value of $\partial F(\mathbf{S})/\partial u_q$ 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 ${}^p\mathbf{A}_j$, at the same origin $\sum_j {}^pX_0^j\,{}^p\mathbf{A}_j$. 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 ${}^p\mathbf{A}_j$ 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 ${}^p\mathbf{A}_j$ 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). B**24**, 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

respect to the crystallographic axes to evaluate structure factors and it is not necessary to transform the parameters back to the crystallographic axial system for the purpose of evaluating differentials for least-squares equations (Rae, 1975*a*,*b*). Parameters obtained for one axial system are transformations of parameters obtained for a different axial system and it should be emphasized that the use of an inappropriate axial system makes it extremely difficult to interpret the variance–covariance matrix of refined parameters.

Schomaker & Trueblood (1968) have derived a general description of rigid-body motion in a general axial system and interpretation of this description is obtained by transformation back to the variable space that could have been used initially.

Pawley (1970), while noting that unconstrained **TLS** refinements can give meaningless results, was unable to determine the cause of this problem because of the choice of a fixed axial system to describe the refinement. As will be seen in the following derivation the intermixing of parameters that best describe the thermal motion can be quite complex if an inappropriate axial system and choice of variables is used.

The displacement of an atom in a rigid molecule may be described using six linearly independent components. We choose these components as three translational movements and three rotational movements about mutually orthogonal non-intersecting axes. The displacements of these axes from the centre of mass and orientation of these axes with respect to the principal inertial axes of the rigid molecule constitute nine degrees of freedom which may be chosen to simplify description of the system.

We let X_n^1, X_n^2, X_n^3 be the equilibrium position of the nth atom with respect to an intersecting set of orthonormal axes located at some origin. The three axes of rotation are parallel to these axes and are displaced by amounts $0, {}^1r^2, {}^1r^3;\ {}^2r^1, 0, {}^2r^3;\ {}^3r^1, {}^3r^2, 0$ respectively. The atomic displacements u_1, u_2, u_3 arising from the six linearly independent movements are given by

$$\begin{aligned} u_1 &= t_1 + \lambda_2(X_n^3 - {}^2r^3) - \lambda_3(X_n^2 - {}^3r^2) \\ u_2 &= t_2 + \lambda_3(X_n^1 - {}^3r^1) - \lambda_1(X_n^3 - {}^1r^3) \\ u_3 &= t_3 + \lambda_1(X_n^2 - {}^1r^2) - \lambda_2(X_n^1 - {}^2r^1) \end{aligned} \quad (1)$$

using the six variables t_i (translation), λ_i (rotation), $i=1,2,3$. (Throughout this paper equations omitted may be obtained from cyclic permutation of indices as may be seen in the above example.)

Thus

$$\begin{aligned} u_1u_1 &= t_1t_1 + \lambda_2t_1 2(X_n^3 - {}^2r^3) - \lambda_3t_1 2(X_n^2 - {}^3r^2) \\ &\quad + \lambda_2\lambda_2(X_n^3 - {}^2r^3)^2 + \lambda_3\lambda_3(X_n^2 - {}^3r^2)^2 \\ &\quad - 2\lambda_2\lambda_3(X_n^2 - {}^3r^2)\,(X_n^3 - {}^2r^3) \\ u_1u_2 &= t_1t_2 - \lambda_1t_1(X_n^3 - {}^1r^3) + \lambda_2t_2(X_n^3 - {}^2r^3) \\ &\quad + \lambda_3t_1(X_n^1 - {}^3r^1) - \lambda_3t_2(X_n^2 - {}^3r^2) \\ &\quad - \lambda_1\lambda_2(X_n^3 - {}^1r^3)\,(X_n^3 - {}^2r^3) \\ &\quad + \lambda_3\lambda_1(X_n^2 - {}^3r^2)\,(X_n^3 - {}^1r^3) \\ &\quad + \lambda_2\lambda_3(X_n^3 - {}^2r^3)\,(X_n^1 - {}^3r^1)\,. \end{aligned} \quad (2)$$

