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

\[
\sum_k R_{jk}(R^{-1})_{kj} = \delta_{jl}.
\]

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 \( \mathbf{S} \) 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 \( \mathbf{A}_k = \mathbf{B}_k, \quad \mathbf{r} \mathbf{A}_k = p \mathbf{B}_k \) and \( \mathbf{A}_k = \sum_I p U_{ki} \mathbf{A}_i \) where \( p U_{ki} = \mathbf{A}_k \cdot p \mathbf{B}_i = \mathbf{B}_k \cdot p \mathbf{A}_i \). If we describe any point \( \mathbf{r} \) in real space as

\[
\mathbf{r} = \sum_I p X^i \mathbf{A}_i
\]

and any point \( \mathbf{S} \) in reciprocal space as

\[
\mathbf{S} = \frac{1}{2\pi} \sum_I p t_i \mathbf{B}_i
\]

then

\[
p X^i = \sum_k X^k p U_{ki} \quad \text{and} \quad p t_i = \sum_k (p U^{-1})_{ik} t_k = \sum_k p U_{ki} t_k.
\]

Also \( \mathbf{a}_j = \sum_I p R_{ij} \mathbf{A}_i \) etc. where

\[
p R_{ij} = \sum_k R_{jk} p U_{ki}.
\]

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
\[ \psi_n(S) = \exp \left( i \sum_j \kappa_n^j t_j + \frac{i^2}{2!} \sum_{jk} \kappa_n^{jk} t_j t_k \right) \]
\[ + \frac{i^3}{3!} \sum_{jkl} \kappa_n^{jkl} t_j t_k t_l + \frac{i^4}{4!} \sum_{jkim} \kappa_n^{jkim} t_j t_k t_l t_m + \ldots \] (1)

where \( i^2 = -1 \) and the first four cumulant tensors \( \kappa_n^j, \kappa_n^{jk}, \kappa_n^{jkl}, \kappa_n^{jkim} \) describe the mean, the variance covariance, the skewness and the kurtosis of the \( n \)th 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

\[ S = \frac{1}{2\pi} \sum_k t_k B_k. \]

Pawley (1972) has pointed out that there is no reason why the cumulant tensors cannot be refined in an orthonormal space. The tensor quantities \( \kappa_n \) are defined in units of \( (\AA)^n \) if we use orthonormal basis vectors when \( |A_i| = 1\ \AA \). Pawley advocates the use of a single axial system (Patterson, 1959) in which \( A_1 = a_1/a_1, \quad A_2 = A_3 \times A_1, \quad \) and \( A_3 = b_3/b_3 \), making

\[ R_{jk} = \begin{pmatrix} a_1 & 0 & 0 \\ a_2 \cos \alpha_1 & a_2 \sin \alpha_1 & 0 \\ a_3 \cos \alpha_2 & -a_3 \sin \alpha_2 \cos \beta_1 & 1/|B_3| \end{pmatrix} \]

where \( \alpha_1, \beta_1 \) are the interaxial angles of the crystallographic unit cell in real space and reciprocal space respectively. This choice contrasts with the orthonormal basis vectors \( B_1 = b_1/b_1, \quad B_2 = B_3 \times B_1, \quad \) and \( B_3 = a_3/a_1 \) 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 reflections 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 (Schoemaker & 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 \( \partial F(S)/\partial u_q \) for various parameters \( u_q \).

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

\[ \frac{\partial F(S)}{\partial u_q} = \sum \frac{\partial F(S)}{\partial v_i} \frac{\partial v_i}{\partial u_q}, \] (2)

where both \( S \) 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 \((\theta_m, d_m)\) is a symmetry operation where \((\theta_m, d_m)r = \theta_m r + d_m\) then the structure factor may be described as

\[ F(S) = \sum_m F_m(S) \]

\[ F_m(S) = \exp \left( 2\pi i d_m \cdot S \right) \sum_n a_n f_n(S) \psi_n(\theta_m^{-1} S) ; \] (3)

\( a_n \) is the occupancy factor, \( f_n(S) \) the scattering factor and \( \psi_n(S) \) 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 \( d_m \cdot S \) and \( \theta_m^{-1} S = \sum_j h_m j \)

where the \( h_{mj} \) values are simple combinations of the Miller indices (Busing, Martin & Levy, 1962).

From (1) it is seen that

\[ \ln \psi_n(S) = i \sum_j \kappa_n^j t_j + \frac{i^2}{2!} \sum_{jk} \kappa_n^{jk} t_j t_k \]
\[ + \frac{i^3}{3!} \sum_{jkl} \kappa_n^{jkl} t_j t_k t_l + \frac{i^4}{4!} \sum_{jkim} \kappa_n^{jkim} t_j t_k t_l t_m \] (4)

and since \( \psi_n(S) = \exp \left( \ln \psi_n(S) \right) \) it follows that

\[ \frac{\partial \psi_n(S)}{\partial u_q} = \psi_n(S) \frac{\partial \ln \psi_n(S)}{\partial u_q} \]

and

\[ \frac{\partial F(S)}{\partial u_q} = \sum_{mn} \exp \left( 2\pi i d_m \cdot S \right) a_n f_n(S) \psi_n(\theta_m^{-1} S) \]
\[ \times \frac{\partial \ln[a_n \psi_n(\theta_m^{-1} S)]}{\partial u_q} . \] (5)
If we describe the qth parameter \( u_q \) with respect to the pth orthonormal axial system, then
\[
\theta_m^* S = \sum_{t} p t_{lm} \hat{p} \mathbf{B}_t
\]
where
\[
\hat{p} \mathbf{B}_t = \mathbf{p} \mathbf{A}_t = \sum_{jk} R_{jk} u_{k1} \mathbf{b}_j = \sum_{jk} \mathbf{p} U_{k1} (R^{-1})_{kj} a_j
\]
and
\[
pt_{lm} = \sum_{jk} \mathbf{p} U_{k1} (R^{-1})_{kj} r_{hmj}.
\]
(6)

