

Effective Spatial Averaging for NMR Second Moment Calculation

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A very effective method of spatial averaging for Van Vleck's second moment calculation for polycrystalline materials with internal rotation of atoms is presented. Compared with other methods of spatial averaging described in literature, the method presented in this paper is tens of times faster. The details of calculation presented in this paper enable their immediate application in numerical evaluation of the second moment for structures with internal reorientation. © 1998 Academic Press

INTRODUCTION

Calculation of the NMR second moment for polycrystalline material with internal rotation of atoms cannot be performed analytically, except for very simple models, such as the interaction between two atoms, one in the center of the sphere, the other moving continuously over the entire surface of this sphere. In a general case—different groups of atoms moving independently—only a numerical approach is feasible. In such calculations the most time consuming task is the spatial averaging required to get the second moment value for a polycrystalline sample.

An isotropic average of function $F(\gamma, \delta)$, where γ and δ are the polar and the azimuthal angles of any arbitrary direction on which the function F depends, is given by

$$\bar{F} = \frac{\int_0^{2\pi} \int_0^\pi F(\gamma, \delta) \sin \gamma d\gamma d\delta}{\int_0^{2\pi} \int_0^\pi \sin \gamma d\gamma d\delta}. \quad [1]$$

For the means of numerical evaluation of this average, we must replace integrals by sums, which leads to

$$\overline{F}_{num} = \frac{\sum_{k=0}^{N-1} \sum_{l=0}^{M-1} F(l\Delta\gamma, k\Delta\delta) \sin(l\Delta\gamma) \Delta\gamma \Delta\delta}{\sum_{k=0}^{N-1} \sum_{l=0}^{M-1} \sin(l\Delta\gamma) \Delta\gamma \Delta\delta}, \quad [1a]$$

where

$$\Delta\gamma = \pi/M \quad \text{and} \quad \Delta\delta = 2\pi/N.$$

The numerically calculated average \overline{F}_{num} would be equal to the exact average \bar{F} in the unrealistic limit $N \rightarrow \infty$ and $M \rightarrow \infty$. For any practical calculations, where the evaluation of function $F(l\Delta\gamma, k\Delta\delta)$ might require minutes of CPU time for every value of l and k , N and M must be kept as small as possible from the accuracy point of view. Different methods were developed to optimize the relation between the values of N , M , and the final accuracy. One of the latest papers concerning this problem (*1*) gives references to the previously presented solutions.

In this paper we show that in the case of the NMR second moment calculation, averaging over the azimuthal angle δ with $N = 3$ is exactly equivalent to averaging with integrating over this angle. This leads to a tremendous decrease in computational time compared with any previously described method for “fast” averaging.

DETAILED CONSIDERATION

We wish to compute the NMR second moment for the polycrystalline material with internal rotation of atoms. For the clarity of the presentation we will consider the dipole–dipole interaction between two atoms only. Any more complicated structure would require additional summation, which can be very easily added to the computer program, but would make our consideration more difficult to follow.

Let us consider two atoms i and j which can reorient independently. We denote their positions in the Cartesian coordinate system as $x_i, y_i, \text{ and } z_i$ for the atom i and $x_j, y_j, \text{ and } z_j$ for the j atom. Atom i can take n positions denoted $1, 2, \dots, n$, and atom j can take m positions denoted $1, 2, \dots, m$. The direction of magnetic field H_0 is defined by the polar angle γ and the azimuthal angle δ in the same coordinate system. This situation is depicted in Fig. 1. For our calculation we need to consider the vector r_{ij} connecting these two atoms, and the angle Θ_{ij} between this vector and the H_0 directions.

As a function to be averaged we choose the expression

$$B_{ij} = (3 \cos^2 \Theta_{ij} - 1) r_{ij}^{-3}, \quad [2]$$

as it is the only orientation dependent part in the NMR second moment formulae (2). The constants required in Eq.

