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A Model for a Torsional Oscillator in Crystallographic Least-Squares Refinements*

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For an axially symmetric group of n atoms in torsional oscillation about the symmetry axis and with no other modes of motion, the contribution to the structure factor assuming a Gaussian distribution for the angular displacement from the mean angular position is given by a Bessel-function series expression of the same form as the King & Lipscomb [*Acta Cryst.* (1950). **3**, 155–158] expression for a hindered rotator except that their factors $I_m(b)/I_0(b)$ are replaced by factors $\exp[-n^2 m^2 \beta^2/2]$, where β^2 is the mean-square angular displacement. Expressions for the real and imaginary parts of the structure-factor contribution and the derivatives required for least-squares refinement are given. With minor changes the formalism of these expressions applies to the King–Lipscomb hindered rotator. With the addition of factors for other modes of motion, the case with $n=1$ has been programmed and successfully applied by Brown & Chidambaram in the paper following this one.

Introduction

A number of authors have discussed the problem of devising a proper structure-factor expression for an atom in librational motion. For such motion the usual six-parameter thermal factor is not appropriate, since it is derived on the assumption of independent rectilinear harmonic motions in three degrees of freedom. For general discussions and leading references see Cruickshank (1956), Johnson (1970*a, b*), Johnson & Levy (1972), and Maslen (1970). This paper describes a model for use in least-squares refinement for an atom having as principal mode of motion a libration of large amplitude about a single axis. The circumstances leading to the development of the model and the details of its application to the methyl hydrogen atom in copper(II) acetate monohydrate were described preliminarily by Brown & Chidambaram (1967) and are detailed in the accompanying paper by Brown & Chidambaram (1973).

Derivation

Bloch (1932) showed that for the linear quantum-mechanical harmonic oscillator at a given temperature the probability distribution function for displacements x is Gaussian. In analogy, we make the assumption that for an atom in torsional oscillation about a single axis the probability distribution function of positions θ about the mean position γ on a circular arc is the Gaussian function

$$P(\theta) = (2\pi\delta^2)^{-1/2} [\exp -(\theta - \gamma)^2/2\delta^2], \quad (1)$$

where δ^2 is the mean value of $(\theta - \gamma)^2$. Normal probability distributions have been used by Kay & Behrendt (1963) in developing a structure-factor expression for an atom in two-dimensional librational motion and also by Maslen (1968, 1970) for the one-dimensional case. Our treatment differs from that of Kay & Behrendt and that of Maslen in that we do not make the approximation that $\sin \theta = \theta$ in order to obtain an expression in closed form; instead, we develop a series expression, following very closely the derivation of King & Lipscomb (1950) for a hindered rotator. The expression is also generalized for the case of a group of n equal atoms with an n -fold axis of symmetry to corre-

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spond to King & Lipscomb's general expression for a hindered rotator with a potential function of n -fold symmetry.

Suppose an atom R rigidly bonded to atom Q is in librational motion about the center C on the axis through atoms P and Q (Fig. 1). Let the vector \mathbf{r} be defined by the equation

$$\mathbf{r} = {}_R\mathbf{x} - {}_C\mathbf{x}, \quad (2)$$

where ${}_R\mathbf{x}$ and ${}_C\mathbf{x}$ are vectors from the unit-cell origin to R and C , respectively. Let \mathbf{r} , ${}_R\mathbf{x}$, and ${}_C\mathbf{x}$ be the column matrices of components of these three vectors referred to the base vectors $\mathbf{a}_i (i=1, 2, 3)$ of the unit cell. The vector \mathbf{r} can also be specified by the magnitude r and the angle θ measured as shown in Fig. 1 from the line through C parallel to the projection on the r, θ plane of the reciprocal vector \mathbf{h} specified by the column matrix \mathbf{h} of the indices. In Fig. 1, both the reciprocal vector and its projection are drawn through C for convenience.

