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Crystal Structure Refinement using a Number of Orthonormal Axial Systems

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A least-squares refinement procedure is developed in which different groups of parameters are defined with respect to different axial systems. The parameters are refined by describing the reciprocal-lattice vector for a given reflexion with respect to the relevant axial system for each refinable parameter. With this procedure features of the structure can be refined in the space most suitable for their description and correlations between parameters are either reduced or at least more readily understood. Constrained refinement is much simpler algebraically and can be made to be extremely flexible.

Introduction

It has been traditional to describe crystal structures in terms of axial systems imposed by the repeating nature of the crystal using basis vectors $\mathbf{a}_j$ and a corresponding set of reciprocal-space vectors $\mathbf{b}_k$ where $\mathbf{a}_j \cdot \mathbf{b}_k = \delta_{jk}$ ($\delta_{jk} = 0$ if $j \neq k$, $\delta_{jk} = 1$ if $j = k$; $j, k = 1$ to 3).

However there is no need to be restricted to such an axial system. For example we can consider a real-space set of basis vectors $\mathbf{A}_j$ and a corresponding set of basis vectors in reciprocal space $\mathbf{B}_k$ where $\mathbf{A}_j \cdot \mathbf{B}_k = \delta_{jk}$. If $\mathbf{a}_j \cdot \mathbf{B}_k = R_{jk}$ it follows that

$$\mathbf{a}_j = \sum_k R_{jk} \mathbf{A}_k , \quad \mathbf{B}_k = \sum_j R_{jk} \mathbf{b}_j ,$$

$$\mathbf{A}_k = \sum_j (R^{-1})_{kj} \mathbf{a}_j , \quad \mathbf{b}_j = \sum_k (R^{-1})_{kj} \mathbf{B}_k$$

and

$$\mathbf{b}_j \cdot \mathbf{A}_k = (R^{-1})_{kj}$$

where

$$\sum_k R_{jk} (R^{-1})_{kl} = \delta_{jl} .$$

Any point $\mathbf{r}$ in real space may be described as

$$\mathbf{r} = \sum_j x^j \mathbf{a}_j = \sum_k X^k \mathbf{A}_k$$

where

$$X^k = \sum_j x^j R_{jk} \quad \text{and} \quad x^j = \sum_k X^k (R^{-1})_{kj} .$$

Any point S in reciprocal space may be described as

$$\mathbf{S} = \sum_j h_j \mathbf{b}_j = \frac{1}{2\pi} \sum_k t_k \mathbf{B}_k$$

where

$$t_k = 2\pi \sum_j (R^{-1})_{kj} h_j \quad \text{and} \quad 2\pi h_j = \sum_k R_{jk} t_k .$$

If we have two different sets of orthonormal basis vectors in real space with corresponding vectors in reciprocal space then $\mathbf{A}_k = \mathbf{B}_k$, $^p\mathbf{A}_k = {}^p\mathbf{B}_k$ and $\mathbf{A}_k = \sum_l {}^pU_{kl} {}^p\mathbf{A}_l$ where $^pU_{kl} = \mathbf{A}_k \cdot {}^p\mathbf{B}_l = \mathbf{B}_k \cdot {}^p\mathbf{A}_l$. If we describe any point $\mathbf{r}$ in real space as

$$\mathbf{r} = \sum_l {}^pX^l {}^p\mathbf{A}_l$$

and any point S in reciprocal space as

$$\mathbf{S} = \frac{1}{2\pi} \sum_l {}^pt_l {}^p\mathbf{B}_l$$

then

$$^pX^l = \sum_k X^k {}^pU_{kl} \quad \text{and} \quad {}^pt_l = \sum_k ({}^pU^{-1})_{lk} t_k = \sum_k {}^pU_{kl} t_k .$$

Also $\mathbf{a}_j = \sum_l {}^pR_{jl} {}^p\mathbf{A}_l$ etc. where

$$^pR_{jl} = \sum_k R_{jk} {}^pU_{kl} .$$

The characteristic function or Fourier transform of a probability density function of the position of an atom in a crystal is expressible in the form

$$\psi_n(\mathbf{S}) = \exp\,(i\;\sum_j {}^1\kappa_n^j t_j + \frac{i^2}{2!}\sum_{jk}{}^2\kappa_n^{jk}t_j t_k$$

$$+ \frac{i^3}{3!}\sum_{jkl}{}^3\kappa_n^{jkl}t_j t_k t_l + \frac{i^4}{4!}\sum_{jklm}{}^4\kappa_n^{jklm}t_j t_k t_l t_m + \ldots)\quad(1)$$

where $i^2 = -1$ and the first four cumulant tensors ${}^1\kappa_n, {}^2\kappa_n,$ ${}^3\kappa_n, {}^4\kappa_n$ describe the mean, the variance covariance, the skewness and the kurtosis of the nth probability density function. The relationship between this and other descriptions of thermal motion is discussed by Johnson (1970). Equation (1) is obtained by describing the reciprocal-lattice vector as

$$\mathbf{S} = \frac{1}{2\pi}\sum_k \mathbf{t}_k \mathbf{B}_k\;.$$

Pawley (1972) has pointed out that there is no reason why the cumulant tensors cannot be refined in an orthonormal space. The tensor quantities ${}^s\kappa_n$ are defined in units of $(\text{Å})^s$ if we use orthonormal basis vectors when $|\mathbf{A}_k| = 1$ Å. Pawley advocates the use of a single axial system (Patterson, 1959) in which $\mathbf{A}_1 = \mathbf{a}_1/a_1$, $\mathbf{A}_2 = \mathbf{A}_3 \times \mathbf{A}_1$, and $\mathbf{A}_3 = \mathbf{b}_3/b_3$, making

$$R_{jk} = \begin{pmatrix} a_1 & 0 & 0 \\ a_2\cos\alpha_3 & a_2\sin\alpha_3 & 0 \\ a_3\cos\alpha_2 & -a_3\sin\alpha_2\cos\beta_1 & 1/b_3 \end{pmatrix}$$

where α_i, β_i are the interaxial angles of the crystallographic unit cell in real space and reciprocal space respectively. This choice contrasts with the orthonormal basis vectors $\mathbf{B}_1 = \mathbf{b}_1/b_1$, $\mathbf{B}_2 = \mathbf{B}_3 \times \mathbf{B}_1$, and $\mathbf{B}_3 = \mathbf{a}_3/a_3$ used by Busing & Levy (1967) as a reference frame for data collection.

It should be pointed out however that Miller indices are still the obvious way to index reflexions and that probability density maps can be calculated much more rapidly using Miller indices and fractional coordinates.

The real benefits of orthonormal axial systems are noted when attempts are made to analyse thermal parameters (Schomaker & Trueblood, 1968) and when constraints are used in the least-squares refinement (Pawley, 1972) since the algebra is then simplified. The evaluation of principal axes of vibration (Waser, 1955; Busing & Levy, 1958) and the graphical representation of structures (Johnson, 1965) is also much simplified.

However the real reason for transforming a refinement problem is to reduce correlations between refinable parameters so that little error will occur in parameters when other parameters are either held constant or omitted. For each refinement cycle we need to set up least-squares equations requiring the evaluation of $\partial F(\mathbf{S})/\partial u_q$ for various parameters u_q.

If the parameters u_q are described with respect to different axial systems then $\partial F(\mathbf{S})/\partial u_q$ is most easily evaluated by describing the reciprocal-lattice vector $\mathbf{S}$ relative to the axes associated with u_q. Since $F(\mathbf{S})$ is formed as the sum of various products of terms dependent on $(\mathbf{S})$, the parameters describing each term may be associated with any axial choice, provided the axial

choice is known. Failure to recognize this fact has led to the unnecessary complication of the algebra of group refinements by saying

$$\frac{\partial F(\mathbf{S})}{\partial u_q} = \sum_i \frac{\partial F(\mathbf{S})}{\partial v_i}\frac{\partial v_i}{\partial u_q}\,,\quad(2)$$

where both $\mathbf{S}$ and the parameters v_i are defined with respect to a fixed reference frame of axes. However parameters need never be defined with respect to a common reference frame unless so desired.

Parameters u_q need only be described in terms of other parameters v_i if we wish to use parameters which are combinations of parameters on different atoms and this combination may be evaluated using parameters v_i which are themselves defined with respect to whatever reference frame of axes most simplifies the evaluation of $\partial v_i/\partial u_q$.

The advantages of refining parameters other than those associated with a single reference frame of axis are:

(a) the results of refinements can be much more readily described,

(b) the application of constraints has greatly simplified algebra, and

(c) correlations between parameters may be reduced and more readily understood.

Theory

If $(\theta_m, \mathbf{d}_m)$ is a symmetry operation where $(\theta_m, \mathbf{d}_m)\mathbf{r} = \theta_m\mathbf{r} + \mathbf{d}_m$ then the structure factor may be described as $F(\mathbf{S}) = \sum_m F_m(\mathbf{S})$ where

$$F_m(\mathbf{S}) = \exp\,(2\pi i\mathbf{d}_m \cdot \mathbf{S})\sum_n a_n f_n(\mathbf{S})\psi_n(\theta_m^{-1}\mathbf{S})\;;\quad(3)$$

a_n is the occupancy factor, $f_n(\mathbf{S})$ the scattering factor and $\psi_n(\mathbf{S})$ the Fourier transform of the probability density function of an atom in the asymmetric unit. The use of the crystallographic unit-cell axial system simplifies the evaluation of $\mathbf{d}_m \cdot \mathbf{S}$ and $\theta_m^{-1}\mathbf{S} = \sum_j h_{mj}\mathbf{b}_j$ where the h_{mj} values are simple combinations of the Miller indices (Busing, Martin & Levy, 1962).

