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An Efficient Method for Evaluating the Effect of Lattice Vibrations on the NMR Second Moment

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An improved algorithm for the evaluation of intra- and inter-molecular contributions to the NMR second moment is presented. The final expressions are given in terms of quadratic forms of the second moment tensor which depends on the equilibrium crystal structure as well as on parameters describing average atomic and molecular motion, assuming the latter to be expressible by the rigid body motion formalism. These parameters are readily available once the crystal structure of the compound considered has been determined by X-ray or neutron diffraction methods, and may serve for the evaluation of second moments of single-crystal as well as polycrystalline specimens. The use of the second moment tensor formulation considerably reduces the computational effort which is required by such calculations when the Van Vleck formula is being directly evaluated.

An explicit introduction of crystal symmetry into the second moment tensor formalism, presented in this paper, further enhances the efficiency and ease of application of the proposed method.

INTRODUCTION

The mean square half width of NMR absorption line from a dipolarly coupled solid, known as the NMR second moment and calculable from Van Vleck's equation (*1*), depends on the equilibrium positions of the nuclear spin carriers as well as on their average motion (*2*). A general treatment of the effects of motion on this quantity, is obviously a rather difficult undertaking. However, in the important case of harmonically vibrating rigid groups of atoms (not necessarily chemical molecules) it was shown (*3, 4, 5*) that the effect of group vibrations on the NMR second moment can be estimated for single crystal and for crystalline powder specimens. This was done by averaging a Taylor expansion of the dipolar interaction term about the equilibrium positions of the nuclei, over nuclear displacements, and an expression of

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the following general form has been obtained (*5*)

$$\langle(3\cos^2\theta_{ij}-1)/r_{ij}'^3\rangle=(3\cos^2\theta_{ij}-1)/r_{ij}^3+f_1(\hat{\mathbf{H}};\mathbf{r}_{ij},\langle\mathbf{d}_{ij}\rangle)$$
$$+f_2(\hat{\mathbf{H}};\mathbf{r}_{ij},\langle\mathbf{d}_{ij}\mathbf{d}_{ij}^T\rangle)\qquad[1]$$

where $\hat{\mathbf{H}}$ is a unit vector along the external magnetic field, $\mathbf{r}_{ij}'$ and $\mathbf{r}_{ij}$ are instantaneous and equilibrium internuclear vectors respectively, relating nuclei i and j, and $\mathbf{d}_{ij}=\mathbf{r}_{ij}'-\mathbf{r}_{ij}$ is the difference of instantaneous displacements of nuclei i and j from their equilibrium positions. The averages $\langle\mathbf{d}\rangle$ and $\langle\mathbf{d}\mathbf{d}^T\rangle$ have been expressed in terms of atomic (*6*) and rigid-group (*7*) vibration tensors, which are readily available from structure determinations by X-ray and neutron diffraction. The above procedure enables one to evaluate the contributions, to the vibration-affected second moment, of nuclei i and j belonging to the same rigid group or to different groups, and thus the effect of vibrations on the intramolecular, intermolecular and intersegment contributions (cf. *5*) can be accounted for. Another merit of the above method is that it employs experimentally available vibration parameters which have a sound lattice dynamical interpretation (*8*, *9*). However, the computation of the second moment, using [1] for a large number of magnetic field orientations, is not very economical since all the lattice summations involved must be evaluated anew for each orientation of $\hat{\mathbf{H}}$. This problem is less disturbing in calculations of the second moment for powder specimens (*3*, *4*) since all the orientations of the magnetic field are then averaged out.