Let ${}^i\mathbf{u} (i=1, 2, 3)$ be the unit base vectors of a right-handed Cartesian coordinate system such that ${}^1\mathbf{u}$ has the direction P to Q , ${}^2\mathbf{u}$ has the direction of \mathbf{r} for the mean position of atom R (that is, of \mathbf{r} for $\theta = \gamma$), and ${}^3\mathbf{u}$ is along the tangent to the circle at the mean position of R . Let ${}^i u_j$ be the column matrix of components ${}^i u_j$ of ${}^i\mathbf{u}$ referred to the reciprocal base vectors $\mathbf{a}' (j=1, 2, 3)$ of the crystal. The position of C can be specified by the equation

$${}_C\mathbf{x} = {}_Q\mathbf{x} + M({}_Q\mathbf{x} - {}_P\mathbf{x}), \quad (3)$$

where

$$M \equiv L_{CQ}/L_{QP}, \quad (4)$$

and the distances L_{CQ} and L_{QP} (see Fig. 1) are given by the equations

$$L_{CQ} = \sum_i ({}_R x^i - {}_Q x^i) \mathbf{a}_i \cdot {}^i\mathbf{u} \quad (5)$$

$$= \sum_i {}^1 u_i ({}_R x^i - {}_Q x^i), \quad (6)$$

$$L_{QP} = [({}_Q \tilde{\mathbf{x}} - {}_P \tilde{\mathbf{x}}) \mathbf{g} ({}_Q \mathbf{x} - {}_P \mathbf{x})]^{1/2}. \quad (7)$$

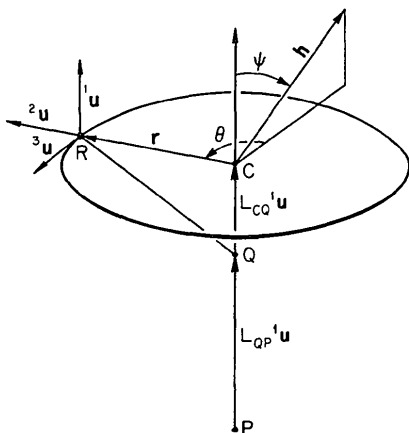


Fig. 1. (See text.)

In (7) \mathbf{g} is the metric tensor for the crystal coordinate system; *i.e.* $g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$. The matrix ${}_Q \tilde{\mathbf{x}}$ is the transpose of ${}_Q \mathbf{x}$, *etc.*

The contribution of atom R to the structure factor $F(\mathbf{h})$ is then written as

$$F_R(\mathbf{h}) = f_R(\mathbf{h}) \exp(2\pi i \tilde{\mathbf{h}} {}_C \mathbf{x}) \int_{\theta} (2\pi \delta^2)^{-1/2} \times \exp[-(\theta - \gamma)^2 / 2\delta^2] \exp(2\pi i \tilde{\mathbf{h}} \mathbf{r}) d\theta, \quad (8)$$

where $f_R(\mathbf{h})$ is the scattering factor of R . Defining h as the magnitude of the reciprocal vector \mathbf{h} and α as $2\pi h r \sin \psi(\mathbf{h})$, where $\psi(\mathbf{h})$ is the angle between ${}^1\mathbf{u}$ and \mathbf{h} , we can write

$$2\pi i \tilde{\mathbf{h}} \mathbf{r} = i\alpha \cos \theta. \quad (9)$$

The exponential $\exp(i\alpha \cos \theta)$ may be written as a uniformly convergent series (Watson, 1948, p. 22; McLachlan, 1955, p. 57):

$$\exp(i\alpha \cos \theta) = \sum_{m=0}^{\infty} i^m \epsilon_m J_m(\alpha) \cos(m\theta), \quad (10)$$

where $J_m(\alpha)$ is the Bessel function of the first kind of order m and ϵ_m is 1 for $m=0$ and 2 otherwise. The integral in equation (8) may then be written

$$I = (2\pi \delta^2)^{-1/2} \sum_{m=1}^{\infty} i^m \epsilon_m J_m(\alpha) \int_{\theta} \exp[-(\theta - \gamma)^2 / 2\delta^2] \times \cos(m\theta) d\theta. \quad (11)$$