When averaged over all motions $\langle u_iu_j\rangle = U_{ij}$, $\langle t_it_j\rangle = T_{ij}$, $\langle \lambda_it_j\rangle = S_{ij}$, $\langle \lambda_i\lambda_j\rangle = L_{ij}$ so that

$$\begin{aligned} U_{11} &= T'_{11} + S'_{21}2X_n^3 - S'_{31}2X_n^2 + L'_{22}X_n^3X_n^3 \\ &\quad + L'_{33}X_n^2X_n^2 - 2L'_{23}X_n^2X_n^3 \\ U_{12} &= T'_{12} - (S'_{11} - S'_{22})X_n^3 + S'_{31}X_n^1 - S'_{32}X_n^2 \\ &\quad - L'_{33}X_n^1X_n^2 - L'_{12}X_n^3X_n^3 + L'_{31}X_n^2X_n^3 + L'_{23}X_n^3X_n^1\,, \end{aligned} \quad (3)$$

where

$$\begin{aligned} T'_{11} &= T_{11} - 2S_{21}{}^2r^3 + 2S_{31}{}^3r^2 + L_{22}({}^2r^3)^2 \\ &\quad + L_{33}({}^3r^2)^2 - 2L_{23}{}^3r^{22}r^3 \\ T'_{12} &= T_{12} + S_{11}{}^1r^3 - S_{22}{}^2r^3 - S_{31}{}^3r^1 + S_{32}{}^3r^2 - L_{33}{}^3r^{13}r^2 \\ &\quad - L_{12}{}^1r^{32}r^3 + L_{31}{}^3r^{21}r^3 + L_{23}{}^2r^{33}r^1 \\ S'_{21} &= S_{21} - L_{22}{}^2r^3 + L_{23}{}^3r^2 \\ S'_{12} &= S_{12} + L_{11}{}^1r^3 - L_{31}{}^3r^1 \\ S'_{11} - S'_{22} &= S_{11} - S_{22} - L_{12}({}^1r^3 + {}^2r^3) + L_{31}{}^3r^2 \\ &\quad + L_{23}{}^3r^1 \quad \text{and} \quad L'_{ij} = L_{ij}\,. \end{aligned} \quad (4)$$

We see that the libration tensor **L** is independent of, but the translation tensor **T** and interaction tensor **S** are dependent on, the displacement parameters. The values $T'_{ij}, S'_{ij}, L'_{ij}$ are the values obtained for zero displacement parameters.

We also wish to see how parameters $T'_{ij}, S'_{ij}, L'_{ij}$ vary with change of axis directions but no change of origin. The principal values $({}^pL_{11}, {}^pL_{22}, {}^pL_{33})$ and principal axes $({}^p\mathbf{A}_1, {}^p\mathbf{A}_2, {}^p\mathbf{A}_3)$ of the **L** tensor are independent of axial choice and are related to an initial choice of axes $(\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3)$ by relationships $\mathbf{A}_i = \sum_j R_{ij}{}^p\mathbf{A}_j$ and ${}^p\mathbf{A}_j = \sum_i R_{ij}\mathbf{A}_i$ where $R_{ij} = \mathbf{A}_i \,.\, {}^p\mathbf{A}_j$, if orthonormal axial systems are assumed. We shall use the prefix p to imply an axial system corresponding to the principal directions of the **L** tensor and the absence of a prefix to imply the initial axial system.

A vector quantity **t** is describable as $\mathbf{t} = \sum_i t_i\mathbf{A}_i = \sum_j {}^pt_j{}^p\mathbf{A}_j$ where $t_i = \mathbf{A}_i \,.\, \mathbf{t}$. Thus $t_i = \sum_j R_{ij}{}^pt_j$ and ${}^pt_j = \sum_i R_{ij}t_i$.

Likewise

$${}^pu_j = \sum_i R_{ij}u_i\,, \quad {}^p\lambda_j = \sum_i R_{ij}\lambda_i$$

and

$${}^pX_n^j = \sum_i R_{ij}X_n^i\,. \quad (5)$$

It follows that

$${}^pU_{kl} = \sum_{ij} U_{ij}R_{ik}R_{jl}\,, \quad {}^pL'_{kl} = \sum_{ij} L'_{ij}R_{ik}R_{jl}\,,$$
$${}^pS'_{kl} = \sum_{ij} S'_{ij}R_{ik}R_{jl}$$

