

The Temperature Factor of an Atom in a Rigid Vibrating Molecule.

II. Anisotropic Thermal Motion

BY G. S. PAWLEY

Department of Natural Philosophy, Edinburgh University, Scotland

AND B. T. M. WILLIS

Atomic Energy Research Establishment, Harwell, Berkshire, England

(Received 16 July 1969)

The analysis in part I is generalized to any crystal containing rigid molecules which undergo anisotropic translational and librational motion about a site fixed by symmetry. The treatment is correct to terms in $\langle u_i^2 \rangle$ and $\langle \omega_i^2 \rangle$, where $\langle u_i^2 \rangle$ is the mean-square translational displacement of the molecule along the i th axis and $\langle \omega_i^2 \rangle$ is the mean-square angular libration about the same axis. The first-order treatment to terms in $\langle u_i^2 \rangle$ and $\langle \omega_i^2 \rangle$ is shown to be equivalent to the rigid-body theory in current use.

1. Introduction

It has recently been shown by Johnson (1969) that the conventional model for least-squares structure refinement, based on individual atomic temperature factors, can be improved by the addition of higher cumulants. Cumulants of the first order are simply the positional parameters for the atoms, and the second-order cumulants are the anisotropic (Gaussian) temperature factors. For an atom on a site of point symmetry 1, there are ten third-order cumulants giving rise to terms with triple products of the Miller indices; these terms are added to the first-order cumulants in the structure-factor expression. Likewise the fourth-order cumulants give rise to extra terms added to the temperature factors. In order to fit ten third-cumulant parameters and fifteen fourth-cumulant parameters per atom, a large amount of accurate data is required, unless some physically reasonable model can be put forward which imposes constraints on the values of these cumulants and so reduces the number of variable parameters.

In this paper we show how third- and fourth-order cumulants can be evaluated for a rigid molecule undergoing anisotropic thermal motion, without introducing any more parameters than those needed for specifying the second-order cumulants. The molecule must be such that there is a point within it which is fixed by symmetry. The maximum number of variable parameters for each molecule, other than atomic positional parameters, is twelve – six representing the mean-square translational displacement tensor \mathbf{T} of the molecule and six representing the mean-square libration tensor \mathbf{L} . The corresponding calculation for isotropic motion and its application to the analysis of neutron diffraction data on hexamethylenetetramine are described in papers I (Willis & Pawley, 1970) and III (Duckworth, Willis & Pawley, 1970). Our notation follows that in I.

2. Atomic temperature factors

We assume that the internal modes of vibration of the molecule make a negligible contribution to the atomic temperature factors $\exp[-W_{\kappa}(\mathbf{Q})]$, so that these factors are determined entirely by the tensors \mathbf{T} and \mathbf{L} . Within the harmonic approximation, \mathbf{T} gives rise to second-cumulant terms only in the expression for $\exp[-W_{\kappa}(\mathbf{Q})]$, whereas \mathbf{L} gives rise to higher-cumulant terms also. In this section we shall calculate the second and higher-cumulant terms contributed by the libration tensor \mathbf{L} .

Referring to equation (2.4b) of paper I, the quantity

$$-W^{\text{lib}}(\mathbf{Q}) = \ln \langle \exp(i\mathbf{Q} \cdot \mathbf{u}^{\text{lib}}) \rangle$$

must be expressed in terms of \mathbf{L} for a molecule with a unique fixed point. The completely general case of a molecule without such a unique point involves a considerably more complicated analysis.

2.1 Expression for $\langle \exp(i\mathbf{Q} \cdot \mathbf{u}^{\text{lib}}) \rangle$

Let us consider the molecule in a unit orthogonal coordinate system. If the equilibrium position for any atom in the molecule is denoted by $\mathbf{r} = (r_1, r_2, r_3)$, the thermal displacement of the atom due to libration is given by equation (I. 2.7). It is not possible to transform the molecular axes to make

$$r_1 = r_2 = 0$$

as in paper I, and so the expression for the librational displacement must be written out in full. The first component of this expression is

$$u_1^{\text{lib}} = (\omega_2 r_3 - \omega_3 r_2) \left(1 - \frac{1}{6}\omega^2\right) + [\omega_1(\omega_2 r_2 + \omega_3 r_3) - (\omega_2^2 + \omega_3^2)r_1] \left(\frac{1}{2} - \frac{1}{4}\omega^2\right) \quad (1)$$

where

$$\omega^2 = \omega_1^2 + \omega_2^2 + \omega_3^2.$$

The other two components can be obtained by cyclic permutation of indices.