If δ^2 is not too large, the exponential term will decrease so rapidly with increasing value of $\theta - \gamma$ that the integral I can be evaluated with negligible error by using the limits $-\infty$ and $+\infty$ in equation (11). Using tabulated integrals, the expression for $F_R(\mathbf{h})$ becomes

$$F_R(\mathbf{h}) = f_R(\mathbf{h}) \exp(2\pi i \tilde{\mathbf{h}} {}_C \mathbf{x}) \sum_{m=1}^{\infty} i^m \epsilon_m J_m(\alpha) \times \cos(m\gamma) \exp(-m^2 \delta^2 / 2) \quad (12)$$

$$= A_R(\mathbf{h}) + iB_R(\mathbf{h}). \quad (13)$$

To correspond with the general King & Lipscomb expression for the hindered rotator with potential function of n -fold symmetry, an expression can be derived by a generalization of our method for a group of equal atoms with n -fold axial symmetry. In equation (8) the factor $\exp(2\pi i \tilde{\mathbf{h}} \mathbf{r})$, equivalent to $\exp(i\alpha \cos \theta)$, is replaced by $\sum_{l=1}^n i\alpha \cos(\theta + 2\pi l/n)$; individual terms in this sum are expanded as in equation (10); each resulting function $\cos[m(\theta + 2\pi l/n)]$ is expanded as the cosine of the sum of two angles; finally, after some simplification and an integration corresponding to that equation (11), the resulting structure-factor contribution is

$$F_{nR}(\mathbf{h}) = n f_R(\mathbf{h}) \exp(2\pi i \tilde{\mathbf{h}} \cdot \mathbf{c} \cdot \mathbf{x}) \sum_{m=0}^{\infty} i^{nm} \varepsilon_m J_{nm}(\alpha) \times \cos(nm\gamma) \exp(-n^2 m^2 \delta^2 / 2) \quad (14)$$

$$= A_{nR}(\mathbf{h}) + i B_{nR}(\mathbf{h}). \quad (15)$$

The angle γ in equation (14) defines the rest position on the circle of one reference atom of the n atoms of the group. The expression for $F_{nR}(\mathbf{h})$ in equation (14) is of the same form as the King-Lipscomb general expression, except that the exponential $\exp(-n^2 m^2 \delta^2 / 2)$ in (14) replaces the King-Lipscomb factor $I_m(b)/I_0(b)$, where $I_m(b)$ is the modified Bessel function and $b = V_o / 2kT$.

Johnson & Levy (1972) have pointed out that our procedure in deriving equation (14) is equivalent to using the generalization for n -fold axial symmetry of the probability distribution function for Brownian diffusion on a circle, which is also called the 'wrapped-up' normal distribution in the mathematical literature (Stephens, 1963; Gumbel, Greenwood & Durand, 1953; Wintner, 1933). They also point out that the King-Lipscomb derivation amounts to application of a generalization of the 'circular normal' distribution (von Mises, 1918; Breitenberger, 1963; Stephens, 1963; Gumbel, Greenwood & Durand, 1953). We prefer our own derivation and that of King & Lipscomb because they are more physical, but it is useful to know that there is a body of literature on these distributions. For example, it is known (Stephens, 1963) that for the unimodal case ($n=1$ in our notation) for values of b up to 4.0 the circular normal distribution used by King & Lipscomb may be closely approximated by the wrapped-up normal distribution by appropriate choice of values of the parameter δ^2 . The close correspondence of the two distributions in this sense suggests that at least for the unimodal case, the only one we have applied, our method and the King-Lipscomb method should be nearly equivalent. Our preference for our own method is basically a preference for dealing in programming with exponential functions instead of modified Bessel functions. The King-Lipscomb assumption of a cosine potential function is no less arbitrary than our assumption of a Gaussian distribution.