From (1) it is seen that

$$\ln\,\psi_n(\mathbf{S}) = i\;\sum_j {}^1\kappa_n^j t_j + \frac{i^2}{2!}\sum_{jk}{}^2\kappa_n^{jk}t_j t_k$$

$$+ \frac{i^3}{3!}\sum_{jkl}{}^3\kappa_n^{jkl}t_j t_k t_l + \frac{i^4}{4!}\sum_{jklm}{}^4\kappa_n^{jklm}t_j t_k t_l t_m\quad(4)$$

and since $\psi_n(\mathbf{S}) = \exp\,(\ln\,\psi_n(\mathbf{S}))$ it follows that

$$\frac{\partial\psi_n(\mathbf{S})}{\partial u_q} = \psi_n(\mathbf{S})\frac{\partial\,\ln\,\psi_n(\mathbf{S})}{\partial u_q}$$

and

$$\frac{\partial F(\mathbf{S})}{\partial u_q} = \sum_{mn}\exp\,(2\pi i\mathbf{d}_m \cdot \mathbf{S})a_n f_n(\mathbf{S})\psi_n(\theta_m^{-1}\mathbf{S})$$

$$\times\,\partial\,\ln[a_n\psi_n(\theta_m^{-1}\mathbf{S})]/\partial u_q\,.\quad(5)$$

If we describe the qth parameter u_q with respect to the pth orthonormal axial system, then $\theta_m^{-1}S = \sum_l {}^p t_{lm}{}^p B_l$ where

$$^p B_l = {}^p A_l = \sum_{jk} R_{jk}{}^p U_{kl} b_j = \sum_{jk} {}^p U_{kl}(R^{-1})_{kj}\, a_j$$

and

$$^p t_{lm} = \sum_{jk} {}^p U_{kl}(R^{-1})_{kj} h_{mj} \,. \tag{6}$$

The pth orthonormal axial system is related to the axial system $A_1 = a_1/a_1$, $A_2 = A_3 \times A_1$, $A_3 = b_3/b_3$ [$A_k = B_k = \sum_j (R^{-1})_{kj} a_j$] by the pth unitary transformation $^p B_l = \sum_k {}^p U_{kl} B_k$.

If a crystal structure has an inversion centre at the origin of the unit cell then $\theta_m^{-1}S = -S$ for this symmetry operation and $\psi_n(-S) = \psi_n^*(S)$ where $\psi_n^*(S)$ is the complex conjugate of $\psi_n(S)$. Thus two centrosymmetrically related atoms make a contribution to $F(S)$ of $f_n(S) a_n[\psi_n(S) + \psi_n^*(S)]$ and the differential of this contribution with respect to u_q is

$$f_n(S)\left[\frac{\partial a_n \psi_n(S)}{\partial u_q} + \left(\frac{\partial a_n \psi_n(S)}{\partial u_q}\right)^*\right].$$

Refinement of the reference frame

We can describe the reciprocal-space vector S with respect to estimates of the pth axial system by saying

$$2\pi S = \sum_l {}^p \hat{t}_l{}^p \hat{B}_l = \sum_l {}^p t_l{}^p B_l$$

where

$$^p \hat{t}_l = \sum_j {}^p t_j{}^p V_{jl}, \quad {}^p \hat{B}_l = \sum_k {}^p V_{kl}{}^p B_k \quad \text{and}$$

$$\sum_l {}^p V_{jl}{}^p V_{kl} = \delta_{jk}.$$

The $^p B_j$ are the initial choice of axis directions and the $^p \hat{B}_l$ are the directions of the best choice of the pth axial system for describing the parameters associated with it.

For the pth reference frame

$$^p V_{jk} = \begin{pmatrix} C_3 & S_3 & 0 \\ -S_3 & C_3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} C_2 & 0 & -S_2 \\ 0 & 1 & 0 \\ S_2 & 0 & C_2 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & C_1 & S_1 \\ 0 & -S_1 & C_1 \end{pmatrix}$$

$$= \begin{pmatrix} C_3 C_2 & C_3 S_2 S_1 + S_3 C_1 & -C_3 S_2 C_1 + S_3 S_1 \\ -S_3 C_2 & -S_3 S_2 S_1 + C_3 C_1 & S_3 S_2 C_1 + C_3 S_1 \\ S_2 & -C_2 S_1 & C_2 C_1 \end{pmatrix}, \tag{7}$$

where $C_i = \cos \varphi_i$, $S_i = \sin \varphi_i$, $i = 1$ to 3. We see that if $C_3 = S_2 = C_1 = 1$ then

$$^p V_{jk} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

and

$$\partial^p V_{jk}/\partial \varphi_i = \begin{pmatrix} -\delta_{12} & \delta_{11} + \delta_{13} & 0 \\ 0 & 0 & \delta_{11} + \delta_{13} \\ 0 & 0 & -\delta_{12} \end{pmatrix}.$$

This possible ill-conditioning of matrices describing axial transformations is well known. However this problem is minimized by describing the axis transformation relative to the initial directions for the axes in the unit cell rather than to the unit cell itself. In this instance our initial values of φ_i are zero, making $^p V_{jk} = \delta_{jk}$ and $^p V_{jk}/\partial \varphi_i = \varepsilon_{ijk}$ where $\varepsilon_{ijk} = +1$ for a cyclic permutation of $1,2,3$, $\varepsilon_{ijk} = -1$ for a non-cyclic permutation of $1,2,3$, $\varepsilon_{ijk} = 0$ otherwise. The approximation $^p V_{jk} \simeq \delta_{jk} + \sum_i \varepsilon_{ijk} \Delta \varphi_i$ implied by the least-squares refinement takes no account of the sequence of the three matrices making up $^p V_{jk}$ but this effect is small if $\Delta \varphi_i$ is small. The ill-conditioning is minimized by putting the matrices in a sequence where the smallest $\Delta \varphi_i$ is associated with the second matrix when (7) is used to give the new axial directions $^p \hat{B}_l = {}^p \hat{A}_l = \sum_j {}^p \hat{U}_{jl} A_j$ where $^p \hat{U}_{jl} = \sum_k {}^p U_{jk}{}^p V_{kl}$ and $A_j = B_j$ are the orthonormal axes $a_1/a_1, A_3 \times A_1, b_3/b_3$ to which all the unitary transformations are referred.

Positional parameters

Positional parameters are associated with the first term in the expansion of $\ln \psi_n(S)$ described in (4). This term may be expressed as $2\pi i r_n \cdot S$ and $r_n = {}^p R + {}^p r_n$ where $^p R$ is the position of the origin of the pth axial system in real space and $^p r_n$ is the position of mean of the probability density function of the nth atom measured relative to the origin of the pth axial system.

We define the positional parameters using the most convenient axial systems. If we define r_n by the best orientation of the pth axial system then

$$^p R = \sum_k {}^p X_0^k{}^p \hat{A}_k \quad \text{and} \quad {}^p r_n = \sum_k {}^p X_n^k{}^p \hat{A}_k .$$

We define $2\pi S$ using the initially assumed orientation of the pth axial system saying $2\pi S = \sum_j {}^p t_j{}^p B_j$. These directions are related by the transformation $^p \hat{B}_k = {}^p \hat{A}_k = \sum_j {}^p V_{jk}{}^p B_j$ where $^p V_{jk}$ is described in terms of parameters φ_i in (7).

Thus

$$2\pi i r_n \cdot S = i \sum_{kj} ({}^p X_0^k + {}^p X_n^k) \, {}^p V_{jk}{}^p t_j$$

and from (5) we see that this term makes a zero contribution to the evaluation of $\partial F(S)/\partial u_q$ unless $u_q = {}^p X_0^j, {}^p X_n^j$ or φ_j. Thus

$$(2\pi i r_n \cdot S)_0 = i \sum_j ({}^p X_0^j + {}^p X_n^j)^p t_j$$

$$\left(\frac{\partial 2\pi i r_n \cdot S}{\partial^p X_0^j}\right)_0 = \left(\frac{\partial 2\pi i r_n \cdot S}{\partial^p X_n^j}\right)_0 = i^p t_j$$

and from (7) when all $\varphi_j = 0$

$$\left(\frac{\partial 2\pi i r_n \cdot S}{\partial \varphi_1}\right)_0 = -i({}^p X_n^2 {}^p t_3 - {}^p X_n^3 {}^p t_2)$$

$$\left(\frac{\partial 2\pi i r_n \cdot S}{\partial \varphi_2}\right)_0 = -i({}^p X_n^3 {}^p t_1 - {}^p X_n^1 {}^p t_3)$$

and

$$\left(\frac{\partial 2\pi i \mathbf{r}_n \cdot \mathbf{S}}{\partial \varphi_3}\right)_0 = -i(^pX_n^1\,{}^pt_2 - {}^pX_n^2\,{}^pt_1) \qquad (8)$$

where the subscript 0 implies evaluation for the initial values.