In a recent study of the second moment (*10*) and its applications (*10*, *11*), Van Vleck's equation (*1*) was represented as a quadratic form of the second moment tensor (*10*) and thereby a separation of crystal-dependent and field-dependent quantities has been achieved. This was done by writing

$$\langle(3\cos^2\theta_{ij}'-1)/r_{ij}'^3\rangle=\hat{\mathbf{H}}^T\langle\mathbf{Q}\rangle_{ij}\hat{\mathbf{H}}\qquad[2]$$

where

$$\mathbf{Q}_{ij}=\frac{3\mathbf{r}_{ij}'\mathbf{r}_{ij}'^T}{r_{ij}'^5}-\frac{\mathbf{I}}{r_{ij}'^3}\qquad[3]$$

and by a subsequent reduction of the quadratic form in [2] to a scalar product. Thus, as shown in (*10*)

$$\hat{\mathbf{H}}^T\langle\mathbf{Q}\rangle\mathbf{H}=\sum_{k=1}^{5}q_k\bar{a}_k\qquad[4]$$

where

$$q_k\doteq 2\pi^{1/2}\phi_k(\hat{\mathbf{H}}),\qquad a_k=\frac{4\pi^{1/2}}{5r'^3}\phi_k(\mathbf{r}')$$

and the functions $\phi(p)$ are the real spherical harmonics, listed in Table 1. The second moment is therefore given by

$$M_2\propto\sum_{i=1}^{N}\sum_{j}\langle\langle(3\cos^2\theta_{ij}'-1)/r_{ij}'^3\rangle^2\rangle\equiv\mathbf{q}^T\mathbf{M}\mathbf{q}\qquad[5]$$

TABLE 1

THE REAL SECOND-ORDER SPHERICAL HARMONICS AS FUNCTIONS OF $\mathbf{p} = (p_1, p_2, p_3)$ [a]

$\phi_1 = (5/16\pi)^{1/2}[(p_1^2 + p_2^2 - 2p_3^2)/|\mathbf{p}|^2]$
$\phi_2 = (15/16\pi)^{1/2}[(p_1^2 - p_2^2)/|\mathbf{p}|^2]$
$\phi_3 = (15/4\pi)^{1/2}(p_1p_2/|\mathbf{p}|^2)$
$\phi_4 = (15/4\pi)^{1/2}(p_1p_3/|\mathbf{p}|^2)$
$\phi_5 = (15/4\pi)^{1/2}(p_2p_3/|\mathbf{p}|^2)$

[a] The vector $\mathbf{p}$ represents the magnetic field or the interproton vector and its components p_i, $i = 1, 2, 3$, are referred to a cartesian system, constructed with the aid of basis vectors of the crystal and/or reciprocal lattices. For example, $\mathbf{p} = \hat{\mathbf{e}}_1 p_1 + \hat{\mathbf{e}}_2 p_2 + \hat{\mathbf{e}}_3 p_3$, where $\hat{\mathbf{e}}_1 = \mathbf{a}/|\mathbf{a}|$, $\hat{\mathbf{e}}_2 = \mathbf{b}^*/|\mathbf{b}^*|$ and $\hat{\mathbf{e}}_3 = \hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2$. If a crystal is transferred from an automatic diffractometer to the NMR spectrometer, its orientation matrix (*16*) can be used to advantage.

where

$$\mathbf{M} = \sum_{i=1}^{N} \sum_{j} \langle \bar{\mathbf{a}}_{ij} \bar{\mathbf{a}}_{ij} \rangle \qquad [6]$$

is the second moment tensor and N is the number of relevant nuclei in the unit cell. The inner brackets in [5] and the bar over $\mathbf{a}$ in [4] and [6] denote averaging over vibrations and fast reorientations while the outer brackets in [5] and [6] imply averaging over slow motions and orientations of crystallites in a powder sample.

Apart from the advantageous separation, shown in [4] and [5], which permits one to evaluate only once all the lattice sums needed for $\mathbf{M}$, thus considerably improving the efficiency of second moment calculation, this formulation has several advantages over Van Vleck's formula: (a) the second moment of crystalline powder is simply $\mathrm{Tr}(\mathbf{M})$, (b) it is possible to introduce crystal symmetry into the second moment formula, and reduce further the computing effort and (c) the second moment tensor [6] can be used to evaluate relaxation constants.

Regarding the influence of motion, an expression for the tensor $\mathbf{M}$, taking into account the intramolecular contribution of rigid-body librations, has been derived (*10*) and was found to be equivalent to the corresponding Van Vleck-type expression (*3*). This libration-affected second moment formula (*10*) was further elaborated elsewhere (*12*).