The pth orthonormal axial system is related to the axial system \( \mathbf{A}_1 = \mathbf{a}_1 / \mathbf{a}_1, \mathbf{A}_2 = \mathbf{A}_3 \times \mathbf{A}_1, \mathbf{A}_3 = \mathbf{b}_2 / \mathbf{b}_3 \) \( \mathbf{A}_k = \mathbf{B}_k = \sum (R^{-1})_{kj} a_j \) by the pth unitary transformation
\[
\mathbf{p} \mathbf{B}_t = \sum_{k} \mathbf{p} U_{k1} \mathbf{B}_k.
\]

If a crystal structure has an inversion centre at the origin of the unit cell then \( 0 \mathbf{S} = - \mathbf{S} \) for this symmetry operation and \( V(-\mathbf{S}) = (\mathbf{S})^* \) where \( (\mathbf{S})^* \) is the complex conjugate of \( \mathbf{S} \). Thus two centrosymmetrically related atoms make a contribution to \( F(\mathbf{S}) \) of \( f(\mathbf{S}) \alpha_{\mathbf{r}} [\mathbf{S} + (\mathbf{S})^*] \) and the differential of this contribution with respect to \( u_q \) is
\[
\left( \frac{\partial}{\partial u_q} V(\mathbf{S}) \right) = \left( \frac{\partial}{\partial u_q} V(\mathbf{S}) \right)^*.
\]

**Refinement of the reference frame**

We can describe the reciprocal-space vector \( \mathbf{S} \) with respect to estimates of the pth axial system by saying
\[
2 \pi \mathbf{S} = \sum_{t} \mathbf{p} t_{lm} \mathbf{B}_t = \sum_{t} \mathbf{p} t_{lm} \mathbf{B}_t
\]
where
\[
\mathbf{p} t_{lm} = \sum_{j} \mathbf{p} V_{jl} \mathbf{V}_{kl} \mathbf{B}_t = \sum_{k} \mathbf{p} V_{kl} \mathbf{B}_k \quad \text{and} \quad \sum_{k} \mathbf{p} V_{kl} \mathbf{V}_{kl} = \delta_{jk}.
\]

The \( \mathbf{p} \mathbf{B}_t \) are the initial choice of axis directions and the \( \mathbf{p} \mathbf{B}_t \) are the directions of the best choice of the pth axial system for describing the parameters associated with it.

For the pth reference frame
\[
\mathbf{p} V_{jk} = \begin{pmatrix} C_3 & S_3 & 0 \\ -S_3 & C_3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} C_2 & 0 & -S_2 \\ 0 & 1 & 0 \\ S_2 & 0 & C_2 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} C_1 & S_1 \\ -S_1 & C_1 \end{pmatrix}
\]
\[
= \begin{pmatrix} C_2 C_3 & C_2 S_3 S_1 + S_2 C_1 & -C_1 S_2 C_3 + S_1 S_3 \\ -S_2 C_2 & S_2 S_3 S_1 + C_1 C_3 & C_1 S_2 C_3 + S_3 S_1 \end{pmatrix}
\]
\[
(7)
\]
where \( C_1 = \cos \phi_1, S_1 = \sin \phi_1, i = 1 \) to 3. We see that if \( C_3 = S_2 = C_1 = 1 \) then
\[
\mathbf{p} V_{jk} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}
\]
and
\[
\mathbf{p} V_{jk} / \partial \phi_i = \begin{pmatrix} -\delta_{12} & \delta_{14} + \delta_{13} & 0 \\ 0 & 0 & \delta_{12} + \delta_{13} \\ 0 & \delta_{12} & -\delta_{13} \end{pmatrix}
\]
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 \( \phi_i \) are zero, making \( \mathbf{p} V_{jk} / \partial \phi_i = \delta_{12} \) and \( \mathbf{p} V_{jk} / \partial \phi_i = \delta_{13} \) for a cyclic permutation of 1, 2, 3, \( \delta_{12} = +1 \) for a non-cyclic permutation of 1, 2, 3, and \( \delta_{13} = 0 \) otherwise. The approximation \( \mathbf{p} V_{jk} \approx \delta_{jk} + \sum_{i} \delta_{1jk} \mathbf{p} \phi_i \) implied by the least-squares refinement takes no account of the sequence of the three matrices making up \( \mathbf{p} V_{jk} \) but this effect is small if \( \delta_{1jk} \) is small. The ill-conditioning is minimized by putting the matrices in a sequence where the smallest \( \delta_{1jk} \) is associated with the second matrix when (7) is used to give the new axial directions \( \mathbf{p} \mathbf{B}_t = \mathbf{p} \mathbf{A}_t = \sum_{k} \mathbf{p} U_{jk} \mathbf{A}_k \) where \( \mathbf{p} \mathbf{U}_{jk} = \sum_{k} \mathbf{p} \mathbf{V}_{kl} \mathbf{V}_{jk} \) and \( \mathbf{A}_k = \mathbf{B}_k \) are the orthonormal axes \( \mathbf{a}_1 / \mathbf{a}_1, \mathbf{A}_3 \times \mathbf{A}_1, \mathbf{b}_3 / \mathbf{b}_3 \) to which all the unitary transformations are referred.

