.

10. U. Haeberlen, *Advan. Magn. Res.* Supplement New York, Academic Press, 1976 and references therein.

11. W. H. Jones, T. P. Graham, R. G. Barns, *Phys. Rev.* **132**, 1898 (1963).

12. J. F. Baugher, P. C. Taylor, T. Oja, P. J. Bray, *J. Chem. Phys.* **50**, 4914 (1969).

13. J. T. Cheng, J. C. Edwards, P. D. Ellis, *J. Phys. Chem.* **94**, 553 (1990).

14. W. P. Power, R. E. Wasylishen, S. Mooibroek, B. A. Pettitt, W. Danchura, *J. Phys. Chem.* **94**, 591 (1990).

15. M. E. Rose, "Elementary Theory of Angular Momentum" New York, John Wiley (1957).

16. K. Narita, J.-I. Umeda, H. Kusumoto, *J. Chem. Phys.* **44**, 2719 (1966).

17. J. S. Waugh, M. M. Maricq and R. Cantor, *J. Magn. Res.* **29**, 183 (1978).

18. D. Müller, *Ann. Phys.* **39**, 451 (1982).

19. J. Kim, J. L. Eglin, A. S. Ellaboudy, L. E. H. McMills, S. Huang, J. L. Dye, *J. Phys. Chem.* **100**, 2885 (1996).

20. K. Y. Lee, T. H. Kim, Y. W. Shin, J. Kim, *Bull. Korean Chem. Soc.* **25**, 529 (2004).

21. D. W. Alderman, M. S. Solum, D. M. Grant, *J. Chem. Phys.* **84**, 3717 (1986).

22. L. K. White, R. L. Belford, *J. Am. Chem. Soc.* **98**, 4428 (1976).

PROGRAM XTALNMR

C

C   AUTHOR

C   JINEUN KIM

C   DEPARTMENT OF CHEMISTRY

C   GYEONGSANG NATIONAL UNIVERSITY

C   CHINJU 660-701 KOREA

C   JAMES L. DYE

C   DEPARTMENT OF CHEMISTRY

C   MICHIGAN STATE UNIVERSITY

C   EAST LANSING, MI 48824 U.S.A.

C   APRIL 16, 1990

C

C   THE PROGRAM "XTALNMR.FOR" COMPUTES CHEMICAL SHIFTS CORRESPONDING

C   TO NUCLEAR MAGNETIC RESONANCE TRANSITIONS WHICH RESULT FROM

C   THE SPIN HAMILTONIAN WITH NUCLEAR ZEEMAN, QUADRUPOLE AND CHEM-

C   ICAL SHIFT TERMS. THE QUADRUPOLE AND CHEMICAL SHIFT TERMS ARE

C   TREATED AS PERTURBATIONS ON THE ZEEMAN TERM, AND ARE CORRECT

C   THROUGH SECOND ORDER AND FIRST ORDER, RESPECTIVELY.

C   THE SINGLE CRYSTAL NMR PEAK POSITIONS ARE CALCULATED BY SETTING

C   THE EULERIAN ANGLES, ALPHA, BETA, AND GAMMA, WHICH ARE DEFINED

C   WITH RESPECT TO THE GONIOMETER AXIS SYSTEM. IF BOTH TENSORS ARE

C   AXIALLY SYMMETRIC AND PRINCIPAL AXES ARE COINCIDENT, THE

C   EULERIAN ANGLE ALPHA IS MEANINGLESS. IT CAN BE AN ARBITRARY NUMBER.