and

$$ {}^{p}T'_{kl}=\sum_{ij} T'_{ij}R_{ik}R_{jl} . \qquad (6) $$

As $\sum_{ij}\delta_{ij}R_{ik}R_{jl}=\delta_{kl}$ ($\delta_{ij}=0$ if $i\neq j$, $\delta_{ii}=1$) it is seen that the value of $S'_{11}+S'_{22}+S'_{33}$ does not alter the values of ${}^{p}S'_{kl}$ and $({}^{p}S'_{kk}-{}^{p}S'_{ll})$ when $k\neq l$. It should be noted that $({}^{p}S'_{kl}-{}^{p}S'_{lk})=\sum_{ij}(S'_{ij}-S'_{ji})R_{ik}R_{jl}$ so that an origin shift that would make $\mathbf{S}'$ symmetric would also make ${}^{p}\mathbf{S}'$ symmetric and if $\mathbf{S}'$ is symmetric then so is ${}^{p}\mathbf{S}'$.

This unique origin shift can be obtained from (4) by putting ${}^{2}r^{1}={}^{3}r^{1}=X^{1}_{0}$, ${}^{3}r^{2}={}^{1}r^{2}=X^{2}_{0}$, ${}^{1}r^{3}={}^{2}r^{3}=X^{3}_{0}$ and $S_{ij}=S_{ji}$.

Thus

$$ S'_{12}-S'_{21}=(L'_{11}+L'_{22})X^{3}_{0}-L_{31}X^{1}_{0}-L_{23}X^{2}_{0} \qquad (7) $$

or for the transformed axes

$$ {}^{p}X^{3}_{0}=({}^{p}S'_{12}-{}^{p}S'_{21})/({}^{p}L'_{11}+{}^{p}L'_{22}) \qquad (8) $$

where

$$ {}^{p}X^{j}_{0}=\sum_{i} R_{ij}X^{i}_{0} . $$

If we use the principal axial system (${}^{p}L_{ij}=0$ for $i\neq j$), equations (4) become

$$ \begin{aligned}
{}^{p}T'_{11}&={}^{p}T_{11}-2{}^{p}S_{21}{}^{2}r^{3}+2{}^{p}S_{31}{}^{3}r^{2}+{}^{p}L_{22}({}^{2}r^{3})^{2}\\
&\quad+{}^{p}L_{33}({}^{3}r^{2})^{2},\\
{}^{p}T'_{12}&={}^{p}T_{12}+({}^{p}S_{11}-{}^{p}S_{22})\,({}^{1}r^{3}+{}^{2}r^{3})/2\\
&\quad+({}^{p}S_{11}+{}^{p}S_{22})\,({}^{1}r^{3}-{}^{2}r^{3})/2-{}^{p}S_{31}{}^{3}r^{1}\\
&\quad+{}^{p}S_{32}{}^{3}r^{2}-{}^{p}L_{33}{}^{3}r^{13}r^{2},\\
{}^{p}S'_{21}&={}^{p}S_{21}-{}^{p}L_{22}{}^{2}r^{3},\ {}^{p}S'_{12}={}^{p}S_{12}+{}^{p}L_{11}{}^{1}r^{3},\\
{}^{p}S'_{11}-{}^{p}S'_{22}&={}^{p}S_{11}-{}^{p}S_{22},\ {}^{p}L'_{ij}={}^{p}L_{ij} .
\end{aligned} \qquad (9) $$

It is seen we can make ${}^{p}S_{ij}=0$ for $i\neq j$ by having

$$ \begin{aligned}
&{}^{2}r^{1}={}^{p}S'_{23}/{}^{p}L'_{22},\ {}^{3}r^{2}={}^{p}S'_{31}/{}^{p}L'_{33},\\
&{}^{1}r^{3}={}^{p}S'_{12}/{}^{p}L'_{11},\ {}^{3}r^{1}=-{}^{p}S'_{32}/{}^{p}L'_{33},\\
&{}^{1}r^{2}=-{}^{p}S'_{13}/{}^{p}L'_{11},\ {}^{2}r^{3}=-{}^{p}S'_{21}/{}^{p}L_{22} .
\end{aligned} \qquad (10) $$

Since $S_{ii}-S_{jj}$ values rather than S_{ii} values are determined from (3) it is seen that ${}^{p}T_{12}$ is only precisely determined if ${}^{1}r^{3}={}^{2}r^{3}$.