**Positional parameters**

Positional parameters are associated with the first term in the expansion of \( \ln V(\mathbf{S}) \) described in (4). This term may be expressed as \( 2 \pi \mathbf{r}_n \cdot \mathbf{S} \) and \( \mathbf{r}_n = \mathbf{R} + \mathbf{r}_n \) where \( \mathbf{R} \) is the position of the origin of the pth axial system in real space and \( \mathbf{r}_n \) 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 \( \mathbf{r}_n \) by the best orientation of the pth axial system then
\[
\mathbf{r}_n = \sum_k \mathbf{p} X_{nk} \mathbf{A}_k \quad \text{and} \quad \mathbf{r}_n = \sum_k \mathbf{p} X_{nk} \mathbf{A}_k.
\]

We define \( 2 \pi \mathbf{r}_n \) using the initially assumed orientation of the pth axial system saying \( 2 \pi \mathbf{r}_n = \sum \mathbf{p} t_{lm} \mathbf{B}_t \). These directions are related by the transformation \( \mathbf{p} \mathbf{B}_t = \sum_{k} \mathbf{p} V_{jk} \mathbf{B}_k \) where \( \mathbf{p} V_{jk} \) is described in terms of parameters \( \phi_i \) in (7).

Thus
\[
2 \pi \mathbf{r}_n \cdot \mathbf{S} = i \sum_{kl} (\mathbf{p} X_{k1} + \mathbf{p} X_{k2}) \mathbf{p} V_{jk} \mathbf{t}_j
\]
and from (5) we see that this term makes a zero contribution to the evaluation of \( \partial F(\mathbf{S}) / \partial u_q \) unless \( u_n = \mathbf{p} X_{l0} / \mathbf{p} X_{l1} \) or \( \phi_j \). Thus
\[
(2 \pi \mathbf{r}_n \cdot \mathbf{S})_0 = i \sum_{kl} (\mathbf{p} X_{k1} + \mathbf{p} X_{k2}) \mathbf{p} V_{jk} \mathbf{t}_j
\]
and from (7) when all \( \phi_j = 0 \)
\[
(2 \pi \mathbf{r}_n \cdot \mathbf{S})_0 = -i (\mathbf{p} X_{l0} \mathbf{r}_3 - \mathbf{p} X_{l3} \mathbf{r}_0)
\]
\[
(2 \pi \mathbf{r}_n \cdot \mathbf{S})_0 = -i (\mathbf{p} X_{l3} \mathbf{r}_1 - \mathbf{p} X_{l1} \mathbf{r}_3)
\]
and
\[
\mathbf{S} = -i \left( pX_n^1 \mathbf{p}_f_2 - pX_n^2 \mathbf{p}_f_1 \right)
\]
(8)
where the subscript 0 implies evaluation for the initial values.

**Higher-order cumulants**

The higher-order terms in the expansion of ln \( \psi_n(S) \) are associated with the distribution of the probability density function of the \( n \)th atom about its mean and may be described with respect to any axial system. If \( A_k = \sum \mathbf{p}_f_1 \mathbf{p}_A_1 \) then \( p_t_1 = \sum \mathbf{p}_k \mathbf{p}_t_k \) and \( t_k = \sum \mathbf{p}_k \mathbf{p}_t_1 \). The values of the components of the cumulant tensors depend on the axial directions chosen to evaluate \( t_j \). Thus

\[
pX_n^j = \sum_j X_n^j \mathbf{p}U_{jj'}, \quad X_n^j = \sum_{j'} pX_n^j \mathbf{p}U_{jj'},
\]
(9)

where the symbol \( p \) denotes the reference frame for the cumulant and the omission of this symbol implies the orthonormal axes \( \mathbf{a}_A / \mathbf{a}_A \times \mathbf{A}_3 \times \mathbf{A}_1 \). 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

\[
\sum_{jkl} 2\kappa^j t_j t_k = A_1 (t_1^2 + t_2^2 + t_3^2) + A_2 (2t_2^2 - t_2^2 - t_3^2)
\]

\[
+ A_3 (t_3^2 - t_2^2) + A_4 t_2 t_3 + A_5 t_3 t_4 + A_6 t_2 t_4
\]
(10)
making

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

\[
2\kappa^{11} = A_1 - A_2/2 + A_3, \quad 2\kappa^{22} = A_1 - A_2/2 - A_3
\]

\[
2\kappa^{33} = A_1 + A_2, \quad A_1 = 4(2\kappa^{11} + 2\kappa^{22} + 2\kappa^{33}), \quad
\]

\[
A_2 = 2\kappa^{33} - 3(2\kappa^{12} + 2\kappa^{23} + 2\kappa^{33}), \quad
\]

\[
A_3 = 4(2\kappa^{11} - 2\kappa^{22}).
\]
(11)

\[
2\kappa^{11}, \quad 2\kappa^{22}, \quad 2\kappa^{33}
\]
have multiplicity 1 and \( 2\kappa^{12}, \quad 2\kappa^{13}, \quad 2\kappa^{23} \) have multiplicity 2. If we choose the \( p \)th axial system to make the primary axis of the imposed point symmetry parallel to \( \mathbf{p}_A_3 \) and the secondary axis parallel to \( \mathbf{p}_A_1 \) 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**

<table>
<thead>
<tr>
<th>Laue symmetry</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( A_1, A_2, A_3, A_4, A_5, A_6 )</td>
</tr>
<tr>
<td>2/m</td>
<td>( A_1, A_2, A_3 )</td>
</tr>
<tr>
<td>mmm</td>
<td>( A_1, A_2 )</td>
</tr>
<tr>
<td>( \tilde{m}, m )</td>
<td>( A_1 )</td>
</tr>
</tbody>
</table>

Also

\[
\sum_{jkl} 3\kappa^j t_j t_k t_l = B_1(3/2)(t_1^2 + t_2^2 + t_3^2) + B_2(3/2)(t_1^2 + t_2^2 + t_3^2)
\]

\[
+ B_3(3/2)(t_1^2 + t_2^2 + t_3^2) + B_4 t_1 t_2 t_3 + B_5 t_1 t_3 t_2 + B_6 t_2 t_3 t_1
\]

\[
+ B_7 t_1 t_2 t_3 + B_8 t_1 t_2 t_3 + B_9 t_1 t_2 t_3
\]

\[
(12)
\]