C   FOR NONCOINCIDENT SYSTEMS, THE TRANSFORMATION OF THE CSA TENSOR TO

C   THE EFG TENSOR PRINCIPAL AXIS SYSTEM IS PERFORMED WITH THE EULERIAN

C   ANGLES, ALPHA', BETA', AND GAMMA'. THE ANGLE VAN IS DEFINED AS AN

C   ANGLE BETWEEN MAGNETIC FIELD DIRECTION AND THE ROTATION

C   (GONIOMETER Z AXIS) AXIS. THE TRANSFORMATIONS ARE DONE BY ROTATION

C   MATRICES SUCH AS R(A,B,C)=R(C)z'R(B)y'R(A)z DESCRIBED IN

```
C   "ELEMENTARY THEORY OF ANGULAR MOMENTUM" BY M. E. ROSE.
C   EACH TRANSITION INTENSITY IS PROPORTIONAL TO I(I+1)-M(M-1).
C   TOTAL TRANSITIONS TO BE CALCULATED ARE 2I*TOTAL ANGLE OF
C   ROTATION(ANG)/ANGLE OF ROTATION(XI).
C   EACH TRANSITION INTENSITY IS PROPORTIONAL TO I(I+1)-M(M-1).
C   TOTAL TRANSITIONS TO BE CALCULATED ARE 2I*TOTAL ANGLE OF
C   ROTATION(ANG)/ANGLE OF ROTATION(XI).
C
C   THE FOLLOWING CONVENTION IS CHOSEN TO LABEL THE PRINCIPAL AXES:
C       ABS(D33-D) > or = ABS(D22-D) > or = ABS(D11-D)
C               WHERE D = (D11+D22+D33)/3 AND
C       ABS(V33) > or = ABS(V22) > or = ABS(V11).
C   ASYMMETRY PARAMETERS (ETA=(V11-V22)/V33 AND CETA=(D11-D22)/(D33-D)
C   FOR QUADRUPOLAR AND CHEMICAL SHIFT INTERACTIONS, RESPECTIVELY)
C   ARE IN THE RANGE OF 0 AND 1.
C
C   INPUT
C     TITLE OF RUN                                          18A4
C     SPIN,TRAN,VL,VAN                              FREE FORMAT
C       SPIN          NUCLEAR SPIN I
C       VL            LARMOR FREQUENCY IN MHZ
C       TRAN          SELECTS TRANSITIONS TO BE CALCULATED
C       VAN           POLAR ANGLE BETWEEN FIELD DIRECTION AND GONIOMETER
C                     Z-AXIS IN DEGREE
C     QCC,ETA,D11,D22,D33                           FREE FORMAT
C       QCC           QUADRUPOLAR COUPLING CONSTANT IN MHZ
C       ETA           ASYMMETRIC PARAMETER OF ELECTRIC FIELD
C                     GRADIENT AT   NUCLEAR SITE
C       D11,D22,D33   CHEMICAL SHIFT PARAMETERS IN PPM
C     ALPA,BETA,GAMA,XI,ANG                         FREE FORMAT
C        ALPA.BETA.GAMA:EULERIAN ANGLES IN DEGREE
```

```
C       XI              ANGLE INCREMENT OF EACH ROTATION IN DEGREE(CONSTANT)
C       ANG             MAXIMUM(TOTAL) ANGLE OF ROTATION
C    ACQ,BCQ,GCQ
C     ALPHA',BETA',GAMMA':EULERIAN ANGLES BETWEEN CSA TENSOR PRINCIPAL
C       AXES AND EFG TENSOR PRINCIPAL AXES
C
C   OUTPUT
C     XL,CHEM,DMAG,FIRS,MULTI,SECO,FNN
C       XL              XL*XI = SUM OF THE ANGLE ROTATED
C       CHEM             CHEMICAL SHIFT ANISOTROPY(PPM)
C       DMAG             M
C       FIRS            FIRST ORDER SATELLITE TRANSITION(PPM)
C       MULTI            I(I+1)-M(M-1)
C       SECO             SECOND ORDER SHIFT FOR EACH TRANSITION(PPM)
C       PFREQ            SUM OF CSA, FIRST ORDER, AND SECOND ORDER
C                        QUADRUPOLAR SHIFT(PPM)
C       *****************************************************************
C
C    EXAMPLES OF DATA FILE
C     Cs1.DAT
C       Cs+ AT GNIOMETER Z-AXIS POLAR ANGLE 90
C       3.5,3.5,23.61,90
C       .15,.5,60,40,-30
C       0,90,0,10,180
C       10,90,0
C     Cs2.DAT
C       Cs+ AT A TILTED GONIOMETER(MAS PROBE) WITH AN ANGLE OF 54.7356
C       3.5,3.5,23.61,54.7356
C       .15,.5,60,40,-30
C       0,90,0,10,360
C       10.90.0
```

```
C        ************************************************************
         IMPLICIT REAL*8 (A-H,O-Z)
         CHARACTER*20 F20,F21
         DIMENSION TITLE(18)
         DIMENSION SGM(400),CGM(400),S2G(400),C2G(400)
         DIMENSION A(10),B(10),C(10),INT(10),D(10)
C
C        ********************** OPEN FILES ***********************
C
7        WRITE(*,20)
         READ(*,40,ERR=7) F20
         OPEN(UNIT=1,FILE=F20,STATUS='OLD')
8        WRITE(*,30)
         READ(*,40,ERR=8) F21
         OPEN(UNIT=2,FILE=F21,STATUS='NEW')
C
C        ************************ FORMAT ************************
C
10       FORMAT(/)
20       FORMAT(' ENTER INPUT FILE NAME')
30       FORMAT(' ENTER OUTPUT FILE NAME')
40       FORMAT(A)
50       FORMAT(9H   ALPHA =,F7.3,1X,8H   BETA =,F7.3,1X,9H   GAMMA =,F7.3,
     *   1X,17H VARIABLE ANGLE =,F7.3)
60       FORMAT(8H    SPIN =,F4.1,2X,14HLARMOR FREQ. =,F7.3,
     *   2X,21HQUAD. COUPL. CONST. =,F7.3,2X,13HASYMM. PAR. =,F7.4)
70       FORMAT(29H   CHEM. SHIFT PARAMETERS;D11=,F9.3,1X,4HD22=,F9.3,1X
     *   4HD33=,F9.3)
80       FORMAT(' ISO. CHEM. SHIFT= ',F9.3,1X,'CHEM. SHIFT DELTA= ',F9.3,
     *   1X,'CHEM. SHIFT ETA= ',F5.3)
90       FORMAT(1X,31HDELTA M = 1 TRANSITIONS BETWEEN,F5.1,4H AND,F5.1.
```

```
    *    5H ONLY)
100      FORMAT(3X,'NO',5X,'CSA',6X,'M',2X,'SATELLITE',3X,'MULTI',
    *    2X,'SECOND',2X,'PEAK PPM')
110      FORMAT(1X,F5.1,1X,F9.3,1X,F4.1,1X,F10.3,1X,I4,1X,F9.3,1X,F10.3)
120      FORMAT(9H ALPHA' =,F7.3,1X,8H BETA' =,F7.3,1X,9H GAMMA' =,F7.3,
    *    1X,30H FOR CSA TENSOR TRANSFORMATION)
130      FORMAT(18A4)
140      FORMAT(2X,18A4)
C        *****************************************************************
         READ(1,130)TITLE
         READ(1,*)SPIN,TRAN,VL,VAN
         READ(1,*)QCC,ETA,D11,D22,D33
         READ(1,*)ALPA,BETA,GAMA,XI,ANG
         READ(1,*)ACQ,BCQ,GCQ
C        *****************************************************************