Derivatives and programming

For a structure-factor least-squares calculation using equation (14) the derivatives of $A_{nR}(\mathbf{h})$ and $B_{nR}(\mathbf{h})$ with respect to M , r , γ , and δ^2 are needed. For convenience in presenting expressions for these derivatives, we define several sum functions. Let S_{cgnp} be defined by

$$S_{cgnp} = \sum_{\substack{nm \\ \text{even}}} (-1)^{nm/2} \varepsilon_m n^p m^p J_{nm}(\alpha) \times \cos(nm\gamma) \exp(-n^2 m^2 \delta^2 / 2), \quad (16)$$

where $m=1, 2, \dots, \infty$; let S_{sgnp} be the corresponding sum with $\cos(nm\gamma)$ replaced by $\sin(nm\gamma)$; let S_{cunp} and

S_{sunp} be corresponding sums but over odd values of nm and with the factors $(-1)^{nm/2}$ replaced by factors $(-1)^{(nm+1)/2}$; let S'_{cgnp} and so forth be the corresponding sums with $J_{nm}(\alpha)$ replaced by $J'_{nm}(\alpha)$, the derivative of $J_{nm}(\alpha)$ with respect to α . One can then write for $A_{nR}(\mathbf{h})$ and $B_{nR}(\mathbf{h})$ and their derivatives expressions of the general form

$$\mathcal{F} = W(T_g S_g + T_u S_u) \quad (17)$$

where S_g is one of the even sums defined above (primed or unprimed) and S_u is one of the odd sums. Each of the terms T_g and T_u is always $\pm \cos(\theta_c)$ or $\pm \sin(\theta_c)$, where $\theta_c \equiv 2\pi \tilde{\mathbf{h}} \cdot \mathbf{c} \cdot \mathbf{x}$. The complete expressions are specified in Table 1. The sums involving the derivatives $J'_{nm}(\alpha)$ are evaluated using the recurrence relation

$$J'_k(\alpha) = \frac{J_{k-1}(\alpha) - J_{k+1}(\alpha)}{2}, \quad (18)$$

which reduces to $J'_0(\alpha) = -J_1(\alpha)$ for $k=0$ (McLachlan, 1955, p. 34).

Table 1. Specification of expressions of the form

$$\mathcal{F} = W(T_g S_g + T_u S_u) \text{ for } A_{nR}(\mathbf{h}) \text{ and } B_{nR}(\mathbf{h})$$

and their derivatives with respect to M , r , γ , and δ^2

In the table the simple symbols A , B , f , ψ , COS , and SIN replace $A_{nR}(\mathbf{h})$, $B_{nR}(\mathbf{h})$, $f(\mathbf{h})$, $\psi(\mathbf{h})$, $\cos(\theta_c)$, and $\sin(\theta_c)$, respectively.

\mathcal{F}	W	T_g	S_g	T_u	S_u
A	nf	COS	S_{cgn0}	SIN	S_{cun0}
B	if	SIN	S_{cgn0}	$-COS$	S_{cun0}
$\partial A / \partial M$	$2\pi \tilde{\mathbf{h}}(\rho \mathbf{x} - \rho \mathbf{x})nf$	$-SIN$	S_{cgn0}	COS	S_{cun0}
$\partial B / \partial M$	$2\pi \tilde{\mathbf{h}}(\rho \mathbf{x} - \rho \mathbf{x})if$	COS	S_{cgn0}	SIN	S_{cun0}
$\partial A / \partial r$	$2\pi h n f \sin \psi$	COS	S'_{cgn0}	SIN	S'_{cun0}
$\partial B / \partial r$	$2\pi h n f \sin \psi$	SIN	S'_{cgn0}	$-COS$	S'_{cun0}
$\partial A / \partial \gamma$	nf	$-COS$	S_{sgn1}	$-SIN$	S_{sun1}
$\partial B / \partial \gamma$	if	$-SIN$	S_{sgn1}	COS	S_{sun1}
$\partial A / \partial \delta^2$	$nf/2$	$-COS$	S_{cgn2}	$-SIN$	S_{cun2}
$\partial B / \partial \delta^2$	$if/2$	$-SIN$	S_{cgn2}	COS	S_{cun2}