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

\[
\sum_{jkl} 3\kappa^j t_j t_k t_l = B_1(3/2)(t_1^2 + t_2^2 + t_3^2) + B_2(3/2)(t_1^2 + t_2^2 + t_3^2)
\]

\[
+ B_3(3/2)(t_1^2 + t_2^2 + t_3^2) + B_4 t_1 t_2 t_3 + B_5 t_1 t_3 t_2 + B_6 t_2 t_3 t_1
\]

\[
+ B_7 t_1 t_2 t_3 + B_8 t_1 t_2 t_3 + B_9 t_1 t_2 t_3
\]

\[
(13)
\]

where

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

\[
t_3(t_1^2 + t_2^2 - t_3^2)
\]
and

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

We then obtain

$$3_k^{111} = (\frac{3}{2})B_1 + B_3,$$
$$3_k^{222} = (\frac{3}{2})B_2 + B_7,$$
$$3_k^{333} = (\frac{3}{2})B_3 + B_9,$$
$$3_k^{211} = (\frac{3}{2})B_2 - B_3 - B_9,$$
$$3_k^{311} = (\frac{3}{2})B_3 - B_4 + B_6 + B_{10},$$
$$3_k^{431} = (\frac{3}{2})B_4 + B_6,$$
$$3_k^{322} = (\frac{1}{2})B_5 - B_9 + B_{10},$$
$$B_2 = 3k^{211} + 3k^{322} + 3k^{333},$$
$$B_5 = 3k^{311} + 3k^{322} + 3k^{333},$$
$$B_{10} = \frac{1}{2}(3k^{311} - 3k^{322}) \text{ and } 3_k^{123} = B_4. \quad (14)$$

$3_k^{111}, \ 3_k^{222}, \ 3_k^{333}$ have multiplicity 1, $3_k^{122}, \ 3_k^{232}, \ 3_k^{311}$ have multiplicity 3 and $3_k^{333}$ has multiplicity 6.

If we choose the $p$th 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

<table>
<thead>
<tr>
<th>Point symmetry</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$B_1 B_2 B_3 B_4 B_5 B_6 B_7 B_8$</td>
</tr>
<tr>
<td>2</td>
<td>$B_1 B_2 B_3 B_4 B_5 B_6 B_7 B_8$</td>
</tr>
<tr>
<td>3</td>
<td>$B_1 B_2 B_3 B_4 B_5$</td>
</tr>
<tr>
<td>$3m$</td>
<td>$B_1 B_2 B_3 B_4 B_5$</td>
</tr>
<tr>
<td>$3m'$</td>
<td>$B_1 B_2 B_3 B_4$</td>
</tr>
<tr>
<td>$3m''$</td>
<td>$B_1 B_2$</td>
</tr>
<tr>
<td>$6$, $6m$, $6mm$</td>
<td>$B_1 B_2 B_3 B_4 B_5$</td>
</tr>
<tr>
<td>$222$, $4m_2$, $23$, $43m$</td>
<td>$B_1 B_2 B_3$</td>
</tr>
<tr>
<td>$32$, $6m_2$</td>
<td>$B_1 B_2$</td>
</tr>
<tr>
<td>$422$, $432$, $622$, $T$</td>
<td>None</td>
</tr>
</tbody>
</table>

Also

$$\sum_{jknm} 4_k^{jklm} t_{jk} t_{km} = (\frac{3}{2})C_1(t_1^2 + t_2^2 + t_3^2)^2 + C_2(t_1^2 - t_2^2 + t_3^2) \left(t_1^2 + t_2^2 + t_3^2\right)$$
$$+ C_3(t_1^2 - t_2^2 + t_3^2) \left(t_1^2 + t_2^2 + t_3^2\right) + C_4(2t_1 t_2) \left(t_1^2 + t_2^2 + t_3^2\right)$$
$$+ C_6(2t_2 t_3) \left(t_1^2 + t_2^2 + t_3^2\right) + C_8\left(2t_1 t_3\right) \left(t_1^2 + t_2^2 + t_3^2\right)$$
$$+ C_9\left(2t_2 t_3\right) \left(t_1^2 + t_2^2 + t_3^2\right) + C_{10}\left(4t_1 t_2 t_3\right) \left(t_1^2 + t_2^2 + t_3^2\right)$$
$$+ C_{11}\left(3t_1^2 - t_2^2 - t_3^2\right) \left(t_1^2 + t_2^2 + t_3^2\right)$$
$$+ C_{14}\left(4t_1 t_2 t_3\right) \left(t_1^2 + t_2^2 + t_3^2\right) + C_{15}\left(4t_1 t_2 t_3\right) \left(t_1^2 + t_2^2 + t_3^2\right)$$

making

$$3_k^{111} = (\frac{3}{2})C_1 - \frac{1}{2}C_2 + C_3 - C_4 - C_6,$$
$$3_k^{222} = (\frac{3}{2})C_1 - \frac{1}{2}C_2 + C_3 - C_4 - C_6,$$
$$3_k^{333} = (\frac{3}{2})C_1 + C_2 - C_3 - C_4 - C_6,$$
$$3_k^{112} = (\frac{3}{2})C_1 - C_2 - C_3 - C_4,$$
$$3_k^{113} = (\frac{3}{2})C_1 + (\frac{1}{2})C_2 + (\frac{1}{2})C_3 + C_4,$$
$$3_k^{223} = \frac{1}{2}C_1 + (\frac{1}{2})C_2 - (\frac{1}{2})C_3 + C_4,$$
\[\begin{align*}
-4(6t^2 - t^2 - t^2 - t^2)
+ 2t_1t_2[7t^2 - (t^2 + t^2 + t^2)]
+ 4t_2t_3(3t^2 - t^2)/2
+ 4t_2t_3(3t^2 - t^2)
+ 4t_2t_3(3t^2 - t^2).
\end{align*}\]