We note that

$$ \begin{aligned}
{}^{p}L'_{11}({}^{1}r^{3}-{}^{p}X^{3}_{0})&=-{}^{p}L'_{22}({}^{2}r^{3}-{}^{p}X^{3}_{0})\\
&=({}^{p}L'_{11}{}^{p}S'_{21}+{}^{p}L'_{22}{}^{p}S'_{12})/({}^{p}L'_{11}+{}^{p}L'_{22})
\end{aligned} \qquad (11) $$

if ${}^{i}r^{j}$ values are chosen to satisfy (10).

If we use the principal axis system and choose ${}^{3}r^{1}={}^{2}r^{1}={}^{p}X^{1}_{0}$, ${}^{1}r^{2}={}^{3}r^{2}={}^{p}X^{2}_{0}$, ${}^{2}r^{3}={}^{1}r^{3}={}^{p}X^{3}_{0}$ then new values of $\mathbf{T},\mathbf{S},\mathbf{L}$ are given from equations (9) by

$$ \begin{aligned}
&{}^{p}\hat{L}_{ij}={}^{p}L'_{ij}\quad {}^{p}\hat{S}_{ii}-{}^{p}\hat{S}_{jj}={}^{p}S'_{ii}-{}^{p}S'_{jj}\\
&{}^{p}\hat{S}_{12}={}^{p}\hat{S}_{21}=({}^{p}\hat{L}_{11}{}^{p}S'_{21}+{}^{p}\hat{L}_{22}{}^{p}S'_{12})/({}^{p}\hat{L}_{11}+{}^{p}\hat{L}_{22})\\
&{}^{p}\hat{T}_{11}={}^{p}T'_{11}-[-2{}^{p}\hat{S}_{21}{}^{p}X^{3}_{0}+2{}^{p}\hat{S}_{31}{}^{p}X^{2}_{0}+{}^{p}\hat{L}_{22}{}^{p}X^{3}_{0}{}^{p}X^{3}_{0}\\
&\quad+{}^{p}\hat{L}_{33}{}^{p}X^{2}_{0}{}^{p}X^{2}_{0}]
\end{aligned} $$

$$ \begin{aligned}
{}^{p}\hat{T}_{12}&={}^{p}T'_{12}-[({}^{p}\hat{S}_{11}-{}^{p}\hat{S}_{22})\,{}^{p}X^{3}_{0}-{}^{p}\hat{S}_{31}{}^{p}X^{1}_{0}\\
&\quad+{}^{p}\hat{S}_{32}{}^{p}X^{2}_{0}-{}^{p}\hat{L}_{33}{}^{p}X^{1}_{0}{}^{p}X^{2}_{0}] ,
\end{aligned} \qquad (12) $$

where the terms in square brackets are obtained from previous equations in the set. The new values of ${}^{p}X^{j}_{n}$ are given by ${}^{p}\hat{X}^{j}_{n}={}^{p}X^{j}_{n}-{}^{p}X^{j}_{0}$.

If we use the principal axis system and choose the displacements of (10) then in this final transformation (9) becomes

$$ \begin{aligned}
&{}^{p}L_{ij}={}^{p}\hat{L}_{ij};\ {}^{p}S_{ii}-{}^{p}S_{jj}={}^{p}\hat{S}_{ii}-{}^{p}\hat{S}_{jj};\ {}^{p}S_{ij}=0 \text{ for } i\neq j\\
&{}^{p}T_{11}={}^{p}\hat{T}_{11}+{}^{p}L_{11}\{({}^{3}r^{2}-{}^{p}X^{2}_{0})\,({}^{1}r^{2}-{}^{p}X^{2}_{0})\\
&\quad+({}^{1}r^{3}-{}^{p}X^{3}_{0})\,({}^{2}r^{3}-{}^{p}X^{3}_{0})\}\\
&{}^{p}T_{12}={}^{p}\hat{T}_{12}-{}^{p}S_{11}({}^{1}r^{3}-{}^{p}X^{3}_{0})+{}^{p}S_{22}({}^{2}r^{3}-{}^{p}X^{3}_{0})\\
&\quad+{}^{p}L_{33}({}^{3}r^{1}-{}^{p}X^{1}_{0})\,({}^{3}r^{2}-{}^{p}X^{2}_{0}) .
\end{aligned} \qquad (13) $$

We note that ${}^{p}T_{ij}$ ($i\neq j$) is only precisely determined if ${}^{p}\hat{S}_{ij}=0$ since otherwise we must assume a value for ${}^{p}S_{11}+{}^{p}S_{22}+{}^{p}S_{33}$.