From the derivatives of $A_{nR}(\mathbf{h})$ and $B_{nR}(\mathbf{h})$ with respect to M , r , and γ in Table 1, the derivatives of $A_{nR}(\mathbf{h})$ and $B_{nR}(\mathbf{h})$ with respect to the coordinates x^i ($i=1, 2, 3$) of atoms P , Q , and R are obtained by equations of the form

$$\frac{\partial A_{nR}(\mathbf{h})}{\partial x^i} = \frac{\partial A_{nR}(\mathbf{h})}{\partial M} \frac{\partial M}{\partial x^i} + \frac{\partial A_{nR}(\mathbf{h})}{\partial r} \frac{\partial r}{\partial x^i} + \frac{\partial A_{nR}(\mathbf{h})}{\partial \gamma} \frac{\partial \gamma}{\partial x^i}. \quad (19)$$

By inspection of Fig. 1 the partial derivatives $\partial M / \partial x^i$, $\partial r / \partial x^i$, and $\partial \gamma / \partial x^i$ are readily deduced. For example,

$$\frac{\partial M}{\partial r x^i} = \mathbf{a}_i \cdot \mathbf{u} / L_{QP} \quad (20)$$

$$= \mathbf{u}_i / L_{QP}. \quad (21)$$

Equation (21) also follows directly from equations (4) and (6). The other partial derivatives with respect to coordinates are as follows:

$$\frac{\partial r}{\partial_{\mathbf{R}}x^i} = {}^2u_i \quad (22)$$

$$\frac{\partial \gamma}{\partial_{\mathbf{R}}x^i} = {}^3u_i/r \quad (23)$$

$$\frac{\partial M}{\partial_{\mathbf{P}}x^i} = {}^1u_i M/L_{QP} \quad (24)$$

$$\frac{\partial r}{\partial_{\mathbf{P}}x^i} = {}^2u_i M \quad (25)$$

$$\frac{\partial \gamma}{\partial_{\mathbf{P}}x^i} = {}^3u_i M/r \quad (26)$$

$$\frac{\partial M}{\partial_{\mathbf{Q}}x^i} = -{}^1u_i(1+M)/L_{QP} \quad (27)$$

$$\frac{\partial r}{\partial_{\mathbf{Q}}x^i} = -{}^2u_i(1+M) \quad (28)$$

$$\frac{\partial \gamma}{\partial_{\mathbf{Q}}x^i} = -{}^3u_i(1+M)/r. \quad (29)$$

If the various sum functions used in Table 1 are redefined by replacing factors $\exp(-n^2m^2\gamma^2/2)$ by factors $I_m(b)/I_0(b)$, the table then gives correctly A and B and their derivatives for the King-Lipscomb hindered rotator model, except that the last two lines no longer apply. The derivatives $\partial A/\partial\delta^2$ and $\partial B/\partial\delta^2$ must be replaced by $\partial A/\partial b$ and $\partial B/\partial b$, for which the series expressions are easily written. The partial derivatives of equations (21)–(29) apply without change for the King-Lipscomb model.

In general an atom in large-amplitude librational motion about a single axis will have other motions with smaller amplitudes which must be taken into consideration in structure-factor calculations. These motions, which will include both intramolecular motions and rigid-body or segmented-body motions, will in general have different directions for their maximum amplitudes for the different atoms in the symmetrical torsional oscillator. For this reason we prefer to use equation (12) rather than (14) even when dealing with a symmetrical oscillator such as a methyl group. For each atom an appropriate factor can be multiplied into the right side of equation (12) to allow for the additional thermal motion.

For additional intramolecular motion, we consider an appropriate factor to be

$$T_i = \exp[-2\pi^2\mathbf{s}U\mathbf{s}], \quad (30)$$

where \mathbf{s} is the column matrix of components of the reflection vector referred to the Cartesian system with base vectors ${}^i\mathbf{u}$ defined above, and U is a 3×3 sym-

metric matrix in which U_{33} , U_{13} , and U_{23} are assigned fixed values of zero. The equation $\overline{d^2} = \widetilde{\mathbf{I}}U\mathbf{I}$ gives the mean-square displacement in the direction of a unit vector \mathbf{I} with components l_i parallel to the ${}^i\mathbf{u}$. Let the matrix V be the matrix which transforms the crystal base vectors \mathbf{a}_i to the ${}^i\mathbf{u}$; that is, let

$$V = ({}^1\mathbf{u} \ {}^2\mathbf{u} \ {}^3\mathbf{u})\mathbf{g}^{-1}, \quad (31)$$

according to our previous definition of the column matrices ${}^i\mathbf{u}$. Then

$$T_i = \exp[-2\pi^2\widetilde{\mathbf{h}}\widetilde{V}UV\mathbf{h}]. \quad (32)$$