Thus
\[
4\kappa^{1111} = (\frac{1}{4})C_1 - (\frac{1}{4})C_2 + (\frac{1}{4})C_3 - 2C_7 + (\frac{1}{4})C_8 - C_9,
4\kappa^{2222} = (\frac{1}{4})C_1 - (\frac{1}{4})C_2 + (\frac{1}{4})C_3 - 2C_7 + (\frac{1}{4})C_8 + C_9,
4\kappa^{3333} = (\frac{1}{4})C_1 + (\frac{1}{4})C_2 - 2C_7 + (\frac{1}{4})C_8 + C_9,
4\kappa^{1122} = (\frac{1}{4})C_1 + (\frac{1}{4})C_2 + C_7 - (\frac{1}{4})C_8 + C_9,
4\kappa^{1133} = (\frac{1}{4})C_1 + (\frac{1}{4})C_2 + (\frac{1}{4})C_3 + C_7 - (\frac{1}{4})C_8 + C_9,
4\kappa^{2233} = (\frac{1}{4})C_1 + (\frac{1}{4})C_2 + (\frac{1}{4})C_3 + C_7 - (\frac{1}{4})C_8 - C_9,
C_1 = C_1',
C_2 = C_5' - C_1',
C_3 = 1/2(C_1' - C_2'),
C_7 = (\frac{1}{4})8C_1' + C_8' + C_9',
C_8 = 1/2(2C_1' - C_8' - C_9'),
C_9 = 1/2(C_8' - C_9').
\]

and
\[
4\kappa^{1233} = (\frac{1}{4})C_4 + C_{10},
4\kappa^{1322} = (\frac{1}{4})C_5 + C_{12},
4\kappa^{1231} = (\frac{1}{4})C_5 + C_{14},
4\kappa^{1213} = (\frac{1}{4})C_4 + 1/4C_{10} + C_{11},
4\kappa^{1311} = (\frac{1}{4})C_5 + 1/4C_{10} - C_{11},
4\kappa^{2232} = (\frac{1}{4})C_6 - C_{14} - C_{15},
4\kappa^{1222} = (\frac{1}{4})C_6 + 1/4C_{10} - C_{11},
4\kappa^{1212} = (\frac{1}{4})C_4 + C_{10} - C_{11},
C_4 = C_4',
C_5 = C_5',
C_6 = C_6',
\]

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 \(p\)th 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 \(C_7 = C_8 = 0\) then \(C_9 = (\frac{1}{3})C_7\).

### Table 3. \(C\) parameters to be refined

<table>
<thead>
<tr>
<th>Laue symmetry</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1/m)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
<tr>
<td>(2/m)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
<tr>
<td>(mmm)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
<tr>
<td>(4/m)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
<tr>
<td>(3/m)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
<tr>
<td>(6/m, 6/mmm)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
<tr>
<td>(3/m, 3/m)</td>
<td>(C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9)</td>
</tr>
</tbody>
</table>

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
\[
\Psi(u) \simeq \left[1 + \sum_{j=1}^{m} Q_j(u)\right] \Psi_0(u)
\]
using up to the \((m + 2)\)th cumulant. Rae (1975a) has pointed out that if the normal distribution
\[
\Psi_0(u) = \frac{\text{det}(p)^{1/2}}{(2\pi)^{1/2}} \exp \left\{ -\frac{1}{2} \sum_{jk} p_{jk}(u^j-x^j)(u^k-x^k) \right\}
\]
is chosen such that
\[
1\lambda = 1/\kappa - x^j = 1/\kappa \sum_{kl} 3\kappa^{ijkl} p_{kl}
\]
and
\[
2\lambda_{jk} = 2\kappa^{ijkl} - \sigma_{jk} = 1/\kappa \sum_{lm} 4\kappa^{ijklm} p_{lm}
\]
where
\[
\sum_k \sigma_{jk} p_{kl} = \delta_{jl},
\]
then
\[
Q_j(u) = \frac{1}{3!} \sum_{ijkl} 3\kappa^{ijkl} Z_j Z_k Z_l Z_m - \frac{1}{2} \sum_{jk} 2\kappa^{ijkl} Z_j Z_k Z_l
+ \frac{1}{2} \sum_{ijklm} 3\kappa^{ijklm} Z_j Z_k Z_l Z_m Z_n Z_o + 18Z_j Z_k p_{kl} p_{lm}
- 9Z_j Z_k p_{kl} p_{lm} - 6p_{jk} p_{kl} p_{lm}
\]
and the position \(u=x\) is a position of maximum probability of value \(\Psi_0(x)\) 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
\[
1\lambda = B_1/2A_1, \quad 1\lambda = B_2/2A_1, \quad 1\lambda = B_3/2A_1,
(\frac{1}{2}\lambda_1 + \frac{1}{2}\lambda_2 + \frac{1}{2}\lambda_3)/3 = C_4/4A_1,
2\lambda = (\frac{1}{2}\lambda_1 + \frac{1}{2}\lambda_2 + \frac{1}{2}\lambda_3)/3 = C_4/4A_1
(\frac{1}{2}\lambda_1 + \frac{1}{2}\lambda_2)/2 = C_6/4A_1, \quad 2\lambda_2 = C_6/4A_1,
(\frac{1}{2}\lambda_1 + \frac{1}{2}\lambda_2)/2 = C_6/4A_1, \quad 2\lambda_3 = C_6/4A_1, \quad 2\lambda_3 = C_6/4A_1.
\]