Constraints on the TLS model

An obvious initial axial system for the rigid group of atoms is one that coincides with the centre of mass and the principal inertial axes.

If the group of atoms has an inherent point symmetry then the symmetry elements can be related to the inertial axes. The principal symmetry axis is taken as coincident with the third principal axis of inertia and if applicable a secondary symmetry axis is taken as coincident with the first principal axis of inertia. The coincidence of the centre of mass of the rigid group of atoms with a special position in the crystal imposes constraints on the **TLS** tensors.

It is possible to consider all possible constraints of the **TLS** model to be simply the choice to refine or not to refine certain members of a set of 20 linearly independent variables by appropriate choice of origin and axis directions. We create this set of variables as

$$ \begin{aligned}
&D_1=(L_{11}+L_{22}+L_{33})/3 ,\\
&D_2=L_{33}-(L_{11}+L_{22}+L_{33})/3 ,\quad D_3=(L_{11}-L_{22})/2 ,\\
&D_4=L_{12} ,\quad D_5=L_{13} ,\quad D_6=L_{23} ,\\
&E_1=(T_{11}+T_{22}+T_{33})/3 ,\\
&E_2=T_{33}-(T_{11}+T_{22}+T_{33})/3 ,\quad E_3=(T_{11}-T_{22})/2 ,\\
&E_4=T_{12} ,\quad E_5=T_{13} ,\quad E_6=T_{23} ,\\
&F_1=C_{23}S_{23}-C_{32}S_{32} ,\quad F_2=C_{31}S_{31}-C_{13}S_{13} ,\\
&F_3=C_{12}S_{12}-C_{21}S_{21} ,\\
&F_4=C_{32}S_{23}+C_{23}S_{32} ,\quad F_5=C_{13}S_{31}+C_{31}S_{13} ,\\
&F_6=C_{21}S_{12}+C_{12}S_{21} ,\\
&F_7=(2S_{33}-S_{11}-S_{22})/2 ,\quad F_8=S_{11}-S_{22} \quad \text{where}\\
&C_{ij}=L_{ii}/(L_{ii}^{2}+L_{jj}^{2})^{1/2} .
\end{aligned} \qquad (14) $$

We note that $S_{11}+S_{22}+S_{33}$ cannot be determined.

The inverse relations for inclusion in (3) are

$$L_{11}=D_1-D_2/2+D_3\,,\quad L_{22}=D_1-D_2/2-D_3\,,$$
$$L_{33}=D_1+D_2\,,\quad L_{12}=D_4\,,\quad L_{13}=D_5\,,\quad L_{23}=D_6\,,$$
$$T_{11}=E_1-E_2/2+E3\,,\quad T_{22}=E_1-E_2/2-E_3\,,$$
$$T_{33}=E_1+E_2\,,\quad T_{12}=E_4\,,\quad T_{13}=E_5\,,\quad T_{23}=E_6$$
$$S_{23}=C_{23}F_1+C_{32}F_4\,,\quad S_{31}=C_{31}F_2+C_{13}F_5\,,$$
$$S_{12}=C_{12}F_3+C_{21}F_6\,,\quad S_{32}=-C_{32}F_1+C_{23}F_4\,,$$
$$S_{13}=-C_{13}F_2+C_{31}F_5\,,\quad S_{21}=-C_{21}F_3+C_{12}F_6\,,$$
$$S_{11}-S_{22}=F_8\,,\quad S_{22}-S_{33}=-F_7-F_8/2\,,$$
$$S_{33}-S_{11}=F_7-F_8/2\,. \qquad (15)$$

Symmetry constraints impose zero values on certain of these parameters, D_i, E_i, F_i. The non-zero parameters (refinable parameters) are given in Table 1.