Higher-order cumulants

The higher-order terms in the expansion of $\ln \psi_n(\mathbf{S})$ are associated with the distribution of the probability density function of the nth atom about its mean and may be described with respect to any axial system. If $\mathbf{A}_k = \sum_l {}^pU_{kl}{}^p\mathbf{A}_l$ then ${}^pt_l = \sum_k {}^pU_{kl}t_k$ and $t_k = \sum_l {}^pU_{kl}{}^pt_l$. The values of the components of the cumulant tensors depend on the axial directions chosen to evaluate t_j. Thus

$$^pX_n^{j'} = \sum_j X_n^j\,{}^pU_{jj'}, \quad X_n^j = \sum_{j'} {}^pX_n^{j'}\,{}^pU_{jj'},$$

$$^2_p\kappa_n^{j'k'} = \sum_{jk} {}^2\kappa_n^{jk}\,{}^pU_{jj'}{}^pU_{kk'}, \quad {}^2\kappa_n^{jk} = \sum_{j'k'} {}^2_p\kappa_n^{j'k'}\,{}^pU_{jj'}{}^pU_{kk'},$$

$$^3_p\kappa_n^{j'k'l'} = \sum_{jkl} {}^3\kappa_n^{jkl}\,{}^pU_{jj'}{}^pU_{kk'}{}^pU_{ll'},$$

$$^3\kappa_n^{jkl} = \sum_{j'k'l'} {}^3_p\kappa_n^{j'k'l'}\,{}^pU_{jj'}{}^pU_{kk'}{}^pU_{ll'} \quad \text{etc.,} \qquad (9)$$

where the symbol p denotes the reference frame for the cumulant and the omission of this symbol implies the orthonormal axes $\mathbf{a}_1/a, \mathbf{A}_3 \times \mathbf{A}_1, \mathbf{b}_3/b_3$. Each tensor is invariant to pairwise interchange of the indices so that for a site of symmetry 1 there are 3, 6, 10, 15 unique elements for tensors of order 1, 2, 3, 4 respectively. The components may be arranged so that $j \leq k \leq l \leq m$ and each component given a multiplicity corresponding to the number of distinguishable sequences of $jklm$.

It is possible to contemplate refinement of the values and directions of the three principal axes of vibration as six refinable parameters but such a procedure is dangerous as most atoms are approximately isotropic. However it is possible to constrain the higher-order cumulants. For the cumulant tensor of order s an artificial point symmetry can be assumed for the atom site, imposing restrictions on the possible components of this tensor. This is most easily done if the axial system is made to coincide with the most convenient directions for the simplification of the tensor. In this way it is easy to include higher-order cumulants without over-parametrizing the refinement problem.

Indeed it is possible to choose variables to describe the higher-order cumulants such that the imposition of a symmetry constraint simply implies that certain of the variables are zero.

Thus

$$\sum_{jk} {}^2\kappa^{jk}t_jt_k = A_1(t_1^2+t_2^2+t_3^2) + A_2\tfrac{1}{2}(2t_3^2-t_1^2-t_2^2)$$
$$+ A_3(t_1^2-t_2^2) + A_42t_1t_2 + A_52t_1t_3 + A_62t_2t_3 \qquad (10)$$

making

$$^2\kappa^{12} = A_4, \quad {}^2\kappa^{13} = A_5, \quad {}^2\kappa^{23} = A_6,$$

$$^2\kappa^{11} = A_1 - A_2/2 + A_3,$$

$$^2\kappa^{22} = A_1 - A_2/2 - A_3,$$

$$^2\kappa^{33} = A_1 + A_2,$$

$$A_1 = \tfrac{1}{3}({}^2\kappa^{11} + {}^2\kappa^{22} + {}^2\kappa^{33}),$$

$$A_2 = \kappa^{33} - \tfrac{1}{3}({}^2\kappa^{11} + {}^2\kappa^{22} + {}^2\kappa^{33}),$$

$$A_3 = \tfrac{1}{2}({}^2\kappa^{11} - {}^2\kappa^{22}). \qquad (11)$$

$^2\kappa^{11}, {}^2\kappa^{22}, {}^2\kappa^{33}$ have multiplicity 1 and $^2\kappa^{12}, {}^2\kappa^{13}, {}^2\kappa^{23}$ have multiplicity 2. If we choose the pth axial system to make the primary axis of the imposed point symmetry parallel to $^p\mathbf{A}_3$ and the secondary axis parallel to $^p\mathbf{A}_1$ then for the following centrosymmetric point symmetries we only need to refine the parameters given in Table 1.

Table 1. *A parameters to be refined*

Laue symmetry	Parameters
$\bar{1}$	$A_1A_2A_3A_4A_5A_6$
$2/m$	$A_1A_2A_3A_4$
mmm	$A_1A_2A_3$
$\bar{3}, \bar{3}m, 4/m, 4/mmm, 6/m, 6/mmm$	A_1A_2
$m3, m3m$	A_1

Also

$$\sum_{jkl} {}^3\kappa^{jkl}t_jt_kt_l = B_1'(\tfrac{3}{5})t_1(t_1^2+t_2^2+t_3^2)$$
$$+ B_2'(\tfrac{3}{5})t_2(t_1^2+t_2^2+t_3^2) + B_3'(\tfrac{3}{5})t_3(t_1^2+t_2^2+t_3^2)$$
$$+ B_4'6t_1t_2t_3 + B_5't_1(3t_2^2-t_1^2) + B_6't_1(3t_3^2-t_1^2)$$
$$+ B_7't_2(3t_1^2-t_2^2) + B_8't_2(3t_3^2-t_2^2) + B_9't_3(3t_1^2-t_3^2)$$
$$+ B_{10}'t_3(3t_2^2-t_3^2)$$

making

$$^3\kappa^{111} = (\tfrac{3}{5})B_1' - B_5' - B_6', \quad {}^3\kappa^{222} = (\tfrac{3}{5})B_2' - B_7' - B_8',$$

$$^3\kappa^{333} = (\tfrac{3}{5})B_3' - B_9' - B_{10}', \quad {}^3\kappa^{122} = (\tfrac{1}{5})B_1' + B_5',$$

$$^3\kappa^{211} = (\tfrac{1}{5})B_2' + B_7', \quad {}^3\kappa^{311} = (\tfrac{1}{5})B_3' + B_9',$$

$$^3\kappa^{133} = (\tfrac{1}{5})B_1' + B_6', \quad {}^3\kappa^{233} = (\tfrac{1}{5})B_2' + B_8',$$

$$^3\kappa^{322} = (\tfrac{1}{5})B_3' + B_{10}', \quad B_1' = {}^3\kappa^{111} + {}^3\kappa^{122} + {}^3\kappa^{133},$$

$$B_2' = {}^3\kappa^{211} + {}^3\kappa^{222} + {}^3\kappa^{233}, \quad B_3' = {}^3\kappa^{311} + {}^3\kappa^{322} + {}^3\kappa^{333}$$

and $^3\kappa^{123} = B_4'$. $\qquad (12)$

However, although these functions have a certain attractiveness, it is better to use the expression

$$\sum_{jkl} {}^3\kappa^{jkl}t_jt_kt_l = B_1(\tfrac{3}{5})t_1(t_1^2+t_2^2+t_3^2) + B_2(\tfrac{3}{5})t_2(t_1^2+t_2^2+t_3^2)$$
$$+ B_3(\tfrac{3}{5})t_3(t_1^2+t_2^2+t_3^2) + B_46t_1t_2t_3 + B_5t_1(t_1^2-3t_2^2)$$
$$+ B_63t_1(t_3^2-t_2^2) + B_7t_2(t_2-3t_1^2) + B_83t_2(t_3^2-t_1^2)$$
$$+ B_9\tfrac{1}{2}[5t_3^3-3t_3(t_1^2+t_2^2+t_3^2)] + B_{10}3t_3(t_1^2-t_2^2) \qquad (13)$$

where

$$3t_3(t_1^2-t_2^2) = 6t_3[(t_1+t_2)/\sqrt{2}][t_1-t_2)/\sqrt{2}]$$
$$= t_3(t_3^2-3t_2^2) - t_3(t_3^2-3t_1^2)$$

and

$$5t_3^3 - 3t_3(t_1^2 + t_2^2 + t_3^2) = t_3(t_3^2 - 3t_2^2) + t_3(t_3^2 - 3t_1^2) .$$

We then obtain

$$^3\kappa^{111} = (\tfrac{3}{5})B_1 + B_5 , \qquad ^3\kappa^{222} = (\tfrac{3}{5})B_2 + B_7 ,$$

$$^3\kappa^{333} = (\tfrac{3}{5})B_3 + B_9 , \qquad ^3\kappa^{122} = (\tfrac{1}{5})B_1 - B_5 - B_6 ,$$

$$^3\kappa^{211} = (\tfrac{1}{5})B_2 - B_7 - B_8 , \qquad ^3\kappa^{311} = (\tfrac{1}{5})B_3 - \tfrac{1}{2}B_9 + B_{10} ,$$

$$^3\kappa^{133} = (\tfrac{1}{5})B_1 + B_6 , \qquad ^3\kappa^{233} = (\tfrac{1}{5})B_2 + B_8 ,$$

$$^3\kappa^{322} = (\tfrac{1}{5})B_3 - \tfrac{1}{2}B_9 - B_{10} , \qquad B_1 = {}^3\kappa^{111} + {}^3\kappa^{122} + {}^3\kappa^{133} ,$$

$$B_2 = {}^3\kappa^{211} + {}^3\kappa^{222} + {}^3\kappa^{233} , \qquad B_3 = {}^3\kappa^{311} + {}^3\kappa^{322} + {}^3\kappa^{333} ,$$

$$B_{10} = \tfrac{1}{2}({}^3\kappa^{311} - {}^3\kappa^{322}) \quad \text{and} \quad ^3\kappa^{123} = B_4 . \tag{14}$$

$^3\kappa^{111}$, $^3\kappa^{222}$, $^3\kappa^{333}$ have multiplicity 1, $^3\kappa^{122}$, $^3\kappa^{133}$, $^3\kappa^{211}$, $^3\kappa^{233}$, $^3\kappa^{311}$, $^3\kappa^{322}$ have multiplicity 3 and $^3\kappa^{123}$ has multiplicity 6.

If we choose the pth axial system to coincide with the imposed point symmetry as before then we only need to refine parameters in Table 2.