Also \(Z_j\) is simply \((u^j-x^j)/A_1\) and the shapes associated with the terms \(B_j C_i\) in (13) and (16) are obtained by replacing \(t_j\) by \((u^j-x^j)/A_1\) 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
\[
\frac{1}{2} \sum_{kl} 3\kappa^{ijkl} p_{kl} = 1\lambda^j
\]
if
\[
3\kappa^{ijkl} = (\frac{1}{2})^{(i+1)(j+1)} (3\lambda^i \sigma^j + 3\lambda^j \sigma^i + 3\lambda^i \sigma^j)
\]
where $\lambda_{jkl}^{k}$ is the component of $\lambda_{jkl}$ that leads to a non-zero value of $\lambda_{j}^{k}$. We can then retain the expression

$$\sum_{j=1}^{3} B_{j} f_{j} (t_{1}^{2} + t_{2}^{2} + t_{3}^{2})$$

in (13) by

$$\sum_{j=1}^{3} \lambda_{jkl}^{k} f_{j} t_{l} f_{k} t_{m} = \frac{1}{4} \sum_{j=1}^{3} B_{j} f_{j} \sum_{k} \sigma_{kl}^{m} t_{l} f_{k} / A_{1}.$$ (20)

Likewise it is noted that

$$\lambda_{jk}^{k} = \frac{1}{4} \sum \lambda_{jk}^{k} t_{k} f_{l} t_{m}$$

if

$$\lambda_{jk}^{k} = (\frac{1}{4}) (\lambda_{jk}^{k} \sigma_{lm}^{jk} + 2 \lambda_{jk}^{k} \sigma_{lm}^{jk} + \frac{1}{2} \lambda_{jk}^{k} \omega_{kl}^{m})$$

where

$$\lambda_{jk}^{k} = \frac{1}{4} \delta_{jk} + (\frac{1}{4}) \sigma_{jk}^{m} \sum \lambda_{lm}^{m} t_{m}.$$ (21)

Now if we define $\lambda_{jm}^{k}$ and $\lambda_{km}^{j}$ as $\lambda_{jm}^{k} = A_{1} \sum_{k} \lambda_{jk}^{k} f_{k}$ and $\lambda_{jm}^{k} = A_{1} \lambda_{jk}^{k} f_{k}$ then

$$\lambda_{jm}^{k} - \lambda_{jm}^{k} - \lambda_{jm}^{k} = \lambda_{jm}^{k} - (\lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}) / 3 = (\lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}) / 3,$$

$$\lambda_{jm}^{k} - \lambda_{jm}^{k} - \lambda_{jm}^{k} = \lambda_{jm}^{k} - \lambda_{jm}^{k} / 2 = (\lambda_{jm}^{k} - \lambda_{jm}^{k}) / 2,$$

$$\lambda_{jm}^{k} = \lambda_{jm}^{k} + \lambda_{jm}^{k}, \lambda_{jm}^{k} = \lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}, \lambda_{jm}^{k} = \lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}, \lambda_{jm}^{k} = \lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}, \lambda_{jm}^{k} = \lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}, \lambda_{jm}^{k} = \lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}.$$

but

$$(\lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}) / 3 = \lambda_{jm}^{k} / 3,$$

$$(\lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}) / 3 = \lambda_{jm}^{k} / 3,$$

$$(\lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}) / 3 = \lambda_{jm}^{k} / 3,$$

$$(\lambda_{jm}^{k} + \lambda_{jm}^{k} + \lambda_{jm}^{k}) / 3 = \lambda_{jm}^{k} / 3.$$

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

$$\psi(t) = \psi_{1}(t) \psi_{2}(t),$$

where

$$\psi_{1}(t) = \prod_{n=-\infty}^{\infty} \exp \left[ i (t \cdot u) \psi_{1}(u-r) \right] \psi_{1}(u-r) du \, dr \, dr^{3},$$

$$\psi_{2}(t) = \prod_{n=-\infty}^{\infty} \exp \left[ i (t \cdot r) \psi_{2}(r) dr \right] dr \, dr^{3},$$

and

$$\Psi(u) = \prod_{n=-\infty}^{\infty} \psi_{1}(u-r) \psi_{2}(r) dr \, dr^{3}.$$ (23)

We can of course only observe the overall transform $\psi(t)$ and not the components $\psi_{1}(t)$ and $\psi_{2}(t)$. 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 $\lambda_{jk}^{k}$ and $\lambda_{jk}^{k}$ for an overall probability density function $\Psi(u)$. However the overall cumulant terms associated with parameters $B_{k}$ 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 $\psi_{2}(t) \psi_{2}(t)$ where $\psi_{2}(t)$ is obtained from the cumulants for the inner-shell electrons, then the factor $\psi_{2}(t)$ 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 $\psi_{1}(t) = 1$ 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 \( \mathbf{r}_n = \sum_k p X_n^k \mathbf{A}_k \) is given by

\[
p U_{ij} = \sum_{k,l} p A_{ijk} p X_n^k p X_n^l + \sum_k p B_{ijk} p X_n^k + p T_{ij},
\]

where

\[
p A_{ijk} = \sum_m e_{ilm} e_{jml} L_{kmn},
\]

and

\[
p B_{ijk} = \sum_n \left( e_{iain} S_{nj} + e_{jmk} S_{ni} \right).
\]

The superscript \( p \) indicates the \( p \)th 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 \( n \)th atom

\[
U_{11} = L_{22} X_n^2 X_n^2 + L_{33} X_n^3 X_n^3 + 2 L_{23} X_n^2 X_n^3 + S_{21} 2 X_n^3
- S_{21} 2 X_n^3 + T_{11},
\]

\[
U_{12} = -L_{33} X_n^2 X_n^2 + L_{12} X_n^3 X_n^3 + L_{13} X_n^2 X_n^3 + L_{23} X_n^2 X_n^3
- (S_{11} - S_{22}) X_n^2 + S_{31} X_n^3 - S_{32} X_n^3 + T_{12} \text{ etc.}
\]  