         RAD=3.141592653589793/180.
C   TERMS FOR TRANSFORMATION OF NONCOINCIDENT CSA TENSOR
         TRACQ=2.*RAD*ACQ
         STACQ=DSIN(TRACQ)
         CTACQ=DCOS(TRACQ)
         RBCQ=RAD*BCQ
         SBCQ=DSIN(RBCQ)
         CBCQ=DCOS(RBCQ)
         SQSB=SBCQ*SBCQ
         SQCB=CBCQ*CBCQ
C   EULERIAN ANGLE ALPHA
         TAL=2.*RAD*ALPA
         STP=DSIN(TAL)
         CTP=DCOS(TAL)
         RGA=RAD*(GCQ+ALPA)
         TRGA=2.*RGA
```

```
        SRGA=DSIN(RGA)
        CRGA=DCOS(RGA)
        STRGA=DSIN(TRGA)
        CTRGA=DCOS(TRGA)
C   EULERIAN ANGLE BETA
        BTA=RAD*BETA
        SBT=DSIN(BTA)
        CBT=DCOS(BTA)
        CSB=CBT*SBT
        SSB=SBT*SBT
        CCB=CBT*CBT
C   EULERIAN ANGLE GAMMA
        J=ANG/XI+1
        DO 300 I=1,J
        YI=I-1.
        ROT=RAD*(GAMA+YI*XI)
        TROT=2.*ROT
        SGM(I)=DSIN(ROT)
        CGM(I)=DCOS(ROT)
        S2G(I)=DSIN(TROT)
        C2G(I)=DCOS(TROT)
300     CONTINUE
C   TERMS FOR TRANSFORMATION FROM THE GONIOMETER FRAME TO THE
LABORATORY
C   AXIS SYSTEM
        THE=RAD*VAN
        VSAL=DSIN(THE)
        VCAL=DCOS(THE)
        VSCA=VSAL*VCAL
        VSSA=VSAL*VSAL
        VDCB=1.-2.*VSSA
```

```
        VCCA=.5*(1.+VCAL*VCAL)
        VTCT=.5*(3.*VCAL*VCAL-1.)
        SIX=SQRT(6.)
C   CSA TERMS
        CSISO=(D11+D22+D33)/3.
        CSDEL=D33-CSISO
        IF (CSDEL.EQ.0.) GO TO 350
        CSETA=(D11-D22)/CSDEL
        GO TO 400
350     CSETA=0.
400     ACS=.5*(3.*SQCB-1.+CSETA*SQSB*CTACQ)
        BCS=SBCQ*CBCQ*(3.-CSETA*CTACQ)/SIX
        CCS=CSETA*SBCQ*STACQ/SIX
        DCS=.5*(3.*SQSB+CSETA*(1.+SQCB)*CTACQ)/SIX
        ECS=CSETA*CBCQ*STACQ/SIX
        DCNES=DCS*CTRGA-ECS*STRGA
        DSEC=DCS*STRGA+ECS*CTRGA
        BCCS=BCS*CRGA+CCS*SRGA
        XNBSCC=-BCS*SRGA+CCS*CRGA
        AO=.5*SIX*SSB*DCNES-SIX*CSB*BCCS+.5*(3.*CCB-1.)*ACS
        BR=-CSB*DCNES+(2.*CCB-1.)*BCCS+.5*SIX*CSB*ACS
        CI=SBT*DSEC+CBT*XNBSCC
        DR=.5*(1.+CCB)*DCNES+CSB*BCCS+.25*SIX*SSB*ACS
        EI=CBT*DSEC-SBT*XNBSCC
C   QUADRUPOLAR TERMS
        SS1=SPIN*(SPIN+1.)
        IF(SPIN - 0.5) 450,450,500
450     VQQ = 0.0
        GO TO 550
500     VQQ=3.*QCC/(2.*SPIN*(2.*SPIN-1.))/VL
550     FACT=VQQ*VQQ/12.
```

```
        XMAG=-TRAN+1.
        MAG=1
600     CONTINUE
        XX1=XMAG*(XMAG-1.)
        A(MAG)=24.*XX1-4.*SS1+9.
        B(MAG)=6.*XX1-2.*SS1+3.
        C(MAG)=-VQQ*(XMAG-.5)
        D(MAG)=XMAG
        INT(MAG)=SS1-XX1
        IF(XMAG.GE.TRAN) GO TO 650
        XMAG=XMAG+1.
        MAG=MAG+1
        GO TO 600
650     CONTINUE
        MGMX=MAG
        ECP=ETA*CTP
        XNECP3=3.-ECP
        CON=XNECP3*CSB/SIX
        SON=ETA*SBT*STP/SIX
        CTW=(3.+ECP-XNECP3*CCB)*.5/SIX
        STW=ETA*CBT*STP/SIX
        FR=.5*(-1.+ECP+XNECP3*CCB)
C   ROTATION ANGLE DEPENDENT TERMS
C   CALCULATE SHIFT CONTRIBUTIONS TO EACH TRANSITION
        WRITE(2,100)
        DO 700 M=1,MGMX
        DO 700 L=1,J
        XL=XI*(L-1.)
        CS2L=CON*SGM(L)-SON*CGM(L)
        CS3L=CTW*C2G(L)-STW*S2G(L)
        CS4L=CON*CGM(L)+SON*SGM(L)
```

```
      CS5L=CTW*C2G(L)+STW*S2G(L)
      CS6L=CTW*S2G(L)+STW*C2G(L)
      SAT=.5*SIX*VSSA*CS3L-SIX*VSCA*CS4L+VTCT*FR
      F1R=-VSCA*CS3L+VDCB*CS4L+.5*SIX*VSCA*FR
      F1I=VSAL*CS6L-VCAL*CS2L
      F2R=VCCA*CS3L+VSCA*CS4L+.25*SIX*VSSA*FR
      F2I=VCAL*CS6L+VSAL*CS2L
      CAN=CSDEL*(.5*SIX*VSSA*(DR*C2G(L)-EI*S2G(L))-SIX*VSCA*
    * (BR*CGM(L)+CI*SGM(L))+VTCT*AO)
      DMAG=D(M)
      MULTI=INT(M)
      VLCC=CSISO+CAN
      FST=C(M)*SAT
      SND=FACT*((F1R*F1R+F1I*F1I)*A(M)-(F2R*F2R+F2I*F2I)*B(M))
      CHEM=VLCC
      FIRS=FST*1.E6
      SECO=SND*1.E6
      PFREQ=VLCC+(FST+SND)*1.E6
      WRITE(2,110) XL,CHEM,DMAG,FIRS,MULTI,SECO,PFREQ
700   CONTINUE
C
C     ***************** OUTPUT FOR PARAMETERS ******************
C
      WRITE(2,10)
      WRITE(2,140) TITLE
      WRITE(2,10)
      WRITE(2,60) SPIN,VL,QCC,ETA
      WRITE(2,10)
      WRITE(2,70) D11,D22,D33
      WRITE(2,10)
      WRITE(2,80) CSISO,CSDEL,CSETA
```

```
         WRITE(2,10)
         WRITE(2,50) ALPA,BETA,GAMA,VAN
         WRITE(2,10)
         WRITE(2,90) TRAN,-TRAN
         WRITE(2,10)
         WRITE(2,120) ACQ,BCQ,GCQ
C        **********************************************************
         STOP
         END



         PROGRAM VMAS
C
C        SOLID STATE NMR POWDER PATTERN(STATIC, MAS, AND VAS) SIMULATION
C        PROGRAM FOR NONCOINCIDENT PRINCIPAL AXIS SYSTEMS
C
C        JINEUN KIM
C                DEPARTMENT OF CHEMISTRY
C                GYEONGSANG NATIONAL UNIVERSITY
C                CHINJU 660-701 KOREA
C        JAMES L. DYE
C                DEPARTMENT OF CHEMISTRY
C                MICHIGAN STATE UNIVERSITY
C                EAST LANSING MI 48824 U. S. A.
C
C        THIS PROGRAM IS AN EXTENSION OF QCPE 154 AND QCMP 56.
C                   ***POWPAT PROGRAM***
C        H.S. STORY AND D. KLINE     DEPARTMENT OF PHYSICS
C               STATE UNIVERSITY OF NEW YORK AT ALBANY
C    POWPAT PROGRAM COMPUTES AND PLOTS POWDER PATTERNS AND SPECTRA
C    CORRESPONDING TO NUCLEAR MAGNETIC RESONANCE TRANSITIONS WHICH
```