Table 2. *B parameters to be refined*

Point symmetry	Parameters
1	$B_1B_2B_3B_4B_5B_6B_7B_8B_9B_{10}$
m	$B_1B_2 \quad B_5B_6B_7B_8 \quad B_9B_{10}$
2	$B_3B_4 \qquad B_9B_{10}$
3	$B_3 \quad B_5 \quad B_7 \quad B_9$
mm2	$B_3 \qquad B_9B_{10}$
3m	$B_3 \quad B_7 \quad B_9$
$\bar{4}$	$B_4 \qquad B_{10}$
$\bar{6}$	$B_5 \quad B_7$
4, 4mm, 6, 6mm	$B_3 \qquad B_9$
222, $\bar{4}$m2, 23, $\bar{4}$3m	B_4
32, $\bar{6}$m2	B_7
422, 432, 622, $\bar{1}$	None

Also

$$\sum_{jklm} {}^4\kappa^{jklm} t_j t_k t_l t_m = (\tfrac{3}{5})C_1'(t_1^2 + t_2^2 + t_3^2)^2$$

$$+ C_2'\tfrac{1}{2}(2t_3^2 - t_1^2 - t_2^2)(t_1^2 + t_2^2 + t_3^2)$$

$$+ C_3'(t_1^2 - t_2^2)(t_1^2 + t_2^2 + t_3^2) + C_4'(2t_1t_2)(t_1^2 + t_2^2 + t_3^2)$$

$$+ C_5'(2t_1t_3)(t_1^2 + t_2^2 + t_3^2) + C_6'(2t_2t_3)(t_1^2 + t_2^2 + t_3^2)$$

$$+ C_7'(6t_1^2t_2^2 - t_1^4 - t_2^4) + C_8'(6t_1^2t_3^2 - t_1^4 - t_3^4)$$

$$+ C_9'(6t_2^2t_3^2 - t_2^4 - t_3^4) + C_{10}'(4t_1t_1)(t_1^2 - 3t_3^2)$$

$$+ C_{11}'(4t_1t_2)(t_2^2 - 3t_3^2) + C_{12}'(4t_3t_1)(t_1^2 - 3t_2^2)$$

$$+ C_{13}'(4t_1t_3)(t_3^2 - 3t_2^2) + C_{14}'(4t_3t_2)(t_2^2 - 3t_1^2)$$

$$+ C_{15}'(4t_2t_3)(t_3^2 - 3t_1^2)$$

making

$$^4\kappa^{1111} = (\tfrac{3}{5})C_1' - \tfrac{1}{2}C_2' + C_3' - C_7' - C_8' ,$$

$$^4\kappa^{2222} = (\tfrac{3}{5})C_1' - \tfrac{1}{2}C_2' - C_3' - C_7' - C_9' ,$$

$$^4\kappa^{3333} = (\tfrac{3}{5})C_1' + C_2' - C_8' - C_9' ,$$

$$^4\kappa^{1122} = (\tfrac{1}{5})C_1' - (\tfrac{1}{6})C_2' + C_7' ,$$

$$^4\kappa^{1133} = (\tfrac{1}{5})C_1' + (\tfrac{1}{12})C_2' + (\tfrac{1}{6})C_3' + C_8' ,$$

$$^4\kappa^{2233} = \tfrac{1}{5}C_1' + (\tfrac{1}{12})C_2' - (\tfrac{1}{6})C_3' + C_9' ,$$

$$C_1' = (\tfrac{1}{3})(C_1'' + C_2'' + C_3'') ,$$

$$C_2' = (\tfrac{6}{7})(C_3'' - C_1'') ,$$

$$C_3' = (\tfrac{6}{7})(C_1'' - C_2'')/2 ,$$

$$C_7' = \kappa^{1122} - (\tfrac{1}{35})(4C_1'' + 4C_2'' - C_3'') ,$$

$$C_8' = \kappa^{1133} - (\tfrac{1}{35})(4C_1'' - C_2'' + 4C_3'') ,$$

$$C_9' = \kappa^{2233} - (\tfrac{1}{35})(-C_1'' + 4C_2'' + 4C_3'') ,$$

where

$$C_1'' = {}^4\kappa^{1111} + {}^4\kappa^{1122} + {}^4\kappa^{1133} ,$$

$$C_2'' = {}^4\kappa^{2211} + {}^4\kappa^{2222} + {}^4\kappa^{2233} ,$$

$$C_3'' = {}^4\kappa^{3311} + {}^4\kappa^{3322} + {}^4\kappa^{3333}$$

and

$$^4\kappa^{1233} = (\tfrac{1}{7})C_4'' - C_{10}' - C_{11}' ,$$

$$^4\kappa^{1322} = (\tfrac{1}{7})C_5'' - C_{12}' - C_{13}' ,$$

$$^4\kappa^{2311} = (\tfrac{1}{7})C_6'' - C_{14}' - C_{15}' , \qquad ^4\kappa^{1211} = (\tfrac{3}{7})C_4'' + C_{10}' ,$$

$$^4\kappa^{1311} = (\tfrac{3}{7})C_5'' + C_{12}' , \qquad ^4\kappa^{2322} = (\tfrac{3}{7})C_6'' + C_{14}' ,$$

$$^4\kappa^{1222} = (\tfrac{3}{7})C_4'' + C_{11}' , \qquad ^4\kappa^{1333} = (\tfrac{3}{7})C_5'' + C_{13}' ,$$

$$^4\kappa^{2333} = (\tfrac{3}{7})C_6'' + C_{15}' , \qquad C_4' = (\tfrac{6}{7})C_4'' , \qquad C_5' = (\tfrac{6}{7})C_5'' ,$$

$$C_6' = (\tfrac{6}{7})C_6'' ,$$

where

$$C_4'' = {}^4\kappa^{1211} + {}^4\kappa^{1222} + {}^4\kappa^{1233} ,$$

$$C_5'' = {}^4\kappa^{1311} + {}^4\kappa^{1322} + {}^4\kappa^{1333} ,$$

$$C_6'' = {}^4\kappa^{2311} + {}^4\kappa^{2322} + {}^4\kappa^{2333} . \tag{15}$$

$^4\kappa^{1111}$, $^4\kappa^{2222}$, $^4\kappa^{3333}$ have multiplicity 1, $^4\kappa^{1211}$, $^4\kappa^{1222}$, $^4\kappa^{1311}$, $^4\kappa^{1333}$, $^4\kappa^{2322}$, $^4\kappa^{2333}$ have multiplicity 4, $^4\kappa^{1122}$, $^4\kappa^{1133}$, $^4\kappa^{2233}$ have multiplicity 6 and $^4\kappa^{1233}$, $^4\kappa^{1322}$, $^4\kappa^{2311}$ have multiplicity 12. Again, although these functions have a certain attractiveness it is better to use

$$\sum_{jklm} 4\kappa^{jklm} t_j t_k t_l t_m = (\tfrac{3}{5})C_1(t_1^2 + t_2^2 + t_3^2)^2$$

$$+ (\tfrac{6}{7})C_2\tfrac{1}{2}(2t_3^2 - t_1^2 - t_2^2)(t_1^2 + t_2^2 + t_3^2)$$

$$+ (\tfrac{6}{7})C_3(t_1^2 - t_2^2)(t_1^2 + t_2^2 + t_3^2)$$

$$+ (\tfrac{6}{7})C_4(2t_1t_2)(t_1^2 + t_2^2 + t_3^2) + (\tfrac{6}{7})C_5(2t_1t_3)(t_1^2 + t_2^2 + t_3^2)$$

$$+ (\tfrac{6}{7})C_6(2t_2t_3)(t_1^2 + t_2^2 + t_3^2)$$

$$+ C_72[5(t_1^2t_2^2 + t_1^2t_3^2 + t_2^2t_3^2) - (t_1^2 + t_2^2 + t_3^2)^2]$$

$$+ C_8(\tfrac{5}{7}) [35t_3^4 - 30t_3^2(t_1^2 + t_2^2 + t_3^2) + 3(t_1^2 + t_2^2 + t_3^2)^2]$$

$$+ C_9(t_1^2 - t_2^2) [7t_3^2 - (t_1^2 + t_2^2 + t_3^2)]$$

$$+ C_{10}(2t_1t_2) [7t_3^2 - (t_1^2 + t_2^2 + t_3^2)] + C_{11}(4t_1t_2)(t_1^2 - t_2^2)$$

$$+ C_{12}(4t_3t_1)(3t_2^2 - t_1^2) + C_{13}(4t_3t_1)(t_3^2 - t_1^2)$$

$$+ C_{14}(4t_3t_2)(3t_1^2 - t_2^2) + C_{15}(4t_3t_2)(t_3^2 - t_2^2) , \tag{16}$$

where

$$10(t_1^2t_2^2 + t_1^2t_3^2 + t_2^2t_3^2) - 2(t_1^2 + t_2^2 + t_3^2)^2 = (6t_1^2t_2^2 - t_1^4 - t_2^4)$$

$$+ (6t_1^2t_3^2 - t_1^4 - t_3^4) + (6t_2^2t_3^2 - t_2^4 - t_3^4) ,$$

$$35t_3^4 - 30t_3^2(t_1^2 + t_2^2 + t_3^2) + 3(t_1^2 + t_2^2 + t_3^2)^2$$

$$= (6t_1^2t_2^2 - t_1^4 - t_2^4) - 4(6t_1^2t_3^2 - t_1^4 - t_3^4)$$

$$-4(6t_2^2t_3^2-t_2^4-t_3^4),$$

$$(t_1^1-t_2^2)\,[7t_3^2-(t_1^2+t_2^2+t_3^2)]$$

$$=(6t_1^2t_3^2-t_1^4-t_3^4)-(6t_2^2t_3^2-t_2^4-t_3^4),$$

$$2t_1t_2[7t_3^2-(t_1^2+t_2^2+t_3^2)]$$

$$=[4t_1t_2(3t_3^2-t_2^2)+4t_2t_1(3t_3^2-t_1^2)]/2,$$

$$4t_1t_2(t_1^2-t_2^2)=4t_1t_2(3t_3^2-t_2^2)-4t_2t_1(3t_3^2-t_1^2).$$

Thus

$$^4\kappa^{1111}=(\tfrac{3}{5})C_1-(\tfrac{3}{7})C_2+(\tfrac{6}{7})C_3-2C_7+(\tfrac{6}{5})C_8-C_9,$$