Another representation of the second moment, in terms of a fourth-order tensor, has been proposed (*13*) and the non-vanishing components of this tensor, for the various point groups, have been obtained by analogy with a treatment of the tensor of elastic constants (*14*).

It was noted, during this study, that the second moment tensor can also be represented in a somewhat less elegant but equally efficient manner to that indicated by [4] and [6]. Since $\mathbf{Q}$, as given by [3], is a symmetric second order tensor, we can write

$$\hat{\mathbf{H}}^T\langle\mathbf{Q}\rangle\hat{\mathbf{H}} = \sum_{k=1}^{6} \eta_k F_k \qquad [7]$$

where

$$\boldsymbol{\eta}^T = (H_1^2, H_2^2, H_3^2, 2H_1H_2, 2H_2H_3, 2H_1H_3) \qquad [8]$$

$$\mathbf{F}^T = (\langle Q_{11}\rangle, \langle Q_{22}\rangle, \langle Q_{33}\rangle, \langle Q_{12}\rangle, \langle Q_{23}\rangle, \langle Q_{13}\rangle), \qquad [9]$$

H_i are cartesian components of the unit vector $\hat{\mathbf{H}}$ and $\langle Q_{mn}\rangle$ are independent components of the tensor $\langle\mathbf{Q}\rangle$ (atomic indices are omitted here). We shall refer to [7] as the quadric representation. As will be shown below, it is possible, with [7], to introduce symmetry operators explicitly into the corresponding quadratic form of the new second moment tensor and hence, the simplifications due to any crystal symmetry can readily be incorporated into a computer program designed for second moment calculations.

It is seen from [4] and [7] that, whether the irreducible spherical-harmonics representation or the quadric representation is being used, it is necessary to average all six independent components of the tensor $\mathbf{r}'\mathbf{r}'^T/r'^5$. The purpose of this article is to express these thermal averages in terms of crystallographic vibration parameters and to derive general expressions for the second moment tensors from which the intramolecular, intermolecular and intersegment contributions to the vibration-affected second moment can be conveniently evaluated.

THERMAL AVERAGES

The functions to be averaged over instantaneous displacements of the spin carriers are

$$f'_{mn} = \frac{X'_m X'_n}{r'^5} \quad \text{and} \quad Q_{mn} = 3f'_{mn} - \frac{1}{r'^3}$$

where f_{mn} and Q_{mn} are to be used in conjunction with equations [6] and [7] respectively. The procedure we shall employ consists of expanding either function in a Taylor series about the equilibrium internuclear separation vector and averaging the displacement moments which appear in the second and third terms of the expansion. These are the only correction terms considered since the harmonic approximation is being assumed. Thus, e.g.

$$\langle f'_{mn}\rangle = f_{mn} + \frac{\partial}{\partial X_p}(f_{mn})\langle d_p\rangle + \frac{1}{2}\frac{\partial^2}{\partial X_q \partial X_p}(f_{mn})\langle d_q d_p\rangle \qquad [10]$$

Assuming that each of the nuclei is part of a rigid body, a condition which is approximately satisfied by many organic molecules, it was shown (*5*) that

$$\begin{aligned}\langle \mathbf{d}_{ij}^{AB}\rangle &= \langle \mathbf{u}_i^A\rangle - \langle \mathbf{u}_j^B\rangle \\ &= \tfrac{1}{2}\{[\mathbf{L}^A - \mathrm{Tr}(\mathbf{L}^A)\mathbf{I}]\boldsymbol{\rho}_i^A - [\mathbf{L}^B - \mathrm{Tr}(\mathbf{L}^B)\mathbf{I}]\boldsymbol{\rho}_j^B\}\end{aligned} \qquad [11]$$

where $\mathbf{L}^A$ and $\mathbf{L}^B$ are the libration tensors [7] of the rigid groups A and B to which the nuclei i and j respectively belong, and $\boldsymbol{\rho}_i^A, \boldsymbol{\rho}_j^B$ are equilibrium position vectors of these nuclei, referred to the centers of libration (7) of groups A and B. Furthermore, it was shown (5) that