C   RESULT FROM THE SPIN HAMILTONIAN WITH NUCLEAR ZEEMAN, QUADRUPOLE

C   AND CHEMICAL SHIFT TERMS, SEE, FOR EXAMPLE, NARITA, UMEDA AND

C   KUSUMOTO, J. CHEM. PHYS.44,2719 (1966). OR BAUGHER, TAYLOR, OJA

C   AND BRAY UNPUBLISHED BROWN UNIVERSITY REPORT.

C   THE QUADRUPOLAR AND CHEMICAL SHIFT TERMS ARE TREATED AS

C   PERTURBATIONS ON THE ZEEMAN TERM, AND ARE CORRECT THROUGH

C   SECOND ORDER AND FIRST ORDER, RESPECTIVELY. THE POWDER PATTERN IS

C   SIMULATED BY SETTING THE CRYSTAL AT A LARGE NUMBER OF ANGLES,

C   THETA AND PHI ON A REGULAR GRID IN COSINE THETA SPACE. THE

C   FREQUENCIES ARE THEN COMPUTED AND A DENSITY FUNCTION OR POWDER

C   PATTERN CONSTRUCTED. THE POWDER PATTERN IS THEN CONVOLUTED WITH

C   A GAUSSIAN (OR GAUSSIAN DERIVATIVE TO PRODUCE A SPECTRUM

C   SIMULATING THAT OBTAINED FROM A WIDE-LINED SPECTROMETER

C   (DERIVATIVE MODE)).

C   THIS PROGRAM ASSUMES THAT ALL TRANSITIONS HAVE THE SAME

C   LINEWIDTH.

C   NOTE--- IF THE POWDER PATTERN EXTENDS BEYOND THE RANGE OF PPMIN

C   OR PPMAX, THE RESULTING STEP WILL PRODUCE A RESPONSE IN THE

C   CONVOLUTED SPECTRUM. THUS PEAKS AT THE ENDS OF THE SPECTRA ARE

C   TO BE DISREGARDED.

C

C   ******** DATA ENTRY   FORMAT   *******

C

C   TITLE OF RUN   18A4

C   SPIN,TRAN,VL,PS,PPMIN,PPMAX,DUMMY   FREE

C   QCC,ETA,D11,D22,D33,SIGHZ,WEIGHT,NORM   FREE

C   ALP,ACQ,BCQ,GCQ,ITH   FREE

C

C   DATA LIST

C   SPIN   NUCLEAR SPIN

C   TRAN   SELECTS TRANSITIONS TO BE INCLUDED

C   VL   LARMOR FREQUENCY

C   PS   NUMBER OF FREQUENCIES AT WHICH POWDER

C   PATTERN AND SPECTRUM WILL BE COMPUTED.

C   PPMIN,PPMAX MINIMUM AND MAXIMUM CHEM. SHIFTS IN

C   POWDER PATTERN AND SPECTRUM.

C   DUMMY   NUMBER TO ADD A BACKGROUND SPECTRUM

C

C   QCC   NUCLEAR QUADRUPOLE COUPLING CONSTANT

C   ETA   ASYMMETRY PARAMETER OF ELECTRIC FIELD

C   GRADIENT AT NUCLEAR SITE

C   _____

C   D11,D22,D33 CHEMICAL SHIFT PARAMETERS(NOT SHELDING)

C   ~~~~~

C   SIGHZ   GAUSSIAN BROADENING IN HZ

C   WEIGHT   RELATIVE WEIGHT TO BE ASSIGNED TO SITE

C   NORM   NORMALIZE INTENSITY, IF NORM = 1

C

C   ALP   VARIABLE ANGLE

C   ACQ,BCQ,GCQ EULERIAN ANGLES BETWEEN QUADRUPOLE COUPLING AND

C   CHEMICAL SHIFT TENSORS

C   ITH   NUMBER OF POINTS OF SPHERE DIVISION

C

C   A GRID IS ESTABLISHED IN COSINE THETA, PHI SPACE WITH EACH

C   COORDINATE HAVING XITH INCREMENTS, SO THAT THE GRID IS XITH*XITH

C   IF THE QUADRUPOLE AND CHEMICAL SHIFT TENSORS ARE GENERAL.