$$^4\kappa^{2222}=(\tfrac{3}{5})C_1-(\tfrac{3}{7})C_2-(\tfrac{6}{7})C_3-2C_7+(\tfrac{6}{5})C_8+C_9,$$

$$^4\kappa^{3333}=(\tfrac{3}{5})C_1+(\tfrac{6}{7})C_2-2C_7+(\tfrac{16}{5})C_8,$$

$$^4\kappa^{1122}=(\tfrac{1}{5})C_1-(\tfrac{1}{7})C_2+C_7+(\tfrac{2}{5})C_8,$$

$$^4\kappa^{1133}=(\tfrac{1}{5})C_1+(\tfrac{1}{14})C_2+(\tfrac{1}{7})C_3+C_7-(\tfrac{8}{5})C_8+C_9,$$

$$^4\kappa^{2233}=(\tfrac{1}{5})C_1+(\tfrac{1}{14})C_2-(\tfrac{1}{7})C_3+C_7-(\tfrac{8}{5})C_8-C_9,$$

$$C_1=C_1',$$

$$C_2=C_3''-C_1',$$

$$C_3=\tfrac{1}{2}(C_1''-C_2''),$$

$$C_7=(\tfrac{1}{10})\,(8C_7'+C_8'+C_9'),$$

$$C_8=\tfrac{1}{4}(2C_7'-C_8'-C_9'),$$

$$C_9=\tfrac{1}{2}(C_8'-C_9')$$

and

$$^4\kappa^{1233}=(\tfrac{1}{7})C_4+C_{10},\quad ^4\kappa^{1322}=(\tfrac{1}{7})C_5+C_{12},$$

$$^4\kappa^{2311}=(\tfrac{1}{7})C_6+C_{14},\quad ^4\kappa^{1211}=(\tfrac{3}{7})C_4-\tfrac{1}{2}C_{10}+C_{11},$$

$$^4\kappa^{1311}=(\tfrac{3}{7})C_5-C_{12}-C_{13},\quad ^4\kappa^{2322}=(\tfrac{3}{7})C_6-C_{14}-C_{15},$$

$$^4\kappa^{1222}=(\tfrac{3}{7})C_4-\tfrac{1}{2}C_{10}-C_{11},\quad ^4\kappa^{1322}=(\tfrac{3}{7})C_5+C_{13},$$

$$^4\kappa^{2333}=(\tfrac{3}{7})C_6+C_{15},\quad C_{11}=\tfrac{1}{2}(^4\kappa^{1211}-^4\kappa^{1222}),$$

$$C_4=C_4',\quad C_5=C_5',\quad C_6=C_6',\quad\quad (17)$$

where $C_1',C_7',C_8',C_9',C_1'',C_2'',C_3'',C_4'',C_5'',C_6''$ are previously defined, see (15).

If we make the pth axial system coincide with the imposed point symmetry as before then we only need to refine the parameters in Table 3. We note for the case of $4/mmm$ symmetry a single parameter C_7 may be used if $C_7'=C_8'=C_9'$ whereas if $C_8'=C_9'=0$ then $C_8=(\tfrac{5}{8})C_7'$.

Table 3. C parameters to be refined

Laue symmetry	Parameters			
$\bar{1}$	$C_1C_2C_3C_4C_5C_6C_7C_8C_9C_{10}C_{11}C_{12}C_{13}C_{14}C_{15}$			
$2/m$	$C_1C_2C_3C_4$	$C_7C_8C_9C_{10}C_{11}$		
mmm	$C_1C_2C_3$	$C_7C_8C_9$		
$4/m$	C_1C_2	C_7C_8	C_{11}	
$\bar{3}$	C_1C_2	C_8	C_{12}	C_{14}
$4/mmm$	C_1C_2	C_7C_8		
$\bar{3}m$	C_1C_2	C_8		C_{14}
$6/m, 6/mmm$	C_1C_2	C_8		
$m3, m3m$	C_1	C_7		

The interpretation of the parameters A_i ($i=1$ to 6), B_i ($i=1$ to 10), and C_i ($i=1$ to 15) may be readily understood using the Edgeworth expansion of the probability density function (Johnson, 1970; Rae, 1975a). The probability density can be defined as an expansion

$$\Psi(\mathbf{u})\simeq[1+\sum_{j=1}^{m}Q_j(\mathbf{u})]\Psi_0(\mathbf{u})$$

using up to the $(m+2)$th cumulant. Rae (1975a) has pointed out that if the normal distribution

$$\Psi_0(\mathbf{u})=\frac{[\det(p)]^{1/2}}{(2\pi)^{3/2}}\exp\{-\tfrac{1}{2}\sum_{jk}p_{jk}(u^j-x^j)(u^k-x^k)\}$$

is chosen such that

$$^1\lambda^j={}^1\kappa^j-x^j=\tfrac{1}{2}\sum_{kl}{}^3\kappa^{jkl}p_{kl}$$

and

$$^2\lambda^{jk}={}^2\kappa^{jk}-\sigma^{jk}=\tfrac{1}{4}\sum_{lm}{}^4\kappa^{jklm}p_{lm}$$

where

$$\sum_k\sigma^{jk}p_{kl}=\delta_{jl},$$

then

$$Q_1(\mathbf{u})=\frac{1}{3!}\sum_{jkl}{}^3\kappa^{jkl}Z_jZ_kZ_l$$

where

$$Z_j=\sum_k p_{jk}(u^k-x^k),$$

$$Q_2(\mathbf{u})=\frac{1}{4!}\sum_{jklm}{}^4\kappa^{jklm}Z_jZ_mZ_lZ_m-\tfrac{1}{2}\sum_{jk}{}^2\lambda^{jk}Z_jZ_k$$

$$+\tfrac{1}{72}\sum_{jkl}\sum_{pqr}{}^3\kappa^{jkl}\,{}^3\kappa^{pqr}(Z_jZ_pZ_kZ_qZ_lZ_r$$

$$-9Z_jZ_pZ_kZ_qp_{lr}+18Z_jZ_pp_{kq}p_{lr}-6p_{jp}p_{kq}p_{lr})$$

$$(18)$$

and the position $\mathbf{u}=\mathbf{x}$ is a position of maximum probability of value $\Psi_0(\mathbf{x})$ to a very good approximation.

We note that if the parameters A_2 to A_6 are zero then the parameters B_4 to B_{10} make no contribution to $^1\lambda$ and the parameters C_7 to C_{15} make no contribution to $^2\lambda$ in (18). In this instance

$$^1\lambda^1=B_1/2A_1,\quad ^1\lambda^2=B_2/2A_1,\quad ^1\lambda^3=B_3/2A_1,$$

$$(^2\lambda^{11}+{}^2\lambda^{22}+{}^2\lambda^{33})/3=C_1/4A_1,$$

$$^2\lambda^{33}-(^2\lambda^{11}+{}^2\lambda^{22}+{}^2\lambda^{33})/3=C_2/4A_1,$$

$$(^2\lambda^{11}-{}^2\lambda^{22})/2=C_3/4A_1,\quad ^2\lambda^{12}=C_4/4A_1,$$

$$^2\lambda^{13}=C_5/4A_1,\quad ^2\lambda^{23}=C_6/4A_1.\quad\quad (19)$$

Also Z_j is simply $(u^j-r^j)/A_1$ and the shapes associated with the terms B_i,C_i in (13) and (16) are obtained by replacing t_j by $(u^j-r^j)/A_1$ for incorporation in (18).

For the case when A_2 to A_6 are non-zero, Rae (1975a) has suggested modified expressions to replace the terms involving B_1 to B_3 and C_1 to C_6. It is noted that

$$\tfrac{1}{2}\sum_{kl}{}^3\kappa_1^{jkl}p_{kl}={}^1\lambda^j$$

if

$$^3\kappa_1^{jkl}=(\tfrac{2}{5})\,(^1\lambda^j\sigma^{kl}+{}^1\lambda^k\sigma^{lj}+{}^1\lambda^l\sigma^{jk})$$

where $^3\kappa_1{}^{jkl}$ is the component of $^3\kappa^{jkl}$ that leads to a non-zero value of $^1\lambda$. We can then retain the expression $^1\lambda^j = B_j/2A_1$ from (19) if we replace the terms $\sum_{j=1}^{3} (\frac{2}{5}) B_j t_j (t_1^2 + t_2^2 + t_3^2)$ in (13) by

$$\sum_{jkl} {}^3\kappa_1{}^{jkl} t_j t_k t_l = \sum_{j=1}^{3} (\tfrac{2}{5}) B_j t_j \sum_{kl} \sigma^{kl} t_k t_l / A_1 . \qquad (20)$$

Likewise it is noted that

$$^2\lambda^{jk} = \tfrac{1}{4} \sum_{lm} {}^4\kappa_1{}^{jklm} p_{lm}$$

if

$$^4\kappa_1{}^{jklm} = (\tfrac{4}{7})\,(^2\bar\lambda^{jk}\sigma^{lm} + {}^2\bar\lambda^{lm}\sigma^{jk} + {}^2\bar\lambda^{jl}\sigma^{km}$$
$$+ {}^2\bar\lambda^{km}\sigma^{jl} + {}^2\bar\lambda^{kl}\sigma^{jm} + {}^2\bar\lambda^{jm}\sigma^{kl})$$

where

$$^2\lambda^{jk} = {}^2\bar\lambda^{jk} + (\tfrac{1}{7})\sigma^{jk} \sum_{lm} \bar\lambda^{lm} p_{lm} .$$