Table 1. *Refinable parameters*

Point group*	Parameters
1	$D_1D_2D_3D_4D_5D_6E_1E_2E_3E_4E_5E_6F_1F_2F_3F_4F_5F_6F_7F_8$
2	$D_1D_2D_3D_4\quad E_1E_2E_3E_4\quad F_3\quad F_6F_7F_8$
m	$D_1D_2D_3D_4\quad E_1E_2E_3E_4\quad F_1F_2\quad F_4F_5$
222	$D_1D_2D_3\quad E_1E_2E_3\quad F_7F_8$
*mm*2	$D_1D_2D_3\quad E_1E_2E_3\quad F_3\quad F_6$
3, 4, 6	$D_1D_2\quad E_1E_2\quad F_3\quad F_7$
$\bar{4}$	$D_1D_2\quad E_1E_2\quad F_6\quad F_8$
32, 422, 622	$D_1D_2\quad E_1E_2\quad F_7$
3*m*, 4*mm*, 6*mm*	$D_1D_2\quad E_1E_2\quad F_3$
$\bar{4}2m$	$D_1D_2\quad E_1E_2\quad F_8$
$\bar{6}$, $\bar{6}m2$	$D_1D_2\quad E_1E_2$
23, $\bar{4}3m$, 432	$D_1\quad E_1$

* Point symmetry $\bar{1}$ makes all F_i zero

The values of D_i (or E_i) may be constrained to make **L** (or **T**) spherically symmetric ($i=1$ only), axially symmetric ($i=1$, 2 only), have three principal axes parallel to the principal axes of inertia ($i=1,2,3$ only) or have one axis parallel to the third principal axis of inertia ($i=1,2,3,4$ only).

Pawley (1972) has summarized the usual constraints on the **TLS** model. The **TL** constraint makes the **S** matrix zero for an initial orthonormal axis system intersecting at a point (commonly the centre of mass). Constraining the F_i values to be identically zero then keeps the centre of action fixed. This is a necessary constraint if the rigid group is on a site of symmetry $\bar{1}$ in the crystal. The **TLX** constraint is a **TL** model where the centre of action has to be located.

If the principal axis directions of the **L** tensor are used to describe the **TLS** model it is seen using (10) and (14) that

$$F_1/[({}^pL_{22})^2+({}^pL_{33})^2]^{1/2}$$
$$=[({}^pL_{22})^{22}r^1+({}^pL_{33})^{23}r^1]/[({}^pL_{22})^2+({}^pL_{33})^2]$$
$$F_4/[({}^pL_{22})^2+({}^pL_{33})^2]^{1/2}$$
$$=({}^2r^1-{}^3r^1){}^pL_{22}{}^pL_{33}/[({}^pL_{22})^2+({}^pL_{33})^2]\,. \qquad (16)$$

Thus in such an axial system the **TLX** constraint corresponds to having $F_i=0$ ($i=4$ to 8).

From (8) the centre of action is at

$${}^pX^1_0=({}^pL_{22}{}^2r^1+{}^pL_{33}{}^3r^1)/({}^pL_{22}+{}^pL_{33}),\ etc.$$

so that

$$F^1/[({}^pL_{22})^2+({}^pL_{33})^2]^{1/2}-{}^pX^1_0=[({}^pL_{22}-{}^pL_{33})/$$
$$({}^pL_{22}+{}^pL_{33})]F_4/[({}^pL_{22})^2+({}^pL_{33})^2]^{1/2}\ etc.$$

From (3) the mean-square value of the displacement of an atom at X^1_n, X^2_n, X^3_n is given by

$$(U_{11}+U_{22}+U_{33})=(T'_{11}+T'_{22}+T'_{33})$$
$$-2X^1_n(S'_{23}-S'_{32})-2X^2_n(S'_{31}-S'_{13})$$
$$-2X^3_n(S'_{12}-S'_{21})$$
$$+(L'_{11}+L'_{22}+L'_{33})\,(X^1_nX^1_n+X^2_nX^2_n$$
$$+X^3_nX^3_n)-\sum_{ij}L'_{ij}X^i_nX^j_n\,. \qquad (17)$$

From (7) it is seen that an origin X^1_0, X^2_0, X^3_0 may be chosen to make $S_{ij}-S_{jt}=0$. If the principal axes of the **L** tensor are used as reference axes then it is readily shown using (8) and (12) that transformation to this origin gives

$${}^p\hat{T}_{11}+{}^p\hat{T}_{22}+{}^p\hat{T}_{33}={}^pT'_{11}+{}^pT'_{22}+{}^pT'_{33}$$
$$-[{}^pL_{11}({}^pX^2_n{}^pX^2_n+{}^pX^3_n{}^pX^3_n)$$
$$+{}^pL_{22}({}^pX^3_n{}^pX^3_n+{}^pX^1_n{}^pX^1_n)$$
$$+{}^pL_{33}({}^pX^1_n{}^pX^1_n+{}^pX^2_n{}^pX^2_n)] \qquad (18)$$

and so minimizes the trace of **T**.