In evaluating the three non-zero independent U_{ij} 's, one needs the derivative of $\widetilde{\mathbf{h}}\widetilde{V}UV\mathbf{h}$ with respect to each of them. It is easily shown by the rules for differentiation of matrix products [see, for example, *International Tables for X-ray Crystallography* (1959), p. 15, and references cited therein] that

$$\frac{\partial(\widetilde{\mathbf{h}}\widetilde{V}UV\mathbf{h})}{\partial U_{ij}} = \widetilde{\mathbf{h}}D^{ij}\mathbf{h}, \quad (33)$$

where the general element of the 3×3 matrix D^{ij} is

$$D_{rc}^{ij} = V_{ir}V_{jc} + (1 - \delta_{ij})V_{jr}V_{ic}, \quad (34)$$

where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ otherwise.

To take into account rigid-body motion, we multiply into the expression for $F_R(\mathbf{h})$ an additional anisotropic temperature factor of the usual form,

$$T_R = \exp[-\widetilde{\mathbf{h}}\beta^R\mathbf{h}], \quad (35)$$

for which the parameters β_{ij}^R are presumed to be available from the results of a rigid-body analysis (Cruickshank, 1956; Schomaker & Trueblood, 1968; Johnson, 1970a) or segmented-body analysis (Johnson, 1970b) of the thermal parameters of the atoms not involved in torsional oscillation. The parameters β_{ij}^R are not adjusted in the further crystallographic refinement. The basic assumption in the use of equation (35) is that the torsional motions already treated are independent of the rigid-body motion. There may be cases of interest in which it is a poor approximation. In other cases, it may be impossible or very difficult to do the preliminary rigid-body or segmented-body analysis.

We have modified a version of the least-squares program of Busing, Martin & Levy (1962) to include our torsional-oscillator model for the case $n=1$ [see equation (10) and read 1 for n in Table 1], including the additional temperature factors T_i and T_R explained above. For the purpose of simplifying the programming, the partial derivatives of equations (24)–(29) were not included; therefore, derivatives with respect to the coordinates x^i of atoms P and Q do not include any terms $\partial A_R(\mathbf{h})/\partial x^i$ or $\partial B_R(\mathbf{h})/\partial x^i$. The omission of these terms is consistent with the omission from Table 1 of partial derivatives with respect to the angle ψ . The components of the unit base vectors ${}^i\mathbf{u}$ are calculated anew at the beginning of each cycle.

The subroutine used to generate the Bessel functions was taken from the Control Data Corporation's library of programs for the CDC 1604A computer. The procedure used in the subroutine has been described by Stegun & Abramowitz (1957) and by Goldstein & Corley (1959).

The rate of convergence in each of the series expressions S_o and S_u represented in Table I is a function of the argument α of the functions $J_m(\alpha)$, of the mean-square amplitude δ^2 , and of the symmetry number n . In our work on copper(II) acetate monohydrate (Brown & Chidambaram, 1973), in which n was taken to be 1, the maximum magnitude of α was 10.24. Using estimates for the values of δ^2 for the methyl hydrogen atoms from the preliminary refinement and making reference to tables of Bessel functions, we concluded that including the terms through $m=14$ for the S_o sums and through $m=15$ for the S_u sums would provide satisfactory accuracy. Among all these sums for all the reflections the largest error is in fact about 1×10^{-5} , which is negligible in view of the small magnitudes (about 10 or less) of the coefficients of the sums. The program might be improved by the incorporation of convergence tests.

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