As equation (1) is true for any orthogonal coordinate system, let us choose the system in such a way that the potential function for the librating molecule can be expressed in the form

$$V(\omega) = V_0 + \frac{1}{2} \left(\frac{\omega_1^2}{\Omega_1} + \frac{\omega_2^2}{\Omega_2} + \frac{\omega_3^2}{\Omega_3} \right), \quad (2)$$

where there are no cross terms $\omega_i\omega_j$ for $i \neq j$. (This transformation of coordinates is discussed later in § 2.2.) Notice here that Ω_i are the diagonal components of a 3×3 matrix which must transform as a second-rank tensor. The coordinate system is chosen so that this matrix is diagonal: off-diagonal components disappear from all the equations which follow, making their transformation properties difficult to determine. Further, let us define h_1, h_2, h_3 as the Miller indices transformed into this coordinate system, so that the equation (I. 2.11) becomes

$$\mathbf{Q} = 2\pi(h_1, h_2, h_3). \quad (3)$$

($a_0 = 1$ for a unit orthogonal coordinate system.) Writing $y = \mathbf{Q} \cdot \mathbf{u}^{1b}$, then

$$y = 2\pi \{ [h_1(\omega_2 r_3 - \omega_3 r_2) + \dots + \dots] (1 - \frac{1}{6}\omega^2) + [h_1(\omega_1\omega_2 r_2 + \omega_1\omega_3 r_3 - \omega_2^2 r_1 - \omega_3^2 r_1) + \dots + \dots] \times (\frac{1}{2} - \frac{1}{24}\omega^2) \}. \quad (4)$$

The symbols $+\dots+\dots$ indicate addition of terms related to the first by cyclic permutation of the indices.

By evaluating $\langle y \rangle$, $\langle y^2 \rangle$, $\langle y^3 \rangle$ and $\langle y^4 \rangle$, $\langle \exp(i\mathbf{Q} \cdot \mathbf{u}^{1b}) \rangle$ can be found from equation (I. 2.25) correct to the fourth order in y , where the angular brackets indicate mean values. This equation is

$$\begin{aligned} \ln \langle \exp iy \rangle &= i \langle y \rangle - \frac{1}{2} \langle y^2 \rangle + \frac{1}{6} \langle y^3 \rangle - \frac{i}{6} \langle y^4 \rangle \\ &\quad - \frac{i}{3} \langle y \rangle^3 + \frac{i}{2} \langle y \rangle \langle y^2 \rangle + \frac{1}{24} \langle y^4 \rangle - \frac{1}{4} \langle y \rangle^4 \\ &\quad - \frac{1}{8} \langle y^2 \rangle^2 - \frac{1}{6} \langle y \rangle \langle y^3 \rangle + \frac{1}{2} \langle y \rangle^2 \langle y^2 \rangle. \end{aligned} \quad (5)$$

To obtain $\langle z \rangle$ where z is any function of ω , we use the relation

$$\begin{aligned} \langle z \rangle &= \frac{\iiint_{-\infty}^{\infty} z \exp \left[-\frac{1}{2} \left(\frac{\omega_1^2}{\Omega_1} + \frac{\omega_2^2}{\Omega_2} + \frac{\omega_3^2}{\Omega_3} \right) \right] d\omega_1 d\omega_2 d\omega_3}{\iiint_{-\infty}^{\infty} \exp \left[-\frac{1}{2} \left(\frac{\omega_1^2}{\Omega_1} + \frac{\omega_2^2}{\Omega_2} + \frac{\omega_3^2}{\Omega_3} \right) \right] d\omega_1 d\omega_2 d\omega_3} \end{aligned} \quad (6)$$

Substituting a few simple values for z :

$$\left. \begin{aligned} z = \omega_1^2, \quad \langle z \rangle &= \Omega_1 (2\pi\Omega_1)^{1/2} / (2\pi\Omega_1)^{1/2} = \Omega_1 \\ z = \omega_1^4, \quad \langle z \rangle &= 3\Omega_1^2 \\ z = \omega_2^2 \omega_3^2, \quad \langle z \rangle &= \Omega_2 \Omega_3 \\ z = \omega_1^n, \quad \langle z \rangle &= 0 \text{ for } n \text{ odd} \end{aligned} \right\} \quad (7)$$