C   IF BOTH ARE AXIAL AND COINCIDENT, THE PHI ROTATION IS NOT

C   DONE. VL,PMIN, PMAX, AND QCC ARE IN MEGAHERTZ. ETA AND

C   WEIGHT ARE DIMENSIONLESS. THE PRINCIPAL AXIS SYSTEM OF THE

C   QUADRUPOLAR COUPLING TENSOR (Xq,Yq,Zq) IS DEFINED SO THAT

C   THE ABSOLUTE MAGNITUDE OF Vzz AND Vxx CAN BE THE LARGEST

```
C        AND THE SMALLEST, RESPECTIVELY. ETA IS DEFINED AS: ETA =
C        (Vxx - Vyy)/Vzz. THE ELEMENTS (D11,D22,D33) OF THE CHEMICAL
C        SHIFT TENSOR ARE CHOSEN IN THE SAME PRINCIPAL AXIS SYSTEM AS
C        QUADRUPOLAR COUPLING TENSOR, SPECIFICALLY,
C
C        ********************************************************
C        ** ABS(D33 - Diso) GE. ABS(D22 - Diso) GE. ABS(D11 - Diso) **
C        ********************************************************
C
C        D11, D22, AND D33 ARE IN PPM SCALE. THE TRANSFORMATION OF THE
C        CSA TENSOR TO THE QUADRUPOLAR PRINCIPAL AXIS SYSTEM IS DONE
C        BY THE EULERIAN ANGLES, ACQ, BCQ, AND GCQ.
C        SIG IS THE GAUSSIAN HALFWIDTH EXPRESSED AS A FRACTION OF THE
C        TOTAL RANGE PMAX-PMIN. THE PATTERNS WILL INCLUDE THE INTENSITY
C       FROM ALL ADJACENT LEVEL TRANSITIONS BETWEEN THE TRAN AND-TRAN,
C        I.E. IF TRAN IS SET EQUAL TO .5 FOR HALF ODD-INTEGRAL SPIN, THEN
C        ONLY THE CENTRAL TRANSITION WILL BE DONE. IF TRAN IS SET TO 1.5
C      THEN THE CENTRAL TRANSITION PLUS TWO ADJACENT SATELLITES WILL BE
C        INCLUDED. THE WEIGHTING FACTOR I(I+1)-M(M-1) FOR THE SATELLITE
C        INTENSITIES IS INCLUDED.   I IS THE SPIN AND M IS THE MAGNETIC
C        QUANTUM NUMBER. DIMENSIONS OF PARAMETERS WHICH AGREE WITH
C       EACH OTHER ARE COUPLED AND SHOULD BE RESET ACCORDINGLY.
C    THIS PROGRAM SIMULATES VARIABLE ANGLE SAMPLE SPINNING NMR SPECTRA
C      (NOT SPINNING SIDEBANDS).IF FAST SPINNING CAN AVERAGE   FIRST ORDER
C      SATELLITES TO ZERO, THE SIMULATION PROGRAM WHICH USES AVERAGE
C      HAMILTONIAN THEORY WILL BE APPROPRIATE (M. M. MARICQ AND
C      J. S. WAUGH, J. CHEM. PHYS. 70, 3300(1977).
C      STATIC   SPECTRA CAN BE SIMULATED BY SETTING THE VARIABLE ANGLE
C      ALP = 0.
C      * DUMMY = FACTOR TO DETERMINE IF SIMULATION IS TO BE NORMAL(ANY
C      NUMBER WHICH IS NOT EQUAL TO 2) OR IF SIMULATION IS TO ADD IN A
```

```
C   BACKGROUND SPECTRUM FROM A FILE(SPECTRUM.DAT). THE VL,PPMIN,PPMAX
C       AND PS MUST BE THE SAME TO ADD. THE RELATIVE RATIOS BETWEEN THE
C       SITES SHOULD BE USED. NORM SHOULD BE 0.
C       AN ARRAY P(K) STORES FREQUENCIES.
C       THE UNIT 2 OUTPUT FILE '   F21    ' KEEPS PARAMETERS.
C       THE UNIT 1 OUTPUT FILE '   F22    ' HAS CHEMICAL SHIFTS
C       AND CORRESPONDING FREQUENCIES.
C       THE UNIT 4 FILE IS A DATA FILE TO EXECUTE THIS PROGRAM(TO ADD A
C       SPECTRUM).
C
C VMAS1.DAT                       VMAS2.DAT
C*TEST1 J.PHYS.CHEM. V94, P591 (1990) *TEST2 J.PHYS.CHEM. V94, P591 (1990)
C*3.5,3.5,26.247,1000,-1700,1700,0      *3.5,3.5,26.247,1000,-3500,3500,0
C*0.142,0.11,127,136,-197,200,1,1      *0.142,0.11,127,136,-197,200,1,0
C*0,0,0,0,360                    *0,0,52,0,360
C
C VMAS3.DAT                       VMAS4.DAT
C*TEST3 J.PHYS.CHEM. V94, P591 (1990) *TEST4 J.PHYS.CHEM. V94, P591 (1990)
C*3.5,0.5,50,1000,-1000,1000,0      *3.5,3.5,26.247,1000,-3500,3500,2
C*14,0.2,50,150,-200,200,1,1      *0.373,0.55,-163,-211,59,200,1,0
C*0,0,60,0,360                    *0,90,7,0,360
C
C VMAS5.DAT                       VMAS6.DAT
C*TEST5 J.CHEM.PHYS. V77, P4360 (1982)*TEST6 J.CHEM.PHYS. V77, P4360 (1982)
C*1.5,0.5,95.25,200,-75,25,0      *1.5,0.5,95.25,200,-85,15,0
C*2.6,0,0,0,0,100,1,1              *2.6,0.3,0,0,0,100,1,0
C*54.74,0,0,0,360              *40,0,0,0,360
C
C   1. THE RESULT OF TEST1 IS A Cs NMR SPECTRUM AT 26.247 MHz WHICH SHOWS 7
C    TRANSITIONS WITH BOTH QUADRUPOLAR AND CHEMICAL SHIFT ANISOTROPY.
C
```

```
C  2. THE TEST2 YIELDS A Cs NMR SPECTRUM WITH AN EULERIAN ANGLE BETWEEN
C       QUADRUPOLAR AND CHEMICAL SHIFT TENSORS.
C
C  3. THE TEST3 DEMONSTRATES THE EFFECT OF AN EULERIAN ANGLE BETWEEN