$$\begin{aligned}\langle \mathbf{dd}^T \rangle_{ij} &= \langle \mathbf{u}_i^A(\mathbf{u}_i^A)^T \rangle + \langle \mathbf{u}_j^B(\mathbf{u}_j^B)^T \rangle - \langle \mathbf{u}_i^A(\mathbf{u}_j^B)^T \rangle - \langle \mathbf{u}_j^B(\mathbf{u}_i^A)^T \rangle \\ &\equiv \mathbf{U}_i^A + \mathbf{U}_j^B - \mathbf{U}_{ij}^{AB} - \mathbf{U}_{ji}^{BA} \qquad [12]\end{aligned}$$

The first two tensors on the r.h.s. of [12] are the anisotropic vibration tensors of nuclei i and j, which are experimentally available from X-ray structure analyses, while the other two describe the average correlated motion of these nuclei (cf. equation [3.3] of Ref. (15)).

A detailed analysis of Eq. [12] in terms of the rigid body tensors **T** (translation), **L** (libration) and **S** (screw-motion) [7], and the corresponding coupling tensors describing correlated rigid body motion, has been presented elsewhere (5) and we shall quote here the resulting forms of $\langle \mathbf{dd}^T \rangle$, which are applicable to some important special cases,

(1) Nuclei i and j belong to the same rigid group:

$$\langle \mathbf{dd}^T \rangle_{ij}^A = \mathbf{v}_{ij} \mathbf{L}^A \mathbf{v}_{ij}^T \qquad [13]$$

where

$$\mathbf{v}_{ij} = \begin{pmatrix} 0 & X_3 & -X_2 \\ -X_3 & 0 & X_1 \\ X_2 & -X_1 & 0 \end{pmatrix}$$

X_k being cartesian components of the equilibrium internuclear vector $\mathbf{r}_{ij}^A$.

(2) Nuclei i and j belong to different molecules:

$$\langle \mathbf{dd}^T \rangle_{ij}^{AB} \cong \mathbf{U}_i^A + \mathbf{U}_j^B \qquad [14]$$

In fact, the complete Eq. [12] should have been used in this case, and it will indeed be so employed as soon as the coupling tensors $\mathbf{U}_{ij}^{AB}$ are experimentally available or reliably calculable. One might argue, however, that upon an accumulation of numerous intermolecular internuclear contributions a large number of cancellations will occur and coupling may be negligible. This may be true, but remains to be further examined.

(3) Nuclei i and j belong to different rigid segments of the same non-rigid molecule:

$$\langle \mathbf{dd}^T \rangle_{ij}^{AB} = \mathbf{W}_i^A \mathbf{L}^A (\mathbf{W}_i^A)^T + \mathbf{W}_j^B \mathbf{L}^B (\mathbf{W}_j^B)^T \qquad [15]$$

where

$$\mathbf{W} = \begin{pmatrix} 0 & \rho_3 & -\rho_2 \\ -\rho_3 & 0 & \rho_1 \\ \rho_2 & -\rho_1 & 0 \end{pmatrix},$$

ρ_i^A has the same meaning as in [11] and $\mathbf{L}^A, \mathbf{L}^B$ are libration tensors of the two segments considered. The assumptions underlying [15] are (a) the two segments A

and B have equal translation tensors and (b) the librational motions of A and B are not correlated.

It should be pointed out that the intermolecular vibrational correction to the second moment is usually smaller than the intramolecular one (*4*) and the neglect of correlated motion in cases 2 and 3 above does not appear to be a very drastic approximation.

The required averages, to be used with the two above described tensorial representations of the second moment, are evaluated by carrying out the differentiations indicated in [10] and using the expressions for $\langle \mathbf{d} \rangle$ and $\langle \mathbf{dd}^T \rangle$, presented in this section, for the cases considered.