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

\[
D_1 = (L_{11} + L_{22} + L_{33})/3, \quad D_2 = L_{33} - (L_{11} + L_{22} + L_{33})/3, \quad D_3 = (L_{11} - L_{22})/2, \quad D_4 = L_{12}, \quad D_5 = L_{13}, \quad D_6 = L_{23},
\]

\[
E_1 = (T_{11} + T_{22} + T_{33})/3, \quad E_2 = T_{33} - (T_{11} + T_{22} + T_{33})/3, \quad E_3 = (T_{11} - T_{22})/2, \quad E_4 = T_{12}, \quad E_5 = T_{13}, \quad E_6 = T_{23},
\]

\[
F_1 = C_{23} S_{33} - C_{32} S_{23}, \quad F_2 = C_{31} S_{21} - C_{13} S_{31}, \quad F_3 = C_{12} S_{12} - C_{21} S_{12}, \quad F_4 = C_{23} S_{33} + C_{23} S_{32},
\]

\[
F_5 = C_{13} S_{31} + C_{31} S_{13}, \quad F_6 = C_{12} S_{21} + C_{21} S_{12}, \quad F_7 = (2S_{33} - S_{22} - S_{11})/2, \quad F_8 = S_{33} - S_{22}.
\]

We note that \( S_{11} + S_{22} + S_{33} \) cannot to be determined. The expression \( \sum U_{ij} t_{ij} \) can then be written as

\[
\sum_{i,j} p U_{ij} t_{ij} = D_1 (\hat{t}_1^2 + \hat{t}_2^2 + \hat{t}_3^2) + D_2 (2 \hat{t}_3 - \hat{t}_1^2 - \hat{t}_2^2)/2
+ D_3 (\hat{t}_1^2 - \hat{t}_2^2) + 2D_4 \hat{t}_1 \hat{t}_2 + 2D_5 \hat{t}_1 \hat{t}_3 + 2D_6 \hat{t}_2 \hat{t}_3
+ E_1 (\hat{t}_1^2 + \hat{t}_2^2 + \hat{t}_3^2) + E_2 (2\hat{t}_1^2 - \hat{t}_2^2 - \hat{t}_3^2)/2 + E_3 (\hat{t}_1^2 - \hat{t}_2^2)/2
+ E_4 \hat{t}_1 t_2 + E_5 \hat{t}_1 t_3 + E_6 \hat{t}_2 t_3 + 2F_1 (C_{23} S_{33} - C_{32} S_{23})
+ 2F_2 (C_{23} S_{33} - C_{32} S_{23}) + 2F_3 (C_{12} S_{12} + C_{21} S_{12})
+ 2F_4 (C_{23} S_{33} + C_{23} S_{32}) + 2F_5 (C_{13} S_{31} + C_{31} S_{13})
+ 2F_6 \hat{t}_1 t_2 + F_7 \hat{t}_1 t_3 + F_8 (\hat{t}_1 t_2 - \hat{t}_2 t_3),
\]

where

\[
\hat{t}_1 = X_n^2 t_3 - X_n^3 t_2, \quad \hat{t}_2 = X_n^3 t_1 - X_n^2 t_3 \quad \text{and} \quad \hat{t}_3 = X_n^1 t_2 - X_n^2 t_1,
\]

(26)

If the axial system is chosen to be parallel to the principal libration axes then the definition of \( C_{ij} \) as \( C_{ij} = L_{ij}/(L_{ii} + L_{jj})^{1/2} \) 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 \( A_i \) to \( A_6 \) in (11). If we choose our axial directions \( p \mathbf{A}_k \) to coincide with the imposed point symmetry (primary axis=\( p \mathbf{A}_3 \) and, if applicable, secondary axis=\( p \mathbf{A}_4 \)), then we only need to refine the independent \( F_i \) parameters given in Table 4.

**Table 4.** \( F \) parameters to be refined

<table>
<thead>
<tr>
<th>Point group</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
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<td>( F_1, F_2, F_3, F_4, F_5, F_6, F_8 )</td>
</tr>
<tr>
<td>2</td>
<td>( F_3, F_6 )</td>
</tr>
<tr>
<td>m</td>
<td>( F_1, F_2, F_3, F_5, F_6 )</td>
</tr>
<tr>
<td>222</td>
<td>( F_1, F_2, F_3, F_6 )</td>
</tr>
<tr>
<td>mm2</td>
<td>( F_3, F_6 )</td>
</tr>
<tr>
<td>23, 4, 6</td>
<td>( F_3, F_5 )</td>
</tr>
<tr>
<td>4</td>
<td>None</td>
</tr>
<tr>
<td>32, 422, 622</td>
<td>( F_7 )</td>
</tr>
<tr>
<td>3m, 4mm, 6mm</td>
<td>( F_3 )</td>
</tr>
<tr>
<td>42m</td>
<td>( F_8 )</td>
</tr>
<tr>
<td>6, 6m2, 23, 432, 43m, T</td>
<td>None</td>
</tr>
</tbody>
</table>

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 \( q \)th 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 \( \sum_j S_{ij} \) is undeterminable are obtained using the \( p \)th axial system \( p \mathbf{A}_j = \sum_{i} p U_{ij} \mathbf{A}_i \) located at \( \sum_{i} X_n^i \mathbf{A}_i \). The principal axes
of the $L$ tensor are defined relative to this axial system as $p\bar{A}_k = \sum_j pV_{jk}^p A_j = \sum_i p\bar{U}_{ik} A_i$, where $p\bar{U}_{ik} = \sum_j U_{ij}^p V_{jk}^p$. Keeping the origin fixed we redefine the $TL_i S$ tensors for the $p\bar{A}_k$ axis system as

$$pT_{kl} = \sum_j T_{ij}^p pV_{jk}^p, \quad pS_{kl} = \sum_j S_{ij}^p pV_{jk}^p,$$
$$pL_{kl} = \sum_j L_{ij}^p pV_{jk}^p,$$

where $pL_{kl}^p = 0$ for $k \neq l$. As $\sum_j \delta_{ij}^p pV_{jk}^p = \delta_{kl}$ it is seen that the assumption of a zero value for $\sum_j S_{ij}$ does not alter the values of $pS_{ij}$ and $pS_{ii} = \rho S_{ij}$ when $i \neq j$.