Now if we define λ_1^{jl} and λ_2^{jl} as $\lambda_1^{jl} = A_1 \sum_k \lambda^{jk} p_{kl}$ and $\lambda_2^{jl} = A_1 \sum_k \bar\lambda^{jk} p_{kl}$ then

$$\lambda_1^{33} - (\lambda_1^{11} + \lambda_1^{22} + \lambda_1^{33})/3 = \lambda_2^{33} - (\lambda_2^{11} + \lambda_2^{22} + \lambda_2^{33})/3,$$

$$(\lambda_1^{11} - \lambda_1^{22})/2 = (\lambda_2^{11} - \lambda_2^{22})/2 ,$$

$$2\lambda_1^{12} = 2\lambda_2^{12} , \quad 2\lambda_1^{13} = 2\lambda_2^{13} , \quad 2\lambda_1^{23} = 2\lambda_2^{23}$$

but

$$(\lambda_1^{11} + \lambda_1^{22} + \lambda_1^{33})/3 = (\tfrac{10}{7})\,(\lambda_2^{11} + \lambda_2^{22} + \lambda_2^{33})/3 .$$

We can obtain a modified version of (19), namely

$$(^2\lambda_1^{11} + {}^2\lambda_1^{22} + {}^2\lambda_1^{33})/3 = C_1/4A_1 ,$$

$$^2\lambda_1^{33} - (^2\lambda_1^{11} + {}^2\lambda_1^{22} + {}^2\lambda_1^{33})/3 = C_2/4A_1 ,$$

$$(^2\lambda_1^{11} - {}^2\lambda_1^{22})/2 = C_3/4A_1 , \quad 2\lambda_1^{12} = C_4/4A_1 ,$$

$$2\lambda_1^{13} = C_5/4A_1 , \quad 2\lambda_1^{23} = C_6/4A_1 , \qquad (21)$$

if we replace the terms corresponding to C_1 to C_6 in (16) by

$$\sum_{jklm} {}^4\kappa_1{}^{jklm} t_j t_k t_l t_m = (\tfrac{24}{7}) \sum_{jk} \bar\lambda^{jk} t_j t_k \sum_{lm} \sigma^{lm} t_l t_m .$$

Substituting $\sum_n \lambda_2^{jn}\sigma^{nk}/A_1$ for $\bar\lambda^{jk}$, we obtain

$$\sum_{jklm} {}^4\kappa_1{}^{jklm} t_j t_k t_l t_m$$

$$= [(\tfrac{2}{5})C_1 \sum_{jk} \sigma^{jk} t_j t_k + (\tfrac{6}{7})C_2\tfrac{1}{2}(\sum_j 3\sigma^{3j} t_3 t_j - \sum_{jk} \sigma^{jk} t_j t_k)$$

$$+ (\tfrac{6}{7})C_3 \sum_j (\sigma^{1j} t_1 t_j - \sigma^{2j} t_2 t_j)$$

$$+ (\tfrac{6}{7})C_4 \sum_j (\sigma^{1j} t_2 t_j + \sigma^{2j} t_1 t_j)$$

$$+ (\tfrac{6}{7})C_5 \sum_j (\sigma^{1j} t_3 t_j + \sigma^{3j} t_1 t_j)$$

$$+ (\tfrac{6}{7})C_6 \sum_j (\sigma^{2j} t_3 t_j + \sigma^{3j} t_2 t_j)] \times \sum_{lm} \sigma^{lm} t_l t_m / A_1^2 , \qquad (22)$$

where symmetry constraints apply exactly as before.

We may describe the Fourier transform of the probability density function $\Psi(\mathbf{u})$ as a product

$$\psi(\mathbf{t}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\,(i\mathbf{t} \cdot \mathbf{u})\Psi(\mathbf{u}) du^1 du^2 du^3$$

$$= \psi_1(\mathbf{t})\psi_2(\mathbf{t}) ,$$

where

$$\psi_1(\mathbf{t}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\,[i\mathbf{t} \cdot (\mathbf{u}-\mathbf{r})]\Psi_1(\mathbf{u}-\mathbf{r}) du^1 du^2 du^3 ,$$

$$\psi_2(\mathbf{t}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\,(i\mathbf{t} \cdot \mathbf{r})\Psi_2(\mathbf{r}) dr^1 dr^2 dr^3$$

and

$$\Psi(\mathbf{u}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \Psi_1(\mathbf{u}-\mathbf{r})\Psi_2(\mathbf{r}) dr^1 dr^2 dr^3 . \qquad (23)$$

We can of course only observe the overall transform $\psi(\mathbf{t})$ and not the components $\psi_1(\mathbf{t})$ and $\psi_2(\mathbf{t})$. However this separation can be useful to distinguish internal molecular motions from rigid-body motions. The former are calculable from spectroscopic results and are generally of smaller mean-square amplitude. Equations (21) and (22) make corrections for $^1\lambda^j$ and $^2\lambda^{jk}$ for an overall probability density function $\Psi(\mathbf{u})$. However the overall cumulant terms associated with parameters B_4 to B_{10} and C_7 to C_{14} are more likely to be associated with internal molecular motions and there seems little reason to alter the form of these expressions from that in (13) and (16).

It is also possible to describe the electron density of an atom as the sum of two electron densities, one for the inner-shell electrons and the other for outer-shell electrons. The means of these two distributions need not coincide. The outer-shell electrons may be described using cumulants which are not the same as for the inner-shell electrons, and if we describe the Fourier transform of the probability density function for the outer-shell electrons as $\psi_1(\mathbf{t})\psi_2(\mathbf{t})$ where $\psi_2(\mathbf{t})$ is obtained from the cumulants for the inner-shell electrons, then the factor $\psi_1(\mathbf{t})$ describes the perturbation of a stationary outer shell of electrons associated with the atom's environment. The ability to choose axial systems to facilitate constrained refinement enables a limited number of meaningful parameters to be used to describe this perturbation. If $\psi_1(\mathbf{t}) = 1$ the mean of the unperturbed outer shell of electrons moves during vibration so as to be coincident with the mean of the inner-shell electrons.

Rigid-body motions of groups of atoms

Schomaker & Trueblood (1968) have indicated how the thermal vibrations of a molecule may be analysed on the assumption that the major contributions to the molecule's motion arise from motion of the molecule as a rigid unit. Johnson (1970) has discussed the use of a segmented-body analysis to describe pieces of a molecule moving as a rigid unit. Uncorrelated motions may be treated by regarding the temperature factor of an atom as the product of more than one temperature

factor, see (23). Thus one can include factors obtained from spectroscopic information and from uncorrelated motions of rigid groups of atoms containing various numbers of atoms. The freedom to choose the origin and direction of the reference frame of axes makes constrained refinement easier, as a specific choice of axial system and rigid-body motion greatly reduces the number of refinable parameters. A lattice-dynamical treatment of molecular rigid-body vibration tensors (Scheringer, 1973) shows that an axial system corresponding to the principal inertial axes centred at the centre of mass is the ideal axial system for isolated molecules or ions in a crystal. Such a choice of axial system is unique. Busing & Levy (1964) have discussed the effect of thermal motion on bond-length estimates, emphasizing that the joint distribution of the motions of the atoms must be known or assumed if proper corrections are to be made. Corrections for the displacement of the mean from the position of maximum probability using (19) and (20) can be imposed on the form of the temperature factor if so desired.

Following the procedure of Schomaker & Trueblood (1968), the average motion of an atom at $r_n = \sum_k {}^p X_n^k \, {}^p A_k$

is given by

$$^p U_{ij} = \sum_{kl} {}^p A_{ijkl} {}^p X_n^k {}^p X_n^l + \sum_k {}^p B_{ijk} {}^p X_n^k + {}^p T_{ij} ,$$

where

$$^p A_{ijkl} = \sum_{mn} \varepsilon_{imk} \varepsilon_{jnl} {}^p L_{mn}$$

and

$$^p B_{ijk} = \sum_n (\varepsilon_{ink} {}^p S_{nj} + \varepsilon_{jnk} {}^p S_{ni}) .$$

The superscript p indicates the pth reference frame but will be omitted since (25) and (26) are not dependent on the axial system; we will always assume we are using the most convenient axial system. In particular for the nth atom

$$U_{11} = L_{22} X_n^3 X_n^3 + L_{33} X_n^2 X_n^2 - 2L_{23} X_n^2 X_n^3 + S_{21} 2 X_n^3$$
$$- S_{31} 2 X_n^2 + T_{11}$$

$$U_{12} = - L_{33} X_n^1 X_n^2 - L_{12} X_n^3 X_n^3 + L_{13} X_n^2 X_n^3 + L_{23} X_n^1 X_n^3$$
$$- (S_{11} - S_{22}) X_n^3 + S_{31} X_n^1 - S_{32} X_n^2 + T_{12} \quad etc. \quad (24)$$