The corresponding expressions are given by

$$\langle f'_{mn} \rangle = AR_{mn} + \sum_{p=1}^{3} B_p \frac{\partial}{\partial X_p} (R_{mn}) + C_{mn} \qquad [16]$$

where

$$R_{mn} = X_m X_n$$

$$A = \left[\frac{1}{r^5} - \frac{5}{r^7} \mathbf{r}^T \langle \mathbf{d} \rangle + \frac{35}{2r^9} \mathbf{r}^T \langle \mathbf{dd}^T \rangle \mathbf{r} - \frac{5}{2r^7} \mathrm{Tr}(\langle \mathbf{dd}^T \rangle) \right]$$

$$B_p = \frac{1}{r^5} \langle d_p \rangle - \frac{5}{r^7} \sum_{q=1}^{3} \langle d_p d_q \rangle X_q$$

$$C_{mn} = \frac{1}{r^5} \langle d_m d_n \rangle$$

and

$$\langle Q_{mn} \rangle = 3 \langle f'_{mn} \rangle - \left\langle \frac{1}{r'^3} \right\rangle \qquad [17]$$

where

$$\left\langle \frac{1}{r'^3} \right\rangle = \frac{1}{r^3} - \frac{3}{r^5} \mathbf{r}^T \langle \mathbf{d} \rangle + \frac{15}{2r^7} \mathbf{r}^T \langle \mathbf{dd}^T \rangle \mathbf{r} - \frac{3}{2r^5} \mathrm{Tr}(\langle \mathbf{dd}^T \rangle)$$

The expressions [16] and [17] are completely general, within the framework of the harmonic approximation. Since, however, the intramolecular contribution to the second moment is likely to be of greatest interest, it is worthwhile to present explicit expressions for this particular case. This can be done either by substituting [11], with $A = B$, and [13] into each of [16] and [17], or by the methods of Refs. (*3*) and *10*). The result, in which the summation convention has been implied, is

$$\langle f'_{mn} \rangle = \frac{1}{r^5} \{ R_{mn} + R_{mp} [L_{pn} - \mathrm{Tr}(\mathbf{L}) \delta_{pn}] + R_{nq} [L_{qm} - \mathrm{Tr}(\mathbf{L}) \delta_{qm}] + v_{mp} L_{pq} v_{qn} \qquad [18]$$

and

$$\langle Q_{mn} \rangle = 3 \langle f'_{mn} \rangle - \frac{1}{r^3} \qquad [19]$$

where L_{np} is a component of the libration tensor of the group considered and v_{mp} has the same meaning as in Eq. [13].

As mentioned in the introduction, a result equivalent to [18] has been derived in [10] and was further developed in [12] in connection with applications to quadrupole and dipole interactions in solids.

We shall now discuss the introduction of crystal symmetry into the second moment in its quadratic representation and then proceed to a summary of the method.

THE SECOND MOMENT AND CRYSTAL SYMMETRY

We shall start with the quadric representation outlined in the introduction and rewrite Eqs. [7], [8] and [9]:

$$\hat{\mathbf{H}}^T\langle\mathbf{Q}\rangle\mathbf{H} = \sum_{k=1}^{6} \eta_k F_k \qquad [7]$$

$$\boldsymbol{\eta}^T = (H_1^2, H_2^2, H_3^2, 2H_1H_2, 2H_2H_3, 2H_1H_3) \qquad [8]$$

$$\mathbf{F}^T = (\langle Q_{11}\rangle, \langle Q_{22}\rangle, \langle Q_{33}\rangle, \langle Q_{12}\rangle, \langle Q_{23}\rangle, \langle Q_{13}\rangle) \qquad [9]$$

where the components of $\mathbf{F}$ are given by [17] and [19] for the general and intramolecular cases respectively.