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

$$\sum_i \hat{X}_i^p = \sum_i X_i^p A_i + \sum_k pX_k^p k\bar{A}_k,$$

where

$$pX_k^p = \sum_i e_{ik} pS_{ij}^p (pL_{ij}^p + pL_{jj}^p)$$

and

$$\hat{X}_i^p = X_i^p + \sum_k p\bar{U}_{ik}^p pX_k^p.$$

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

$$pL_{ij}^p = pL_{ij}^p, \quad pS_{ij} = pS_{ij}^p = (pL_{ij}^p S_{ij}^p + pL_{ij}^p S_{ij}^p)/^p,$$

for $i \neq j$, $pL_{ii}^p = pS_{ii}^p = pS_{ii}^p + pS_{ii}^p$, $pT_{11}^p = pT_{11}^p - [2pS_{21}^p X_0^p + 2pS_{11}^p X_0^p + pT_{22}^p X_0^p + pT_{33}^p X_0^p + pT_{33}^p X_0^p + pT_{32}^p X_0^p]$ etc.,

$$pT_{12} = pT_{12}^p - [(pS_{11}^p - pS_{22}^p) X_0^p + pT_{11}^p + pT_{13}^p + pT_{13}^p - pT_{33}^p X_0^p]$$

where the terms in square brackets are obtained from the previous equations and the remaining values of $pT_{il}^p$ and $pT_{ij}^p$ are obtained by permutation of indices.

We thus obtain new starting parameters for the next refinement cycle. The position of the $n$th atom at $\sum_i X_i^p A_i$ with respect to the $p$th axial system $p\bar{A}_k$ at $\sum_i \hat{X}_i^p A_i$ is given by $\sum_k pX_k^p k\bar{A}_k$ where $pX_n^p = \sum_i (X_i^p - \hat{X}_i^p) p\bar{U}_{ik}$ for the evaluation of $\hat{X}_i^p$ 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 $U_{11} + U_{32} + U_{33}$ 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 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 $p\bar{X}_i$ is the component of the displacement on the $i$th direction and is given by $B_i/2A_i$, $i = 1$ 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 $\sum_i X_0^p A_i$ 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 $F_a, F_b, F_c$ (Rae, 1975b).

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

$$p\bar{X}_n^p = -p\bar{X}_n^p (pL_{11}^p + pL_{22}^p)/2, \quad (i \neq j \neq k),$$

where $p\bar{X}_n^p, p\bar{X}_n^p, p\bar{X}_n^p$ is the position of maximum probability and $p\bar{X}_n^p = p\bar{X}_n^p - p\bar{X}_n^p$ where $p\bar{X}_n^p, p\bar{X}_n^p, p\bar{X}_n^p$ 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 $\bar{X}_i$ along the C–H bond direction arising from this motion is given by $-\alpha/2d$ where $d$ is the bond distance and $\alpha$ 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, 1973) 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 $U_{11} + U_{32} + U_{33}$ 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 $\bar{X}_i$. 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

\[
\Delta u_j = \sum_{k=1}^{n} P_{jk} \Delta v_k ,
\]

then changing variables causes the least-squares equation

\[
\sum_{j=1}^{n} A_{ij} \Delta u_j = B_i
\]

to become

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

\[
\sum_{i=1}^{n} C_{ij} \Delta v_i = D_i, \quad (i = 1 \text{ to } n).
\]

If the \((m+1)\)th to \( n \)th variables \( \Delta v_i \) are constrained to have certain fixed values then we solve the \( m \) equations

\[
\sum_{i=1}^{m} C_{ij} \Delta v_i = D_i - \sum_{i=m+1}^{n} C_{ij} \Delta v_i, \quad i = 1 \text{ to } m
\]

and evaluate values of \( \Delta u_j \) 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 \( \partial / \partial v_k = \sum P_{jk} \partial / \partial u_j \).

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 \( \Delta u_j \) 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 \( t \)th internal coordinate is given by

\[
\Delta s_t = \sum_{j=1}^{3N} B_{ij} \Delta r_j \text{ where } B_{ij} = (\partial s_t / \partial r_j)_0,
\]

where \( r_j \) is a positional parameter \( X_j(n = 1 \text{ to } N, \ i = 1 \text{ to } 3) \) and the subscript 0 implies evaluation for all \( \Delta s_t = 0 \). Thus

\[
\Delta r_j = \sum_{t=1}^{3N} (B^{-1})_{ij} \Delta s_t ,
\]

provided we pick a set of \( 3N \) linearly independent internal coordinates and

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

allowing the concepts of (29), (30), (31) to be applied. Values of \( (\partial / \partial s_t)_0 \) for rotation and translation parameters \( (\phi_i \text{ and } X_0^0) \) 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, \( v_m \) so that \( \Delta r_j = \sum R_{jm} \Delta v_n \) where \( R_{jm} \) gives the value of \( \Delta r_j \) when \( \Delta v_n = 1, \Delta v_m = 0 (m \neq n) \). Thus \( (\partial / \partial v_n)_0 = \sum R_{jm} (\partial / \partial r_j)_0 \). 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 \( R_{jm} \) as necessary to make this possible. We note \( \Delta s_t = \sum S_{tn} \) where \( S_{tn} = \sum_{j=1}^{3N} B_{ij} R_{jm} \) if the amount the \( t \)th 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 \( \Delta v_n \) 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 \( pX_2 = 0 \) for these atoms. The axial system may be refined by allowing \( X_0^0, \phi_1 \) and \( \phi_2 \) 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 \( \partial F(S) / \partial u_q \) 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 \( n \)th 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 $\sum pX_h^j pA_j$. 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.

References