Thus to obtain $\langle y^n \rangle$, equation (4) is raised to the n th power, the terms are grouped as coefficients of powers of ω_i , discarding those terms containing ω_i^m , $m \neq 2, 4$, and the remaining terms are substituted with equations (7). This assumes that terms of higher order than ω^4 can be neglected. In this way the following equations are obtained:

$$\begin{aligned} \frac{\langle y \rangle}{2\pi} &= h_1 \left[-\frac{1}{2}\Omega_2 - \frac{1}{2}\Omega_3 + \frac{1}{24}(2\Omega_2\Omega_3 + \Omega_3\Omega_1 + \Omega_1\Omega_2 + 3\Omega_2^2 + 3\Omega_3^2) \right] r_1 + \dots + \dots \\ \frac{\langle y^2 \rangle}{4\pi^2} &= h_1^2 \left[\Omega_2 r_3^2 + \Omega_3 r_2^2 + \Omega_2^2 (\frac{1}{4}r_1^2 - r_3^2) + \Omega_3^2 (\frac{1}{4}r_1^2 - r_2^2) + \Omega_2\Omega_3 (\frac{1}{2}r_1^2 - \frac{1}{3}r_2^2 - \frac{1}{3}r_3^2) + \Omega_3\Omega_1 (\frac{1}{4}r_3^2 - \frac{1}{3}r_2^2) + \Omega_1\Omega_2 (\frac{1}{4}r_2^2 - \frac{1}{3}r_3^2) \right] + \dots + \dots \\ &\quad + h_2 h_3 \left[-2\Omega_1 + \frac{7}{2}\Omega_1^2 + \Omega_2\Omega_3 + \frac{7}{6}\Omega_3\Omega_1 + \frac{7}{6}\Omega_1\Omega_2 \right] r_2 r_3 + \dots + \dots \\ \frac{\langle y^3 \rangle}{8\pi^3} &= h_1^3 \left[-\frac{9}{2}\Omega_2^2 r_3^2 - \frac{9}{2}\Omega_3^2 r_2^2 - \frac{3}{2}\Omega_2\Omega_3 (r_2^2 + r_3^2) \right] r_1 + \dots + \dots \\ &\quad + h_1^2 h_2 \left[\Omega_3^2 (9r_1^2 - \frac{9}{2}r_2^2) + \Omega_2\Omega_3 (3r_1^2 - \frac{9}{2}r_3^2) + \Omega_3\Omega_1 (3r_3^2 - \frac{3}{2}r_2^2) - \frac{9}{2}\Omega_1\Omega_2 r_2^2 \right] r_2 + \dots + \dots \\ &\quad + h_1^2 h_3 \left[\Omega_2^2 (9r_1^2 - \frac{9}{2}r_3^2) + \Omega_2\Omega_3 (3r_1^2 - \frac{9}{2}r_2^2) + \Omega_1\Omega_2 (3r_2^2 - \frac{3}{2}r_3^2) - \frac{9}{2}\Omega_3\Omega_1 r_2^2 \right] r_3 + \dots + \dots \\ &\quad + h_1 h_2 h_3 \left[12(\Omega_2\Omega_3 + \Omega_3\Omega_1 + \Omega_1\Omega_2) r_1 r_2 r_3 \right] \\ \frac{\langle y^4 \rangle}{16\pi^4} &= h_1^4 \left[3\Omega_2^2 r_3^4 + 3\Omega_3^2 r_2^4 + 6\Omega_2\Omega_3 r_2^2 r_3^2 \right] + \dots + \dots \\ &\quad + h_1^3 h_2 \left[-12\Omega_3^2 r_1 r_3^2 - 12\Omega_2\Omega_3 r_1 r_2 r_3^2 \right] + \dots + \dots \\ &\quad + h_1^3 h_3 \left[-12\Omega_2^2 r_1 r_3^2 - 12\Omega_2\Omega_3 r_1 r_2 r_3 \right] + \dots + \dots \\ &\quad + h_1^2 h_2 h_3 \left[24\Omega_2\Omega_3 r_1^2 r_2 r_3 - 12\Omega_3\Omega_1 r_2^2 r_3 - 12\Omega_1\Omega_2 r_2^2 r_3^2 \right] + \dots + \dots \\ &\quad + h_1^2 h_3^2 \left[18\Omega_3^2 r_1^2 r_2^2 + 6\Omega_2\Omega_3 r_1^2 r_3^2 + 6\Omega_3\Omega_1 r_2^2 r_3^2 + 6\Omega_1\Omega_2 r_3^4 \right] + \dots + \dots \end{aligned} \quad (8)$$