If nucleus i belongs to the pth asymmetric unit and nucleus j is anywhere in the crystal, then to the vector $\mathbf{r}_p = \mathbf{r}_j - \mathbf{r}_i$ there corresponds a symmetry related one, $\mathbf{r}_q^{(s)} = \mathbf{P}^{(s)}\mathbf{r}_p$ where $\mathbf{P}^{(s)}$ is the rotational part of the space group operation transforming the pth into the qth asymmetric unit. Hence, the tensor $\langle\mathbf{Q}\rangle$ transforms as

$$\langle\mathbf{Q}\rangle^{(s)} = \mathbf{P}^{(s)}\langle\mathbf{Q}\rangle\mathbf{P}^{(s)T} \qquad [20]$$

or, in component form,

$$\langle Q_{mn}\rangle^{(s)} = P_{mp}^{(s)} P_{nq}^{(s)} \langle Q_{pq}\rangle. \qquad [21]$$

Since $\langle\mathbf{Q}\rangle$ is a symmetric tensor, we have

$$\frac{\partial\langle Q_{mn}\rangle^{(s)}}{\partial\langle Q_{pq}\rangle} = \begin{cases} P_{mp}^{(s)} P_{nq}^{(s)}, & p = q \\ P_{mp}^{(s)} P_{nq}^{(s)} + P_{mq}^{(s)} P_{np}^{(s)}, & p \neq q \end{cases} \qquad [22]$$

where mn and pq refer to the upper triangles of $\langle\mathbf{Q}\rangle^{(s)}$ and $\langle\mathbf{Q}\rangle$ respectively. Comparing [9], [21] and [22], we can obtain a suitable representation of the symmetry operation as a 6×6 matrix $\boldsymbol{\Pi}^{(s)}$, where

$$\mathbf{F}^{(s)} = \boldsymbol{\Pi}^{(s)}\mathbf{F} \quad \text{or} \quad F_k^{(s)} = \Pi_{kl}^{(s)} F_l^{(s)} \qquad [23]$$

The indices k and l in [23] correspond to the three dimensional representation according to

k	1	2	3	4	5	6
mn	11	22	33	12	23	31

If the unit cell contains k asymmetric units, the second moment is proportional to

$$\begin{aligned} M_2' &= \sum_{s=1}^{k} \left(\sum_{i=1}^{N/k} \sum_{j=1}^{\text{all}} (\hat{\mathbf{H}}^T \langle \mathbf{Q} \rangle_{ij}^{(s)} \hat{\mathbf{H}})^2 \right) \\ &= \sum_{s=1}^{k} \sum_{i \neq j}\sum \boldsymbol{\eta}^T \mathbf{F}_{ij}^{(s)} \mathbf{F}_{ij}^{(s)T} \boldsymbol{\eta} \\ &= \sum_{s=1}^{k} \boldsymbol{\eta}^T \boldsymbol{\Pi}^{(s)} \Big(\sum_{i \neq j}\sum \mathbf{F}_{ij} \mathbf{F}_{ij}^T \Big) \boldsymbol{\Pi}^{(s)T} \boldsymbol{\eta}. \end{aligned} \qquad [24]$$

We may now compute the separate contributions of the k asymmetric units for a single direction of the magnetic field or use the contribution of a single unit and k symmetry-related directions of the field vector. The latter approach will reduce the computing time by a factor of (nearly) k and is of course preferable. The second moment thus reduces to

$$M_2 \propto \sum_{s=1}^{k} \boldsymbol{\eta}^{(s)T} \boldsymbol{\sigma} \boldsymbol{\eta}^{(s)} \qquad [25]$$

where

$$\boldsymbol{\eta}^{(s)} = \boldsymbol{\Pi}^{(s)T} \boldsymbol{\eta} \quad \text{and} \quad \boldsymbol{\sigma} = \sum_{i=1}^{N/k} \sum_{j=1}^{\text{all}} \mathbf{F}_{ij} \mathbf{F}_{ij}^T \qquad [26]$$

We have achieved a reduction of the second moment to a sum of quadratic forms which explicitly take into account the crystal symmetry. The appropriately transformed symmetry operations are here applied to the magnetic field dependent vector $\boldsymbol{\eta}$ rather than to the structure which, along with its lattice vibrations and possible reorientations, has to be considered only once.

One of the merits of the quadric representation is that it can directly utilize crystallographic results in their conventional form, as the $\boldsymbol{\Pi}^{(s)}$ matrices are readily constructed from the 3×3 $\mathbf{P}^{(s)}$ symmetry operations with the aid of [22].