C       QUADRUPOLAR AND CHEMICAL SHIFT TENSORS ON A CENTRAL TRANSITION.
C
C  4. IF THERE ARE TWO SITES, THE SUM OF THE SPECTRA CAN BE GENERATED BY
C       USING THE VMAS4.DAT AND THE "SPECTRUM.DAT" WHICH IS RENAMED FROM
C     THE OUTPUT OF VMAS2.DAT("WEIGHT" CAN BE VARIED IN ORDER TO CONSIDER
C       THE RELATIVE RATIO BETWEEN TWO SITES.).
C
C  5. THE TEST5 SIMULATES A MAS SPECTRUM.
C
C  6. THE TEST6 GIVES A VAS POWDER PATTERN WITH A VARIABLE
C       ANGLE 40 DEGREE.
C
C        IMPLICIT REAL*8 (A-H,O-Z)
         CHARACTER*20 F20,F21,F22
         DIMENSION TITLE(18),G(1000),GK(1000),SPTR(1000),PPM(1000)
         DIMENSION ST(720),CT(720),SCT(720),CCT(720),CXCT(720)
         DIMENSION SP(721),CP(721),STP(721),CTP(721),CXP(721)
         DIMENSION HT(1000),BO1(10),BO2(10),BO3(10),BO4(10)
         DIMENSION BO5(10),BO6(10),BO7(10),FINT(10)
C
C        OPEN FILES
C
7        WRITE(*,82)
         READ(*,84,ERR=7) F20
         OPEN(UNIT=4,FILE=F20,STATUS='OLD')
8        WRITE(*,78)
```

```
        READ(*,84,ERR=8) F21
        OPEN(UNIT=1,FILE=F21,STATUS='NEW')
9       WRITE(*,80)
        READ(*,84,ERR=9) F22
        OPEN(UNIT=2,FILE=F22,STATUS='NEW')
C
C       ****************  FORMAT  *************************************
C
12      FORMAT(/)
14      FORMAT(6HSPIN =,F4.1,2X,13HLARMOR FRQ. =,F7.3,1X,3HMHz,2X,
    *   5HQCC =,F7.3,1X,3HMHz,2X,13HASYMM. PAR. =,F7.4)
16      FORMAT(13HSPHERE DIV. =,I4,1X,26HNO. POINTS TO BE PLOTTED =,
    *   F5.0,/,18HMIN. CHEM. SHIFT =,F8.2,1X,18HMAX. CHEM. SHIFT =,
    *   F8.2,3Hppm)
18      FORMAT(28H CHEM. SHIFT PARAMETERS;D11=,F7.2,1X,4HD22=,F7.2,1X,
    *   4HD33=,F7.2,1X,3Hppm)
20      FORMAT('ISO. CHEM. SHIFT =',F7.2,1X,'CHEM. SHIFT DELTA =',F8.3,
    *   1X,'ppm',3X,'CHEM SHIFT ETA=',F7.2)
22      FORMAT(22HGAUSSIAN BROADENNING =,F7.5,1X,20HGAUSSIAN LINEWIDTH
        =,
    *   F10.5,4H kHz)
24      FORMAT(10HDELTA M = ,I1,20H TRANSITIONS BETWEEN,F5.1,
    *   4H AND,F5.1)
28      FORMAT(18A4)
32      FORMAT(2X,17H VARIABLE ANGLE =,F10.7,7H DEGREE,/,
    *   7HALPHA =,F10.6,2X,6HBETA =,F10.6,2X,7HGAMMA =,F10.6,7H DEGREE)
34      FORMAT(2X,'ENTER TITLE')
36      FORMAT(2X,'ENTER SPIN (FOR EXAMPLE I=7/2--->3.5)')
38      FORMAT(8X,'TRANSITIONS TO BE CALCULATED(.5 FOR CENTRAL
    *   TRANSITION)')
40      FORMAT(8X,'LARMOR FREQUENCY IN MHZ')
```

```
42        FORMAT(8X,'NUMBER OF POINTS FOR PLOT    (<1001)')

44        FORMAT(8X,'PLOT MINIMUM IN PPM (FOR EXAMPLE -100)')

46        FORMAT(8X,'PLOT MAXIMUM IN PPM (FOR EXAMPLE 100)')

48        FORMAT(8X,'DUMMY (0 FOR NORM. SIM., 2 TO ADD A SPECTRUM)')

50        FORMAT(34H SPIN,TRAN,VL,PS,PPMIN,PPMAX,DUMMY)

52        FORMAT(2X,'ENTER QUADRUPOLE COUPLING CONSTANT IN MHZ')

54        FORMAT(8X,'ASYMMETRY PARAMETER OF EFG')

56        FORMAT(8X,'3 CSA TENSOR PRINCIPAL COMPONENTS IN PPM')

58        FORMAT(8X,'GAUSSIAN BROADENING IN HZ')

60        FORMAT(8X,'RELATIVE INTENSITY')

62        FORMAT(8X,'1 FOR NORMALIZATION, 0 TO ADD A SPECTRUM')

64        FORMAT(38H QCC,ETA,D11,D22,D33,SIGHZ,WEIGHT,NORM)

66        FORMAT(8X,'VARIABLE ANGLE (54.7356 FOR MASS, 0 FOR STATIC)')

68        FORMAT(8X,'EULERIAN ANGLES, ACQ, BCQ, GCQ')

70        FORMAT(8X,'NUMBER OF POINTS FOR ANGLES (<1001)')

72        FORMAT(20H ALP,ACQ,BCQ,GCQ,ITH)

74        FORMAT(2E12.4)

76        FORMAT('*** THE SPECTRUM.DAT FILE HAS BEEN ADDED.
      *   ADD THE PARAMETER FILE OF THE DATA FILE ***')

78        FORMAT(' ENTER OUTPUT FILE NAME')

80        FORMAT(' ENTER OUTPUT PARAMETER FILE NAME')

82        FORMAT(' ENTER INPUT PARAMETER FILE NAME')

84        FORMAT(A)

86        FORMAT('WEIGHT = ',1F10.6)

88        FORMAT(' PLEASE, DO NOT INTERRUPT.')
          IO=2
C
C         ******   INPUT PARAMETER   *****************************************
C
C         WRITE(*,34)
C         READ(*,28)TITLE
```

```
C       WRITE(*,36)
C       WRITE(*,38)
C       WRITE(*,40)
C       WRITE(*,42)
C       WRITE(*,44)
C       WRITE(*,46)
C       WRITE(*,48)
C       WRITE(*,50)