Substituting equations (8) in equation (5), the terms

$$-\frac{i}{3} \langle y \rangle^3 - \frac{1}{4} \langle y \rangle^4 - \frac{1}{6} \langle y \rangle \langle y^3 \rangle + \frac{1}{2} \langle y \rangle^2 \langle y^2 \rangle$$

can be ignored as these give rise to quantities of order ω^6 . The remaining terms are arranged as coefficients of the products of the indices h_i , ignoring all but the lowest powers of Ω_i within these coefficients. The final expression for $\ln \langle \exp iy \rangle$ works out as

$$\begin{aligned} \ln \langle \exp iy \rangle &= -W^{1b}(\mathbf{Q}) \\ &= 2\pi i h_1 \left[-\frac{1}{2}\Omega_2 - \frac{1}{2}\Omega_3 \right] r_1 + \dots + \dots \end{aligned} \quad (\text{first cumulant})$$

$$\left. \begin{aligned} &+ 4\pi^2 h_1^2 \left[-\frac{1}{2}\Omega_2 r_3^2 - \frac{1}{2}\Omega_3 r_2^2 \right] + \dots + \dots \\ &+ 4\pi^2 h_2 h_3 \left[\Omega_1 r_2 r_3 \right] + \dots + \dots \end{aligned} \right\} \quad (\text{second cumulant})$$

$$\left. \begin{aligned} &+ 8\pi^3 i h_1^3 [(\Omega_2^2 r_3^2 + \Omega_3^2 r_2^2) \frac{1}{2} r_1] + \dots + \dots \\ &+ 8\pi^3 i h_2^3 h_1 [\Omega_3^2 (\frac{1}{2} r_2^2 - r_1^2) \\ &+ (\Omega_2 \Omega_3 - \Omega_3 \Omega_1 + \Omega_1 \Omega_2) \frac{1}{2} r_3^2] r_2 + \dots + \dots \\ &+ 8\pi^3 i h_3^3 h_2 [\Omega_2^2 (\frac{1}{2} r_3^2 - r_1^2) \\ &+ (\Omega_2 \Omega_3 + \Omega_3 \Omega_1 - \Omega_1 \Omega_2) \frac{1}{2} r_2^2] r_3 + \dots + \dots \\ &+ 8\pi^3 i h_1 h_2 h_3 [-(\Omega_2 \Omega_3 + \Omega_3 \Omega_1 \\ &+ \Omega_1 \Omega_2) r_1 r_2 r_3] \end{aligned} \right\} \text{(third cumulant) (9)}$$

where the fourth cumulant vanishes.* If we include the terms in $\Omega_i \Omega_j$ neglected in the first and second cumulant expressions in equation (9), the equation readily reduces to the isotropic form (I. 2.27).

2.2 Expression for temperature factor correct to ω^2

The rigid-body model in current use is accurate only to ω^2 , and it is instructive to derive the corresponding form of equation (9) to this approximation. If equation (9) is rewritten, omitting all terms higher than first order in Ω_i , the resulting expression is

$$\ln \langle \exp(i \mathbf{Q} \cdot \mathbf{u}^{1b}) \rangle = 2\pi i h_1 [-\frac{1}{2} \Omega_2 - \frac{1}{2} \Omega_3] r_1 + \dots + \dots \\ + 4\pi^2 h_1^2 [-\frac{1}{2} \Omega_2 r_3^2 - \frac{1}{2} \Omega_3 r_2^2] + \dots + \dots \\ + 4\pi^2 h_2 h_3 [\Omega_1 r_2 r_3] + \dots + \dots \quad (10)$$

The first term in equation (10) includes the libration correction of Cruickshank (1956), usually applied after refinement is complete, and the remaining terms give the second-order cumulants. These second-order cumulants are equivalent to those used in the refinement procedure of Pawley (1964): they are

$$-2\pi^2 (h_1, h_2, h_3) \begin{pmatrix} 0 & -r_3 & r_2 \\ r_3 & 0 & -r_1 \\ -r_2 & r_1 & 0 \end{pmatrix} \begin{pmatrix} \Omega_1 & 0 & 0 \\ 0 & \Omega_2 & 0 \\ 0 & 0 & \Omega_3 \end{pmatrix} \begin{pmatrix} 0 & r_3 & -r_2 \\ -r_3 & 0 & r_1 \\ r_2 & -r_1 & 0 \end{pmatrix} \begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix} \quad (11)$$

which can be written as a matrix product

$$-2\pi^2 \mathbf{h} \mathbf{V}_i' \mathbf{\Omega} \tilde{\mathbf{V}}_i' \mathbf{h} \quad (12)$$

defining \mathbf{V}_i' for the i th atom. The symbol \sim denotes transpose.