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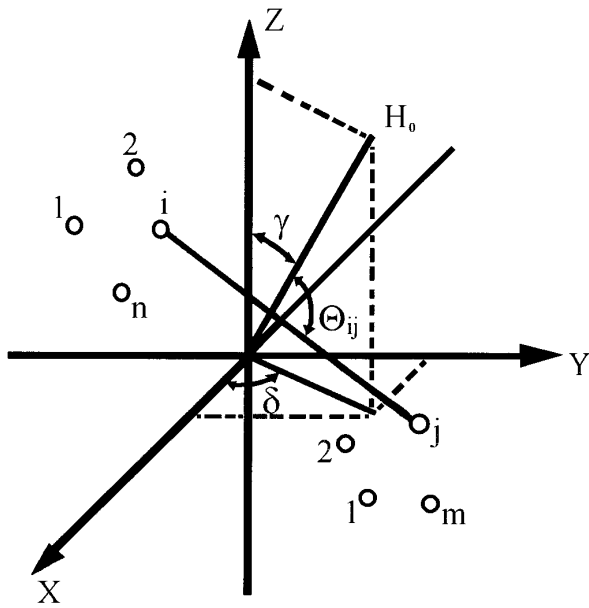


FIG. 1. Schematic representation of the reorienting atoms. The symbols are defined in the text.

[2] for B_{ij} to represent the dipole–dipole interaction between atoms i and j can be omitted from the calculation, as the constant does not influence any type of averaging. For further calculations we will express B_{ij} from Eq. [2] throughout x , y , and z coordinates of atoms i and j . Such an approach is dictated by the fact that in practice we usually know these coordinates from the X-ray studies. Taking

$$r_{ij} = (\Delta x_{ij}^2 + \Delta y_{ij}^2 + \Delta z_{ij}^2)^{1/2}, \quad [3]$$

where

$$\Delta x_{ij} = x_i - x_j, \quad \Delta y_{ij} = y_i - y_j, \quad \text{and} \quad \Delta z_{ij} = z_i - z_j,$$

and calculating the Cartesian components of the magnetic field H_0 ,

$$\begin{aligned} H_x &= H_0 \sin \gamma \cos \delta, \\ H_y &= H_0 \sin \gamma \sin \delta, \\ H_z &= H_0 \cos \gamma, \end{aligned} \quad [4]$$

one can express the $\cos \Theta_{ij}$ as

$$\begin{aligned} \cos \Theta_{ij} &= (\Delta x_{ij} \sin \gamma \cos \delta + \Delta y_{ij} \sin \gamma \sin \delta \\ &\quad + \Delta z_{ij} \cos \gamma) r_{ij}^{-1}. \end{aligned} \quad [5]$$

Finally, the B_{ij} from Eq. [2] can be written as

$$\begin{aligned} B_{ij} &= 3(\Delta x_{ij}^2 \sin^2 \gamma \cos^2 \delta + \Delta y_{ij}^2 \sin^2 \gamma \sin^2 \delta \\ &\quad + \Delta z_{ij}^2 \cos^2 \gamma + 2\Delta x_{ij} \Delta y_{ij} \sin^2 \gamma \sin \delta \cos \delta \end{aligned}$$

$$\begin{aligned} &+ 2\Delta x_{ij} \Delta z_{ij} \sin \gamma \cos \gamma \cos \delta \\ &+ 2\Delta y_{ij} \Delta z_{ij} \sin \gamma \cos \gamma \sin \delta) r_{ij}^{-5} - r_{ij}^{-3}. \end{aligned} \quad [6]$$

We assume reorientation of both atoms, and the average value of B_{ij} with respect to these reorientations we denote by $\langle B \rangle$. It can be calculated from the equation

$$\langle B \rangle = \frac{\sum_{i=1}^n \sum_{j=1}^m B_{ij}}{n \cdot m}. \quad [7]$$