It is seen from (13) that this trace is further minimized by using non-intersecting axes to make **S** diagonal. This result requires ${}^pL_{ii}>0$ which must be true for the **TLS** description to be meaningful.

The fact that three non-intersecting perpendicular axes can be found to make $L_{ij}=S_{ij}=0$ for $i\neq j$ shows that the average motion of a rigid molecule can be described by six separate non-covarying average motions (Schomaker & Trueblood, 1968). These motions are three screw rotations about the perpendicular non-intersecting axes and three translations along a different three orthonormal directions. The ith screw rotation has $\lambda_j=t_j=0$ for $j\neq i$ in (1). The average motion is then described by saying $\lambda_i\lambda_i={}^pL_{ii}$, $\lambda_it_i={}^pS_{ii}$ and hence $t_it_i={}^pS^2_{ii}/{}^pL_{ii}$. Johnson & Levy (1974) have pointed out that $\sum_i {}^pS^2_{ii}/{}^pL_{ii}$ is a minimum if ${}^pS_{11}+{}^pS_{22}+{}^pS_{33}$ has a value such that

$${}^pS_{11}=[({}^pS_{11}-{}^pS_{22})/{}^pL_{22}+({}^pS_{11}-{}^pS_{33})/{}^pL_{33}]/\sum_i {}^pL^{-1}_{ii}\ etc. \qquad (19)$$

thus giving a maximum residual uncorrelated translational motion which may be described as three uncorrelated translational motions in the principal axis directions of the residual **T** tensor.

We see that choosing an axial system parallel to the principal axes of the **L** tensor allows the parameters D_i and F_i to be individually associated with distinct features of the three screw rotations.

Values of the **T**, **L** and **S** tensors are evaluated from either U_{ij} values or else from the least-squares refinement of X-ray or neutron structure factors. If the U_{ij} are known then the evaluation is a linear least-squares

problem [see (3)], and for a fixed weighting scheme convergence occurs in a single cycle. However the estimation of the covariances of the parameters D_i, E_i, F_i which best describe the motion using the best axial system are not easily obtained from a refinement calculated for some other axial system as may be seen from the transformations in (12). Transforming the axial system, the new U_{ij} parameters are a linear combination of the old U_{ij} parameters and so the covariances of the new U_{ij} parameters are easily obtained. The usual least-squares procedure regards U_{ij} values as uncorrelated observations. Using weights of $w=1/\text{var}\,(U_{ij})$ can be expected to give a slightly different description from that obtained in the previous cycle, that is L_{ij} and $S_{ij}-S_{ji}$ $(i\neq j)$ may not be identically zero even though the axial system was chosen from the previous cycle to make this so.

A **TLX** constraint analysis of U_{ij} parameters may be obtained by iteration procedures with F_i set identically zero for $i=4$ to 8. An initial cycle setting $C_{ij}=1/\sqrt{2}$ in (14) may be used to find an initial centre of action and orientation of the **L** tensor. Transforming the axial system to make L_{ij} and $S_{ij}-S_{ji}$ $(i\neq j)$ equal zero enables better values of C_{ij} to be calculated for a further cycle with $F_i=0$ $(i=4$ to 8).

It should be noted that the relaxation of the **TLX** constraint will not alter the value of $U_{11}+U_{22}+U_{33}$ for any atom should the **T** and **L** tensors and the centre of action remain unaltered [see (17)].

Calculation of the **T**, **L** and **S** tensors using the least-squares refinement of structure factors is again best handled by the use of D_i, E_i and F_i parameters. Each cycle the parameters are redefined relative to the axial system that makes L_{ij} and $S_{ij}-S_{ji}$ equal zero for $i\neq j$. Refined variables are then directly associated with features of the axial system that best describes the interpretation of the **TLS** model and allows constraints on the model to be made by setting certain D_i, E_i, F_i parameters as identically zero. The variances calculated from the least-squares equations are then directly associated with meaningful parameters and the covariance and refinability of parameters is more easily understood.