Rae (1975b) has shown that all meaningful constraints on the TLS model can be achieved by judicious choice of axial system and using the variables

$$D_1 = (L_{11} + L_{22} + L_{33})/3 , \quad D_2 = L_{33} - (L_{11} + L_{22} + L_{33})/3 ,$$

$$D_3 = (L_{11} - L_{22})/2 , \quad D_4 = L_{12} , \quad D_5 = L_{13} , \quad D_6 = L_{23} ,$$

$$E_1 = (T_{11} + T_{22} + T_{33})/3 , \quad E_2 = T_{33} - (T_{11} + T_{22} + T_{33})/3 ,$$

$$E_3 = (T_{11} - T_{22})/2 , \quad E_4 = T_{12} , \quad E_5 = T_{13} , \quad E_6 = T_{23} ,$$

$$F_1 = C_{23} S_{23} - C_{32} S_{32} , \quad F_2 = C_{31} S_{31} - C_{13} S_{13} ,$$

$$F_3 = C_{12} S_{12} - C_{21} S_{21} , \quad F_4 = C_{32} S_{23} + C_{23} S_{32} ,$$

$$F_5 = C_{13} S_{31} + C_{31} S_{13} , \quad F_6 = C_{21} S_{12} + C_{12} S_{21} ,$$

$$F_7 = (2 S_{33} - S_{11} - S_{22})/2 , \quad F_8 = S_{11} - S_{22} ,$$

$$\text{where} \quad C_{ij}^2 + C_{ji}^2 = 1 . \quad (25)$$

We note that $S_{11} + S_{22} + S_{33}$ cannot be determined. The expression $\sum U_{ij} t_i t_j$ can then be written as

$$\sum_{ij} U_{ij} t_i t_j = D_1 (\hat{t}_1^2 + \hat{t}_2^2 + \hat{t}_3^2) + D_2 (2\hat{t}_3^2 - \hat{t}_1^2 - \hat{t}_2^2)/2$$

$$+ D_3 (\hat{t}_1^2 - \hat{t}_2^2) + 2 D_4 \hat{t}_1 \hat{t}_2 + 2 D_5 \hat{t}_1 \hat{t}_3 + 2 D_6 \hat{t}_2 \hat{t}_3$$

$$+ E_1 (t_1^2 + t_2^2 + t_3^2) + E_2 (2 t_3^2 - t_1^2 - t_2^2)/2 + E_3 (t_1^2 - t_2^2)$$

$$+ 2 E_4 t_1 t_2 + 2 E_5 t_1 t_3 + 2 E_6 t_2 t_3 + 2 F_1 (C_{23} \hat{t}_2 t_3 - C_{32} \hat{t}_3 t_2)$$

$$+ 2 F_2 (C_{31} \hat{t}_3 t_1 - C_{13} \hat{t}_1 t_3) + 2 F_3 (C_{12} \hat{t}_1 t_2 - C_{21} \hat{t}_2 t_1)$$

$$+ 2 F_4 (C_{32} \hat{t}_2 t_3 + C_{23} \hat{t}_3 t_2) + 2 F_5 (C_{13} \hat{t}_3 t_1 + C_{31} \hat{t}_1 t_3)$$

$$+ 2 F_6 (C_{21} \hat{t}_1 t_2 + C_{12} \hat{t}_2 t_1) + 2 F_7 \hat{t}_3 t_3 + F_8 (\hat{t}_1 t_1 - \hat{t}_2 t_2) ,$$

where

$$\hat{t}_1 = X_n^2 t_3 - X_n^3 t_2 , \quad \hat{t}_2 = X_n^3 t_1 - X_n^1 t_3 \quad \text{and}$$

$$\hat{t}_3 = X_n^1 t_2 - X_n^2 t_1 . \quad (26)$$

If the axial system is chosen to be parallel to the principal libration axes then the definition of C_{ij} as $C_{ij} = L_{ii}/(L_{ii}^2 + L_{jj}^2)^{1/2}$ allows the parameters F_1 to F_6 to be associated with the axial system that best describes the average motion (Rae, 1975b). Symmetry constraints on D_i, E_i, $i = 1$ to 6 are those of A_1 to A_6 in (11). If we choose our axial directions ${}^p A_k$ to coincide with the imposed point symmetry (primary axis $= {}^p A_3$ and, if applicable, secondary axis $= {}^p A_1$), then we only need to refine the independent F_i parameters given in Table 4.

Table 4. *F parameters to be refined*

Point group	Parameters		
1	$F_1 F_2 F_3 F_4 F_5 F_6 F_7 F_8$		
2	F_3	$F_6 F_7 F_8$	
m	$F_1 F_2$	$F_4 F_5$	
222			$F_7 F_8$
$mm2$	F_3	F_6	
3, 4, 6	F_3	F_7	
$\bar{4}$		F_6	F_8
32, 422, 622		F_7	
$3m$, $4mm$, $6mm$	F_3		
$\bar{4}2m$			F_8
$\bar{6}$, $\bar{6}m2$, 23, $\bar{4}32$, $\bar{4}3m$, $\bar{1}$	None		

It is not necessary to refine positional parameters using the same axial system. Likewise, not all thermal parameters need be defined with respect to the same axial system. As seen from (5), it is only necessary to define the axial system used to define the qth parameter. Choice of axial system allows sensible constrained refinement to be simply the choice to refine or not to refine a parameter.

The interpretation of the TLS description of rigid-body motion uses an axial system parallel to the principal axes of the L tensor located at the centre of action, which is defined as the unique point which makes $S_{ij} = S_{ji}$. Parameters $T'_{ij}, L'_{ij}, S'_{ij}$ where $\sum_i S'_{ii}$ is undeterminable are obtained using the pth axial system ${}^p A_j = \sum_i {}^p U_{ij} A_i$ located at $\sum_i X_0^i A_i$. The principal axes

of the **L** tensor are defined relative to this axial system as $^p\hat{A}_k = \sum_j {}^pV_{jk}{}^p A_j = \sum_i {}^p\hat{U}_{ik}A_i$ where $^p\hat{U}_{ik} = \sum {}^pU_{ij}{}^pV_{jk}$. Keeping the origin fixed we redefine the **T,L,S** tensors for the $^p\hat{A}_k$ axis system as

$$^pT'_{kl} = \sum_{ij} T'_{ij}{}^pV_{ik}{}^pV_{jl} , \quad ^pS'_{kl} = \sum_{ij} S'_{ij}{}^pV_{ik}{}^pV_{jl} ,$$

$$^pL'_{kl} = \sum_{ij} L'_{ij}{}^pV_{ik}{}^pV_{jl} ,$$

where $^pL'_{kl} = 0$ for $k \neq l$. As $\sum_{ij}\delta_{ij}{}^pV_{ik}{}^pV_{jl} = \delta_{kl}$ it is seen that the assumption of a zero value for $\sum_{ij} S'_{ij}$ does not alter the values of $^pS'_{ij}$ and $^pS'_{ii} - {}^pS'_{jj}$ when $i \neq j$.

The $^p\hat{A}_k$ axes are then relocated at

$$\sum_i \hat{X}_0^i A_i = \sum_i X_0^i A_i + \sum_k {}^pX_0^k {}^p\hat{A}_k ,$$

where

$$^pX_0^k = \sum_{ij} \varepsilon_{ijk}{}^pS'_{ij}/({}^pL'_{ii} + {}^pL'_{jj})$$

and

$$\hat{X}_0^i = X_0^i + \sum_k {}^p\hat{U}_{ik}{}^pX_0^k .$$

This redefines the elements of the **TLS** tensors (Rae, 1975b) as

$$^p\hat{L}_{ij} = {}^pL'_{ij} , \quad ^p\hat{S}_{ij} = {}^p\hat{S}_{ji} = ({}^p\hat{L}_{ii}{}^pS'_{ji} + {}^p\hat{L}_{jj}{}^pS'_{ij})/$$

$$({}^p\hat{L}_{ii} + {}^p\hat{L}_{jj}) \quad \text{for} \quad i \neq j , \quad ^p\hat{S}_{ii} - {}^p\hat{S}_{jj} = {}^pS'_{ii} - {}^pS'_{jj} ,$$

$$^p\hat{T}_{11} = {}^pT'_{11} - [-2{}^p\hat{S}_{21}{}^pX_0^3 + 2{}^p\hat{S}_{31}{}^pX_0^2 + {}^p\hat{L}_{22}{}^pX_0^3 \, {}^pX_0^3$$

$$+ {}^p\hat{L}_{33}{}^pX_0^2 \, {}^pX_0^2]$$

$$^p\hat{T}_{12} = {}^pT'_{12} - [({}^p\hat{S}_{11} - {}^p\hat{S}_{22}){}^pX_0^3 - {}^p\hat{S}_{31}{}^pX_0^1 + {}^p\hat{S}_{32}{}^pX_0^2$$

$$- {}^p\hat{L}_{33}{}^pX_0^1{}^pX_0^2] \quad etc. , \tag{27}$$

where the terms in square brackets are obtained from the previous equations and the remaining values of $^p\hat{T}_{ii}$ and $^p\hat{T}_{ij}$ are obtained by permutation of indices.

We thus obtain new starting parameters for the next refinement cycle. The position of the nth atom at $\sum_i X_n^i A_i$ with respect to the pth axial system $^p\hat{A}_k$ at $\sum_i \hat{X}_0^i A_i$ is given by $\sum_k {}^pX_n^{kp}\hat{A}_k$ where $^pX_n^k = \sum_i(X_n^i - \hat{X}_0^i){}^p\hat{U}_{ik}$ for the evaluation of $\hat{t}_i$ values in (26).

It has been shown (Rae, 1975b) that the **TLX** constraint is equivalent to setting $F_i = 0$, $i = 4$ to 8 in this localized axial system and the application of this constraint at this stage does not alter the values of $U_{11} + U_{22} + U_{33}$ for any atom. Nor does it alter the displacement of the mean from the position of maximum probability for any atom.

Correction of interatomic distances

Approximations of these corrections have been summarized by Johnson & Levy (1974). Rae (1975a) has shown how a displacement of the mean of the probability distribution of an atom from the position of maximum probability may be described using parameters B_1, B_2, B_3 [see (21)] where $^1\lambda^i$ is the component of the displacement on the ith direction and is given by $B_i/2A_1$, $i = 1$ to 3. The mean-square motion of an atom in a rigid group may be considered to arise from six non-covariant contributions, i.e. three screw rotations and three translations. For the origin at $\sum_i \hat{X}_0^i A_i$ the screw rotations may be described as parallel to the principal axes of the **L** tensor but displaced from this origin by amounts given by the parameters F_4, F_5, F_6 (Rae, 1975b).