Substituting B_{ij} from Eq. [6] into Eq. [7], we get

$$\begin{aligned} \langle B \rangle &= a_1 \sin^2 \gamma \cos^2 \delta + a_2 \sin^2 \gamma \sin^2 \delta \\ &\quad + a_3 \cos^2 \gamma + a_4 \sin^2 \gamma \sin \delta \cos \delta \\ &\quad + a_5 \sin \gamma \cos \gamma \cos \delta \\ &\quad + a_6 \sin \gamma \cos \gamma \sin \delta - a_7, \end{aligned} \quad [8]$$

with

$$\begin{aligned} a_1 &= 3 \langle \Delta x_{ij}^2 r_{ij}^{-5} \rangle, \\ a_2 &= 3 \langle \Delta y_{ij}^2 r_{ij}^{-5} \rangle, \\ a_3 &= 3 \langle \Delta z_{ij}^2 r_{ij}^{-5} \rangle, \\ a_4 &= 6 \langle \Delta x_{ij} \Delta y_{ij} r_{ij}^{-5} \rangle, \\ a_5 &= 6 \langle \Delta x_{ij} \Delta z_{ij} r_{ij}^{-5} \rangle, \\ a_6 &= 6 \langle \Delta y_{ij} \Delta z_{ij} r_{ij}^{-5} \rangle, \end{aligned}$$

and

$$a_7 = \langle r_{ij}^{-3} \rangle.$$

The $\langle \rangle$ brackets denote average with respect to the reorientations.

Now we need to square $\langle B \rangle$ from Eq. [8], which results in

$$\begin{aligned} \langle B \rangle^2 &= a_1^2 \sin^4 \gamma \cos^4 \delta + a_2^2 \sin^4 \gamma \sin^4 \delta + a_3^2 \cos^4 \gamma \\ &\quad + a_4^2 \sin^4 \gamma \sin^2 \delta \cos^2 \delta + a_5^2 \sin^2 \gamma \cos^2 \gamma \cos^2 \delta \\ &\quad + a_6^2 \sin^2 \gamma \cos^2 \gamma \sin^2 \delta + a_7^2 + 2a_1 a_2 \sin^4 \gamma \\ &\quad \times \sin^2 \delta \cos^2 \delta + 2a_1 a_3 \sin^2 \gamma \cos^2 \gamma \cos^2 \delta \\ &\quad + 2a_1 a_4 \sin^4 \gamma \sin \delta \cos^3 \delta + 2a_1 a_5 \sin^3 \gamma \\ &\quad \times \cos \gamma \cos^3 \delta + 2a_1 a_6 \sin^3 \gamma \cos \gamma \sin \delta \cos^2 \delta \\ &\quad - 2a_1 a_7 \sin^2 \gamma \cos^2 \delta + 2a_2 a_3 \sin^2 \gamma \cos^2 \gamma \sin^2 \delta \\ &\quad + 2a_2 a_4 \sin^4 \gamma \sin^3 \delta \cos \delta + 2a_2 a_5 \sin^3 \gamma \end{aligned}$$

$$\begin{aligned}
& \times \cos \gamma \sin^2 \delta \cos \delta + 2a_2 a_6 \sin^3 \gamma \cos \gamma \sin^3 \delta \\
& - 2a_2 a_7 \sin^2 \gamma \sin^2 \delta + 2a_3 a_4 \sin^2 \gamma \cos^2 \gamma \\
& \times \sin \delta \cos \delta + 2a_3 a_5 \sin \gamma \cos^3 \gamma \cos \delta \\
& + 2a_3 a_6 \sin \gamma \cos^3 \gamma \sin \delta - 2a_3 a_7 \cos^2 \gamma \\
& + 2a_4 a_5 \sin^3 \gamma \cos \gamma \sin \delta \cos^2 \delta + 2a_4 a_6 \sin^3 \gamma \\
& \times \cos \gamma \sin^2 \delta \cos \delta - 2a_4 a_7 \sin^2 \gamma \sin \delta \cos \delta \\
& + 2a_5 a_6 \sin^2 \gamma \cos^2 \gamma \sin \delta \cos \delta - 2a_5 a_7 \sin \\
& \times \gamma \cos \gamma \cos \delta - 2a_6 a_7 \sin \gamma \cos \gamma \sin \delta. \quad [9]
\end{aligned}$$