If atoms in a rigid group are defined with respect to their inertial axes and assumed centre of action (usually the centre of mass) then successive refinement cycles can occur refining E_1, all E_i, all E_i and D_1, D_2, D_3; all D_i, E_i; all D_i, E_i and F_1, F_2, F_3; all D_i, E_i and F_i $(i=1$ to 6) and finally all D_i, E_i, F_i. Symmetry constraints necessarily restrict this choice. If the rigid group is inherently symmetric but lies on a site in the crystal of lower symmetry, the constraints of the higher symmetry on the **L** and **S** tensors can still be imposed by choice of D_i and F_i parameters (see Table 1).

Appropriate expressions for least-squares refinement are given elsewhere (Rae, 1975*b*). It is noted that it is not necessary to transform parameters back to the crystallographic axial system to evaluate differentials for the least-squares equations.

Correction to atom positions

These corrections are best carried out using the orthonormal axial system that has axes parallel to the principal axes of libration. The nth atom is described as being at ${}^pX^1_n, {}^pX^2_n, {}^pX^3_n$ and the centre of action is at ${}^pX^1_0, {}^pX^2_0, {}^pX^3_0$. The corrections arise from rotation about three non-intersecting screw rotation axes displaced from the centre of action by amounts 0, $-{}^p\hat{S}_{13}/{}^p\hat{L}_{11}$, ${}^p\hat{S}_{12}/{}^p\hat{L}_{11}$; ${}^p\hat{S}_{23}/{}^p\hat{L}_{22}$, 0, $-{}^p\hat{S}_{21}/{}^p\hat{L}_{22}$; $-{}^p\hat{S}_{32}/{}^p\hat{L}_{33}$, ${}^p\hat{S}_{31}/{}^p\hat{L}_{33}$, 0 respectively. Thus the nth atom is displaced from the first screw axis by an amount 0, ${}^pX^2_n-{}^pX^2_0+{}^p\hat{S}_{13}/{}^p\hat{L}_{11}$, ${}^pX^3_n-{}^pX^3_0-{}^p\hat{S}_{12}/{}^p\hat{L}_{11}$. The three screw axes are non-covariant and so a single screw rotation may be thought of as acting on an atom, the most probable position of which is the mean of the probability density distribution arising from all other motions. Since $\langle\cos\theta\rangle=1-\langle\theta^2\rangle/2$ for small θ the inclusion of the motion about the first screw axis shortens the mean position of an atom at a distance d from the screw axis by an amount $\frac{1}{2}{}^p\hat{L}_{11}d$. Thus the inclusion of the motion about the first screw axis shifts the mean position of the nth atom by an amount 0, $-({}^pX^2_n-{}^pX^2_0){}^p\hat{L}_{11}/2-{}^p\hat{S}_{13}$, $-({}^pX^3_n-{}^pX^3_0){}^p\hat{L}_{11}/2+{}^p\hat{S}_{12}$.

If the most probable position of the nth atom is regarded as the position ${}^p\hat{X}^1_n, {}^p\hat{X}^2_n, {}^p\hat{X}^3_n$ when all angular displacements are zero, then the inclusion of all three screw rotation movements displaces the mean of the electron density from this point by an amount

$$\begin{aligned}&-({}^p\hat{X}^1_n-{}^pX^1_0)\,({}^p\hat{L}_{22}+{}^p\hat{L}_{33})/2\,,\\&-({}^p\hat{X}^2_n-{}^pX^2_0)\,({}^p\hat{L}_{33}+{}^p\hat{L}_{11})/2\,,\\&-({}^p\hat{X}^3_n-{}^pX^3_0)\,({}^p\hat{L}_{11}+{}^p\hat{L}_{22})/2\end{aligned}\qquad(20)$$

since ${}^p\hat{S}_{ij}={}^p\hat{S}_{ji}$.

It is seen that these corrections are not dependent on the parameters F_4 to F_8. Thus the imposition of the **TLX** constraint neither alters the value of $(U_{11}+U_{22}+U_{33})$ for any atom nor changes the displacement of the mean from the most probable position.

(Rae, 1975*a*) has shown how the displacement of the mean from its most probable position can be allowed for in a structure-factor calculation by using third-rank cumulants permitting the refinement of positions of maximum rather than mean probability in least-squares equations (Rae, 1975*b*).

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