C       READ(*,*)SPIN,TRAN,VL,PS,PPMIN,PPMAX,DUMMY
C       WRITE(*,52)
C       WRITE(*,54)
C       WRITE(*,56)
C       WRITE(*,58)
C       WRITE(*,60)
C       WRITE(*,62)
C       WRITE(*,64)
C       READ(*,*)QCC,ETA,D11,D22,D33,SIGHZ,WEIGHT,NORM
C       WRITE(*,66)
C       WRITE(*,66)
C       WRITE(*,66)
C       WRITE(*,72)
C       READ(*,*)ALP,ACQ,BCQ,GCQ,ITH
        WRITE(*,88)
        READ(4,28)TITLE
        READ(4,*)SPIN,TRAN,VL,PS,PPMIN,PPMAX,DUMMY
        READ(4,*)QCC,ETA,D11,D22,D33,SIGHZ,WEIGHT,NORM
        READ(4,*)ALP,ACQ,BCQ,GCQ,ITH
C       ************************************************************
        IF(ITH.GT.720.) ITH=720.
        IF(PS.GT.1000.) PS=1000.
        IF(ITH.LT.1.) ITH=90.
```

```
        IF(PS.LT.1.) PS=100.
        NS=PS
        XITH=ITH
        PMIN=VL+(PPMIN*VL/1.0E6)
        PMAX=VL+(PPMAX*VL/1.0E6)
        PR=PMAX-PMIN
        GIP=(PS-1.)/PR
        DO 110 K=1,NS
        G(K)=0.
        GK(K)=0.
        SPTR(K)=0.
        XK=K
        PK=PMIN+(XK-1.)*PR/(PS-1.)
        PPM(K)=(PK-VL)*1.0E6/VL
110     CONTINUE
        SIGKC=SIGHZ/1000.
        SIG=SIGHZ/PR*1.E-6
        CSIGMA=(D11+D22+D33)/3.
        CSDEL=D33-CSIGMA
        IF(CSDEL.EQ.0.) GO TO 120
        CSETA=(D11-D22)/CSDEL
        GO TO 130
120     CSETA=0.
130     CISO=CSIGMA/1.E6
        CDEL=CSDEL/1.E6
        RAD=1.745329252E-2
        ANG=RAD*ALP
        CAL=COS(ANG)
        CXC=CAL*CAL
        CTC=CXC*CXC
        THC=.5*(3.*CXC-1.)
```

```
TTC=.5*THC
RTA=2.*RAD*ACQ
SINTA=SIN(RTA)
COSTA=COS(RTA)
RBCQ=RAD*BCQ
SINB=SIN(RBCQ)
COSB=COS(RBCQ)
SQSB=SINB*SINB
SQCB=COSB*COSB
RGCQ=RAD*GCQ
SING=SIN(RGCQ)
COSG=COS(RGCQ)
SINTG=2.*SING*COSG
COSTG=COSG*COSG-SING*SING
VLCL=VL*CDEL*THC
AAB=.5*VLCL*(3.*SQCB-1.+CSETA*SQSB*COSTA)
BAB=.25*VLCL*(3.*SQSB+CSETA*(1.+SQCB)*COSTA)
CAB=.5*VLCL*CSETA*COSB*SINTA
DAB=VLCL*SINB*COSB*(-3.+CSETA*COSTA)
EAB=-VLCL*CSETA*SINB*SINTA
BABS=BAB*SINTG
BABC=BAB*COSTG
CABS=CAB*SINTG
CABC=CAB*COSTG
DABS=DAB*SING
DABC=DAB*COSG
EABS=EAB*SING
EABC=EAB*COSG
BSCC=BABS+CABC
BCNCS=BABC-CABS
DCES=DABC+EABS
```

```
        DSEC=-DABS+EABC
        MPH=ITH+1
        IF(ACQ+BCQ+GCQ.EQ.0.) XITH=2.*XITH
        DO 100 I=1,ITH
        XI=I
        CT(I)=1.-2.*(XI-.5)/XITH
        CCT(I)=CT(I)*CT(I)
        ST(I)=SQRT(1.-CCT(I))
        SCT(I)=ST(I)*CT(I)
        CXCT(I)=CCT(I)*CCT(I)
100     CONTINUE
        IF(ETA+CSETA+ACQ+BCQ+GCQ.EQ.0) MPH=1
        DO 200 M=1,MPH
        XPI=M
        PHI=3.1415927*(XPI-1.)/XITH
        TPHI=2.*PHI
        SP(M)=SIN(PHI)
        CP(M)=COS(PHI)
        STP(M)=SIN(TPHI)
        CTP(M)=COS(TPHI)
        CXP(M)=CTP(M)*CTP(M)
200     CONTINUE
        EE=ETA*ETA
        EE6=EE/6.
        SS1=SPIN*(SPIN+1.)
        IF(SPIN-0.5) 140,140,150
140     VQQ=0.0
        GO TO 160
150     VQQ=3.*QCC/(2.*SPIN*(2.*SPIN-1.))
160     FACT=VQQ*VQQ/(12.*VL)
        VIS=VL*(1.+CISO)-.5*AAB
```

```
        FATA=FACT*ETA
        XMAG=-TRAN+1.
        ITRAN=2*TRAN
        MAG=1
170     CONTINUE
        XX1=XMAG*(XMAG-1.)
        A=24.*XX1-4.*SS1+9.
        B=6.*XX1-2.*SS1+3.
        C=-VQQ*(XMAG-.5)
        VMA=.5*A*(1.-CTC)-.125*B*(1.+6.*CXC+CTC)
        VMB=.5*A*(1.-3.*CXC+4.*CTC)-.5*B*(1.-CTC)
        VMC=1.5*A*(CXC-CTC)-.375*B*(1.-2.*CXC+CTC)
        ETAC=ETA*C
        BO1(MAG)=-TTC*C+FACT*(.375*VMA+EE6*VMB+.25*VMC)
        BO2(MAG)=BCNCS+TTC*ETAC+FATA*(.25*VMA-.5*VMC)
        BO3(MAG)=FACT*EE*(VMA/24.-VMB/6.+.25*VMC)
        BO4(MAG)=1.5*AAB+3.*TTC*C+FACT*((EE6-.75)*VMA
     *  +(1.5-EE6)*VMB-1.5*VMC)
        BO5(MAG)=-BCNCS-TTC*ETAC+FATA*(-VMB+2.*VMC)
        BO6(MAG)=FACT*(.375*VMA-1.5*VMB+2.25*VMC)
        BO7(MAG)=FATA*(-.25*VMA+VMB-1.5*VMC)
        FINT(MAG)=SS1-XX1
        IF(XMAG.GE.TRAN) GO TO 190
180     XMAG=XMAG+1
        MAG=MAG+1
        GO TO 170
190     CONTINUE
        MGMX=MAG
        AMP=WEIGHT/XPI
        DO 300 I=1,ITH
        DO 300 JP=1.MPH
```

```
        DO 300 MAG=1,MGMX
        BOC=BO3(MAG)*CXP(JP)
        EUN1=VIS+BO1(MAG)+BO2(MAG)*CTP(JP)-BSCC*STP(JP)+BOC