DISCUSSION

As shown in the foregoing sections, the second moment can now be efficiently evaluated, while taking into account atomic and molecular motion, via the **U**, **T**, **L** and **S** tensors which are available or derivable from conventional crystal structure analyses.

In order to enhance the ease of application of the expressions derived above, to various types of problems, two quadratic-form representations of the second moment have been proposed. The spherical-harmonics representation, introduced in (*10*) and further developed in this paper, is, because of its irreducibility, the appropriate one to use in attempts at determining structural parameters of hydrogen nuclei from second moment measurements. The general vibration correction to the second moment is evaluated from Eqs. [11], [12] (or the variants [13], [14] and [15]) and [16] which permit, with the aid of Table 1, performing the summation leading to the second moment tensor [6] and the second moment M_2, as given by the r.h.s. of [5].

The other representation, put forward in this paper and termed 'the quadric representation", lead to a (reducible) 6 × 6 second moment tensor and enables one to introduce explicitly the crystal symmetry into the computation of the second moment. It should be noted that no group theoretical arguments are required for the transformation of Van Vleck's equation to the quadratic form of the second moment tensor (cf. [24]) and the required enlarged (6×6) symmetry operation matrices can be constructed in a simple manner using [22] with conventional (3 × 3) matrices of the crystal point group considered. If the construction of a cartesian system, and transformations of vectors and tensors (including symmetry operations) thereto are allowed for, the quadric representation permits an evaluation of the vibrationally corrected second moment, using as input a conventional description of a crystal structure. The second moment calculation proceeds, in the general case, through equations [11], [12], [16] and [17] from which M_2 can be evaluated with the aid of [25] using the second moment tensor given by [26].

It should be pointed out that the two representations of the second moment are completely equivalent and nearly equally efficient. The differences in programming and computing effort are probably marginal and the choice depends mainly on the type of representation the user is accustomed to. For example, it is believed that crystallographers will prefer the quadric representation, which appears in many phases of crystal structure analysis, while spectroscopists will favor the irreducible spherical-harmonics representation. Since the subject discussed here is an interdisciplinary one, it may only benefit from easily accessible approaches.

The second moment tensor, in either representation, can thus be readily used in evaluating efficiently the second moment for an arbitrary orientation of a single crystal relative to the external magnetic field (cf. Eqs. [5] and [25]). The second moment calculation for powder specimens is also quite straightforward. For the spherical-harmonics representation it is given simply by the trace of the corresponding second moment tensor, as shown in (*10*). For the quadric representation, we have

$$M_2(\text{powder}) \propto \frac{k}{15}[3(\sigma_{11}+\sigma_{22}+\sigma_{33})+4(\sigma_{44}+\sigma_{55}+\sigma_{66})+2(\sigma_{12}+\sigma_{23}+\sigma_{13})] \qquad [27]$$

where k is the number of asymmetric units in the unit cell, σ_{ij} are components of the second moment tensor σ appearing in [26] and the numerical coefficients in [27] are related to the non-vanishing integrals of the form $\int_{\text{sph}} \eta_i \eta_j \, d\tau$, which appear in the orientational averaging of equation [25].

The second moment tensor formalism is also applicable to the study of relaxation constants (*11*).

As is evident from the foregoing, the main computational effort is spent on the evaluation of the effects of motion on the intermolecular contribution to the second moment. These effects were, until recently (*4*), neglected altogether without proper justification. The few available examples (*4, 5*) indicate that, in fact, the intramolecular contribution predominates in cases of large libration. This is also consistent with the qualitative arguments presented in (*10*). However, this cannot be regarded as a rule, if only in view of an opposite behavior in pyrene and anthracene (*4*). Generally speaking, the relative importance of intra- and intermolecular contributions depends on the packing arrangement and dynamics of the crystal considered.

Since these properties are specific to any given crystal, it is difficult to make a priori predictions which will permit a decision as to when the neglect of the intermolecular vibrational correction is really justified. It is the opinion of the present authors that this has to be carefully considered in each particular case, depending on the compound studied, and if the purpose of the study in question calls for more than approximate results, that both contributions should be evaluated. It is hoped that the present paper will prove to be useful for this purpose.

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