Consider the matrix \mathbf{M} which transforms from the crystal fractional coordinate system to the unit orthogonal system in which the potential function, equation (2), is diagonal. \mathbf{M} is the product of two transformations $\mathbf{B}\mathbf{A}$, \mathbf{A} transforming from the crystal coordinates to a standard unit orthogonal system and \mathbf{B} then transforming into the final system. Thus \mathbf{B} diagonalizes the mean-square librational tensor \mathbf{L}

$$\mathbf{B}\mathbf{L}\tilde{\mathbf{B}} = \mathbf{\Omega}.$$

The expression (12) can be written

$$-2\pi^2 (\mathbf{h}\mathbf{M}) \mathbf{A}^{-1} (\tilde{\mathbf{B}}\mathbf{V}_i' \mathbf{B}) (\tilde{\mathbf{B}}\mathbf{\Omega}\mathbf{B}) (\tilde{\mathbf{B}}\tilde{\mathbf{V}}_i' \mathbf{B}) \tilde{\mathbf{A}}^{-1} (\tilde{\mathbf{M}}\mathbf{h})$$

using $\mathbf{B}^{-1} = \tilde{\mathbf{B}}$ and $\tilde{\mathbf{M}} = \tilde{\mathbf{A}}\tilde{\mathbf{B}}$. This reduces to

$$-2\pi^2 \mathbf{H} \mathbf{A}^{-1} \mathbf{V}_i \mathbf{L} \tilde{\mathbf{V}}_i' \tilde{\mathbf{A}}^{-1} \tilde{\mathbf{H}} \quad (13)$$

where $\mathbf{H} = (H_1, H_2, H_3)$ are the Miller indices in the crystal system and \mathbf{V}_i is as defined by Pawley (1964). The librational contribution to the temperature factor in equation (1) of Pawley (1964) differs from expression (13) above only in the factor $2\pi^2$: this difference arises because in the present paper we define the mean-square librational tensor in the same units as those of Cruickshank (1956).

The above argument establishes the tensor properties of \mathbf{L} . It is important to note that (13) does not contain the transformation \mathbf{B} . Indeed \mathbf{B} is a necessary variable transformation for the treatment of § 2.1, but its purpose is served in expression (13) by the variable nature of all the six independent tensor components of \mathbf{L} . This fact is used in the program which has been written on the basis of the present theory.

3. Computational

Our programming procedure is as follows. At the start of each least-squares cycle, \mathbf{L} is diagonalized giving the matrix \mathbf{B} . All the third-order cumulants are then obtained and used in calculating the structure factor F , but no use is made of these higher cumulants in calculating the differentials $\partial F / \partial L_{ij}$. These differentials are not strictly accurate, but as structure refinement is an iterative process the effect of the errors is only a slowing down of the refinement. In practice, we have found that the refinement is not perceptibly slower than that using the rigid-body model with second-order cumulants only.

The program has been applied to the analysis of the neutron diffraction data of Pawley & Yeats (1969) for perdeuterophthalene. Structure refinements were carried out with second-order cumulants only, and with second- and third-order cumulants: the R indices were 5.10 and 4.95% respectively. This is only a small improvement, but, as the two models were identical apart from the order of the expansion, it is significant. Data of higher accuracy are required before we can hope to observe appreciable improvements using the present theory.

References

- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.
 DUCKWORTH, J. A. K., WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 263.
 JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187.
 PAWLEY, G. S. (1964). *Acta Cryst.* **17**, 457.
 PAWLEY, G. S. & YEATS, E. A. (1969). *Acta Cryst.* **B25**, 2009.
 WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* **A26**, 254.

* We are indebted to Dr C.K. Johnson and to the referee for pointing out an algebraic error in our original expression for equation (9).