We will perform the spatial averaging defined by Eq. [1] in two steps. First we calculate the integral of $\langle B \rangle^2$ over the polar angle γ , and then over the azimuthal angle δ . Performing the first step yields

$$\begin{aligned}
W &= \int_0^\pi \langle B \rangle^2 \sin \gamma d\gamma \\
&= c_1 \cos^4 \delta + c_2 \sin^4 \delta + c_3 \\
&+ c_4 \sin^2 \delta \cos^2 \delta + c_5 \cos^2 \delta + c_6 \sin^2 \delta \\
&+ c_7 + c_{12} \sin^2 \delta \cos^2 \delta + c_{13} \cos^2 \delta + c_{14} \sin \delta \cos^3 \delta \\
&+ c_{17} \cos^2 \delta + c_{23} \sin^2 \delta + c_{24} \sin^3 \delta \cos \delta \\
&+ c_{27} \sin^2 \delta + c_{34} \sin \delta \cos \delta + c_{37} \\
&+ c_{47} \sin \delta \cos \delta + c_{56} \sin \delta \cos \delta, \quad [10]
\end{aligned}$$

with

$$\begin{aligned}
c_1 &= \frac{16}{15} a_1^2, & c_2 &= \frac{16}{15} a_2^2, & c_3 &= \frac{2}{3} a_3^2, \\
c_4 &= \frac{16}{15} a_4^2, & c_5 &= \frac{4}{15} a_5^2, & c_6 &= \frac{4}{15} a_6^2, \\
c_7 &= 2a_7^2, & c_{12} &= \frac{32}{15} a_1 a_2, & c_{13} &= \frac{8}{15} a_1 a_3, \\
c_{14} &= \frac{32}{15} a_1 a_4, & c_{17} &= -\frac{8}{3} a_1 a_7, & c_{23} &= \frac{8}{15} a_2 a_3, \\
c_{24} &= \frac{32}{15} a_2 a_4, & c_{27} &= -\frac{8}{3} a_2 a_7, & c_{34} &= \frac{8}{15} a_3 a_4, \\
c_{37} &= -\frac{4}{3} a_3 a_7, & c_{47} &= -\frac{8}{3} a_4 a_7, & \text{and } c_{56} &= \frac{8}{15} a_5 a_6.
\end{aligned}$$

The integral over the polar angle γ from the denominator of Eq. [1] gives 2; therefore, the spatial average of $\langle B \rangle^2$ can be written as

$$\overline{\langle B \rangle^2} = \frac{\int_0^{2\pi} W d\delta}{2 \int_0^{2\pi} d\delta}. \quad [11]$$

Substituting W from Eq. [10] into Eq. [11] and evaluating all integrals gives

$$\begin{aligned}
\overline{\langle B \rangle^2} &= \frac{3}{16} c_1 + \frac{3}{16} c_2 + \frac{1}{2} c_3 + \frac{1}{16} c_4 + \frac{1}{4} c_5 \\
&+ \frac{1}{4} c_6 + \frac{1}{2} c_7 + \frac{1}{16} c_{12} + \frac{1}{4} c_{13} \\
&+ \frac{1}{4} c_{23} + \frac{1}{4} c_{17} + \frac{1}{4} c_{27} + \frac{1}{2} c_{37}. \quad [12]
\end{aligned}$$

Now we return to Eq. [11] and replace integration over azimuthal angle δ by summation. We will get

$$\overline{\langle B \rangle_{num}^2} = \frac{\sum_{k=0}^{N-1} W(k\Delta\delta) \Delta\delta}{2 \sum_{k=0}^{N-1} \Delta\delta} = \frac{\sum_{k=0}^{N-1} W(k\Delta\delta)}{2 \cdot N}, \quad [11a]$$

which is the spatial average of $\langle B \rangle^2$ from Eq. [9] calculated through integration over the polar angle γ and summation over the azimuthal angle δ .

Calculating the value of Eq. [11a] for $N \geq 3$, we will get exactly the same value as from the integration over the azimuthal angle δ given in Eq. [12].

CONCLUSIONS

Performing the numerical spatial averaging for the second moment calculation, we can limit the summation over the azimuthal angle to three values (0 , $\frac{2\pi}{3}$, and $\frac{4\pi}{3}$) of this angle and obtain accuracy equal to that achievable by integration over the angle. This means a dramatic decrease in the CPU time needed for calculation compared to any of the methods presented in the literature.

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