        EUN2=BO4(MAG)+BO5(MAG)*CTP(JP)+BSCC*STP(JP)-2.*BOC
        EUN3=BO6(MAG)+BO7(MAG)*CTP(JP)+BOC
        EUN4=DCES*CP(JP)+DSEC*SP(JP)
        FNN=EUN1+EUN2*CCT(I)+EUN3*CXCT(I)+EUN4*SCT(I)-PMIN
        NN=FNN*GIP+1.5
        IF(NN.LT.2.OR.NN.GT.NS) GO TO 300
        GK(NN)=GK(NN)+FINT(MAG)
300     CONTINUE
        DO 210 LL=1,NS
        GK(LL)=GK(LL)*AMP.
210     CONTINUE
        CALL SHIFT(NS,GK)
        CALL CONVOL(NS,SIG,GK,0,SPTR)
        IF(DUMMY.NE.2) GO TO 230
        OPEN(UNIT=3,FILE='SPECTRUM.DAT',STATUS='OLD')
        READ(3,74)(PPM(K),HT(K),K=1,NS)
        WRITE(*,76)
        DO 220 N=1,NS
        SPTR(N)=SPTR(N)+HT(N)
220     CONTINUE
230     IF(NORM.NE.1) GO TO 240
        CALL UNITY(NS,SPTR)
C       ******************  OUTPUT  **********************************
C
240     WRITE(1,74)(PPM(K),SPTR(K),K=1,NS)
C
C       ******** OUTPUT FOR INPUT PARAMETER   *************************
C
```

```
      WRITE(IO,28)TITLE
      WRITE(IO,12)
      WRITE(IO,16)ITH,PS,PPMIN,PPMAX
      WRITE(IO,12)
      WRITE(IO,14)SPIN,VL,QCC,ETA
      WRITE(IO,24)ITRAN,TRAN,-TRAN
      WRITE(IO,12)
      WRITE(IO,18)D11,D22,D33
      WRITE(IO,20)CSIGMA,CSDEL,CSETA
      WRITE(IO,12)
      WRITE(IO,32)ALP,ACQ,BCQ,GCQ
      WRITE(IO,12)
      WRITE(IO,22)SIG,SIGKC
      WRITE(IO,12)
      WRITE(IO,86)WEIGHT
C     ****************************************************************
      STOP
      END
C
      SUBROUTINE CONVOL(NS,SIGMA,G,NDERIV,SA)
C     CONVOL DOES A CONVOLUTION OF THE NTH GAUSSIAN DERIVATIVE WITH
C     AN ARBITRARY FUNCTION. N IS 0,1,2, OR 3. ENTRY IS NS POINTS,
C     SIGMA THE GAUSSIAN HALF-WIDTH, G CONTAINING THE FUNCTION TO BE
C     CONVOLUTED AND NDERIV THE VALUE OF N. THE OUTPUT IS IN SA.
C
C     IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION G(1000),SA(1000),XSTORE(1000)
      IF(SIGMA.LE.0.) RETURN
      RX=1./(2.*(SIGMA*NS)**2)
      SQRX=RX**.5
      DO 28 L=1,NS
```

```
        SA(L)=0.
        XL=L-1
        POW=XL*XL*RX
        IF(POW-30.) 26,27,27
26      XSTORE(L)=EXP(-POW)
29      GO TO 28
27      XSTORE(L)=0.
28      CONTINUE
        IF(NDERIV.LT.0.OR.NDERIV.GT.3) NDERIV=1
        MOVE=NDERIV+1
        GO TO (20,30,40,50) MOVE
20      CONTINUE
        DO 22 I=1,NS
        DO 22 J=1,NS
        XXX=I-J
        IF(XXX) 23,24,24
23      L=J-I+1
        GO TO 22
24      L=I-J+1
22      SA(J)=SA(J)+G(I)*XSTORE(L)
        RETURN
30      CONTINUE
        DO 32 I=1,NS
        DO 32 J=1,NS
        XXX=I-J
        IF(XXX) 33,34,34
33      L=J-I+1
        GO TO 32
34      L=I-J+1
32      SA(J)=SA(J)+G(I)*XSTORE(L)*XXX*SQRX
        RETURN
```

```
40        CONTINUE
          DO 42 I=1,NS
          DO 42 J=1,NS
          XXX=I-J
          IF(XXX) 43,44,44
43        L=J-I+1
          GO TO 42
44        L=I-J+1
42        SA(J)=SA(J)+G(I)*XSTORE(L)*(1.-2.*XXX*XXX*RX)
          RETURN
50        CONTINUE
          DO 52 I=1,NS
          DO 52 J=1,NS
          XXX=I-J
          IF(XXX) 53,54,54
53        L=J-I+1
          GO TO 52
54        L=I-J+1
52        SA(J)=SA(J)-G(I)*XSTORE(L)*(-6.*XXX*SQRX
     *    +4.*XXX*XXX*XXX*RX*SQRX)
          RETURN
          END
C
          SUBROUTINE SHIFT(NS,G)
C             SHIFT SUBTRACTS A FIXED AMOUNT FROM THE POWDER
C             PATTERN TO MINIMIZE THE EFFECTS OF THE CONVOLUTION
C             AT THE ENDS OF THE SIMULATED SPECTRUM.
C
C         IMPLICIT REAL*8 (A-H,O-Z)
          DIMENSION G(1000)
          GMIN=G(1)
```

```
      DO 1 I=2,NS
      IF(GMIN.LE.G(I)) GO TO 1
      GMIN=G(I)
1     CONTINUE
      DO 2 I=1,NS
      G(I)=G(I)-GMIN
2     CONTINUE
      RETURN
      END
C

      SUBROUTINE UNITY(NS,SPTR)
C     UNITY NORMALIZES INTENSITY AFTER CONVOLUTION (MAXIMUM PEAK
C     HEIGHT = 1.).
C     IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION SPTR(1000)
      STMAG=SPTR(1)
      DO 1 I=1,NS
      IF(STMAG.GE.SPTR(I)) GO TO 1
      STMAG=SPTR(I)
1     CONTINUE
      DO 2 I=1,NS
      SPTR(I)=SPTR(I)/STMAG
2     CONTINUE
      RETURN
      END
```