However the displacement of the mean from the position of maximum probability for the nth atom is only dependent on the libration tensor **L** and the distance from the centre of action. For the principal axis system $^p\hat{A}_k$ at $\sum_i \hat{X}_0^i A_i$ this is given by

$$^p\lambda_n^k = -{}^p\hat{X}_n^k({}^pL_{ii} + {}^pL_{jj})/2 , \quad (i \neq j \neq k) , \tag{28}$$

where $^p\hat{X}_n^1, {}^p\hat{X}_n^2, {}^p\hat{X}_n^3$ is the position of maximum probability and $^p\lambda_n^k = {}^pX_n^k - {}^p\hat{X}_n^k$ where $^pX_n^1, {}^pX_n^2, {}^pX_n^3$ is the position of the mean relative to the localized origin.

Riding motions

The total correction of atom positions for libration is evaluated as the vector sum of corrections for individual uncorrelated components of each mode seeing an atom at the mean position for all other modes. The most probable position is regarded as being where all amplitudes of vibration and libration are zero. For example, an H atom on a phenyl ring may be thought to have an extra libration component in excess of the C atoms with a centre of action at the mean position of the adjacent C atom. Thus the component of $^1\lambda$ along the C–H bond direction arising from this motion is given by $-\alpha/2d$ where d is the bond distance and α is the mean-square displacement of the H atom normal to the bond in excess of that predicted assuming the H atom has no excess libration. The contribution of those higher-frequency normal modes which do not maintain the rigid nature of the phenyl group may be evaluated spectroscopically and thus the corrections for excess vibration of H atoms in the phenyl group may be made empirically.

The use of segmented-body analysis (Johnson, 1970) with constraints on the **TLS** model for each segment may require the superposition of a number of corrections such as given in (28). However the use of constraints on the principal axes of libration and the centre of action presupposes a knowledge of intersegment correlation. It should be noted that a **TLX** constraint does not alter the value of $U_{11} + U_{22} + U_{33}$ for any atom, nor does it alter the displacement of the mean from the position of maximum probability for any atom and is often sufficient constraint for small segments to obtain sensible refinements and hence sensible values of $^1\lambda$. The use of variable parameters B_1, B_2, B_3 for an atom completely avoids the need for rigid-body models

to try and obtain correct atomic positions. However rigid-body models use far fewer variable parameters.

Constrained refinement

If we have two different sets of n linearly independent real variables related by the transformation

$$\Delta u_j = \sum_{k=1}^{n} P_{jk}\Delta v_k , \qquad (29)$$

then changing variables causes the least-squares equation

$$\sum_{j=1}^{n} A_{lj}\Delta u_j = B_l$$

to become

$$\sum_{j,k,l=1}^{n} P_{ji}A_{jk}P_{kl}\Delta v_l = \sum_{j} P_{ji}B_j \quad \text{or}$$

$$\sum_{l=1}^{n} C_{il}\Delta v_l = D_i , \quad (i=1 \text{ to } n) . \qquad (30)$$

If the $(m+1)$th to nth variables Δv_l are constrained to have certain fixed values then we solve the m equations

$$\sum_{l=1}^{m} C_{il}\Delta v_l = D_i - \sum_{l=m+1}^{n} C_{il}\Delta v_l , \quad i=1 \text{ to } m \qquad (31)$$

and evaluate values of Δu_j using (29).

If the differentials $\partial/\partial u_j$ refer to single-atom parameters, the transformation to (30) may be done either after the evaluation of A_{ij} or directly using differentials $\partial/\partial v_k = \sum_j P_{jk}\partial/\partial u_j$.

The transformation matrix P_{jk} can be generated from an auxiliary program and provision made for a transformation of the type (29), (30), and (31) to be standard procedure. By arranging the sequence of the variables Δu_j it is possible to block-diagonalize the matrix P_{jk}.

Positional-parameter constraints

It is possible to refine changes in internal coordinates rather than positional parameters. The use of an orthonormal axial system to describe positional parameters allows the application of concepts used for the analysis of normal-mode analysis of vibration (Wilson, Decius & Cross, 1955). If we have N atoms we have $3N$ degrees of freedom to describe changes in positional parameters. The change in the tth internal coordinate is given by $\Delta s_t = \sum_{j=1}^{3N} B_{tj}\Delta r_j$ where $B_{tj} = (\partial s_t/\partial r_j)_0$, where r_j is a positional parameter X_n^i ($n=1$ to N, $i=1$ to 3) and the subscript 0 implies evaluation for all $\Delta s_t = 0$. Thus

$$\Delta r_j = \sum_{t=1}^{3N} (B^{-1})_{tj}\Delta s_t ,$$

provided we pick a set of $3N$ linearly independent internal coordinates and

$$(\partial/\partial s_t)_0 = \sum_{j=1}^{3N} (B^{-1})_{tj}(\partial/\partial r_j)_0$$

allowing the concepts of (29), (30), (31) to be applied. Values of $(\partial/\partial s_t)_0$ for rotation and translation parameters (φ_i and X_0^i) have been given earlier in (8).

It should be noted that s_t can be a linear combination of bond lengths or bond angles. Bonds can be made equivalent by constraining the difference between the bond lengths to change by an amount to make the bond lengths equal. If a symmetry constraint is imposed the only non-zero changes in internal coordinates are those which maintain the equivalence required by symmetry.

The B^{-1} matrix is of dimension $3N$ so that ways of reducing storage requirements warrant consideration. One method is to use artificially created displacement modes, v_n, so that $\Delta r_j = \sum_n R_{jn}\Delta v_n$ where R_{jn} gives the value of Δr_j when $\Delta v_n = 1$, $\Delta v_m = 0$ ($m \neq n$). Thus $(\partial/\partial v_n)_0 = \sum_j R_{jn}(\partial/\partial r_j)_0$. These modes are created in such a way that the nth mode does not alter the $(n+1)$th to $3N$th internal coordinates and need only involve as many non-zero values of R_{jn} as necessary to make this possible. We note $\Delta s_t = \sum_n S_{tn}$ where $S_{tn} = \sum_{j=1}^{3N} B_{tj}R_{jn}$ if the amount the tth internal coordinate changes when $\Delta v_n = 1$, $\Delta v_m = 0$ ($m \neq n$). Constraints are then imposed by giving the $(m+1)$th to $3N$th values of Δv_n fixed values.

It is possible to cut the structure up into segments where no constraints are imposed on the linkages between segments. This enables any constraint to be imposed within segments and enables the most convenient axial system to be chosen for each segment. For example if certain atoms in a segment are constrained to be planar an axial system may be chosen so that $^pX_n^3 = 0$ for these atoms. The axial system may be refined by allowing X_0^3, φ_1 and φ_2 to change value. An atom on a special position such as x,x,z may be refined by defining an axial system rather than writing a patch for the least-squares program. The axes are chosen so that the allowed degrees of freedom for such an atom correspond to changes in axial directions.

It is also possible to achieve equivalence between comparable groups of atoms by the use of pseudosymmetry operators. We define a different axial system for each segment in such a way that the position of an atom in segment 1 relative to the axial system for segment 1 is equal to the position of an atom in segment 2 relative to the axial system for segment 2. A change in atom positions within a segment relative to its axial system is then common to the two segments if equivalence is to be maintained. It is seen from (5) for the evaluation of $\partial F(\mathbf{S})/\partial u_q$ it is only necessary to say that the parameter u_q' describing the n'th atom is the same as the parameter u_q describing the nth atom for the

value of $\partial F(S)/\partial u_q$ to be an easily programmed quantity.

The orientation and location of the axial system for a segment relative to its initial position are refinable parameters. Linear independence of variables must be considered since it is not possible to refine simultaneously all atom positions in a segment as well as all the axial systems. This problem can be avoided if the axial system for one segment is fixed.

A special case of equivalent segment constraint is when a molecule of inherent symmetry is located at a position of lower symmetry in the unit cell. The inherent symmetry can be imposed as a constraint by describing each pseudo-equivalent segment by its own axial system. All these axial systems have a common origin and have a fixed relationship to a reference axial system ^pA_j, at the same origin $\sum_j {}^pX_0^j\, {}^pA_j$. Changes in the atom positions within a segment relative to its axial system are then common to all segments. However only the orientation and location of the reference axial system ^pA_j can be refined if the symmetry constraint is to be observed. This axial system is refined relative to its initial position using initial positions described in the ^pA_j axial system for the pseudo-equivalent atoms.

Conclusion

It has been shown that it is possible to write a program for least-squares refinement so that meaningful constraints can be applied by simply deciding whether or not to refine certain standard parameters. This choice is made possible by the use of a number of orthonormal axial systems. The systematic removal of constraints is also possible in such a system and the significance of those parameters which remove a constraint is more easily assessed.

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Rigid-Body Motion in Crystals – The Application of Constraints on the TLS Model

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A simpler derivation of the equations of Schomaker & Trueblood [*Acta Cryst.* (1968), B24, 63–76] is given. It is shown that the ready interpretation of the meaningfulness of refinable parameters is best achieved by selecting the centre of action as origin and describing the motion with parameters defined relative to the principal axes of libration. A choice of 20 variables is made so that all meaningful constraints on the TLS model correspond to certain of the variables having zero value. It is shown that the five parameters that distinguish the TLS model from the TLX model do not alter the mean-square displacement of any atom. Neither do they alter the displacement of the mean from the position of maximum probability for any atom.

Introduction

There is an unfortunate tendency in X-ray crystallography always to describe structures relative to crystallographic axes. If a non-crystallographic axial system is used to describe some feature of a crystal structure then it is only necessary to know the relationship of the origin and orientation of the axial system with