

On the Rigid-Body Motion of Molecules in Crystals*

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Cruickshank's analysis of the rigid-body motion of molecules in crystals in terms of two symmetric tensors, one for libration and one for translation, has been widely adopted in the interpretation of the results of anisotropic refinements of the structures of molecular crystals. In recent years it has been recognized by several people that this treatment is inadequate when there is no pre-ordained center of libration (*e.g.* a center of symmetry), but in each instance the two-tensor description of molecular motion has been retained, an effective center of libration has been assumed to exist, and its location has been sought by one means or another.

Actually, an additional tensor (which we call **S**) is needed to account for correlations of libration and translation. For a molecule at a sufficiently unsymmetrical site, **S** has eight independent components, one of its diagonal elements being arbitrary, and the contribution to the anisotropic displacement tensors by the rigid-body part of the enormously various actual motions can be described in terms of six uncorrelated simple motions: the three familiar principal mean-square translations plus three *screw (helical)* motions about and along three mutually perpendicular, *non-intersecting* axes.

The problem of fitting the observed atomic displacement tensors in terms of rigid-body translation and screw motion involves in the general case a least-squares fit of twenty independent parameters. If the molecule is at a symmetrical site, some or all of the components of **S** are subject to special restrictions; for example, if the site-symmetry is $\bar{1}$, **S** vanishes completely and the treatment is identical with Cruickshank's. In any event, the fit is always independent of the origin assumed in the description of the motion and is found by a straightforward linear least-squares process. Corrections to intramolecular interatomic distances foreshortened by rigid-body motion are shown to depend only on the libration tensor, which is independent of the assumed origin.

Examples of the application of this analysis are given.

Introduction

Cruickshank's (1956*a*) treatment of the rigid-body motion of molecules in crystals in terms of two symmetric tensors, for libration and translation, has been widely adopted in the interpretation of the results of anisotropic refinements of crystal structures. It is inadequate, however, when the libration axes are not constrained to intersect in a known point (*e.g.* a center of symmetry), as has been recognized by Hirshfeld, Sandler & Schmidt (1963), Pawley (1963), Cruickshank, Jones & Walker (1964), and presumably others as well. In each of these investigations, the two-tensor description was assumed with the understanding that the axes of libration intersected at a point. This point and the two tensors were adjusted by trial and error or by a (necessarily non-linear) least-squares method to give the best obtainable over-all fit between the individual atomic vibration tensors, **U**, as derived in the X-ray analysis

and as calculated from the known molecular geometry by the particular method in question.

Indeed, Hirshfeld *et al.* only stated that the assumption of intersecting axes was 'reasonable', implying that it might not be correct, and in an independent confrontation with the problem in connection with a still unpublished structure worked out by Dr R. P. Dodge, kinematical intuition led us to the conviction that the assumption is in fact not always appropriate. This conviction and a straightforward consideration of the full set of second moments of libration-translation have led to the following discussion of the use of the rigid-body postulate.

The root of the difficulty with the earlier attempts to generalize Cruickshank's treatment is that an additional tensor (here called **S**) is needed to account for the average quadratic correlation of translation and libration. When this tensor is included in the analysis, the fit of observed and calculated **U**'s is independent of the origin, although the components of **S** and the translational tensor, **T**, vary with it. It is necessary to establish conditions to eliminate this arbitrariness, so that data may be reported uniformly, and such a condition – that **S** be symmetric – is developed. This con-

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dition can be applied after **S**, **T**, and the librational tensor, **L**, have been found (by a straightforward linear least-squares treatment) for any arbitrary initial origin. If the site of the molecule is centrosymmetric, **S** is identically zero, and the analysis reduces essentially to Cruickshank's treatment. As shown below, **S** vanishes or is a constant – these two conditions are equivalent when **U** is evaluated, because (see below) $\text{Tr}(\mathbf{S})$ is indeterminate – for a few other symmetries as well.

The present approach should not be confused with the one used to good effect by Pawley (1964, 1966), in which the rigid-body assumption is made in the crystallographic least-squares refinement itself, so that instead of all the individual atomic anisotropic vibration parameters, only the components of the over-all librational and translational tensors **L** and **T** and the coordinates of a presumed origin of libration are considered as parameters and refined. This treatment also can be faulted for the failure to include **S**, and it would be substantially improved if **S** were incorporated and the illusory search for a unique origin of libration were correspondingly omitted. In this case the resulting linearity of the least-squares problem would be of no great consequence because iteration is already essential to the structure-refinement process.

Analysis of the motion*

The most general displacement of a rigid body with a fixed point is a rotation about some axis through that point (Euler's theorem; cf. Goldstein, 1950, p. 118); the corresponding displacement of any other point in the body, originally at **r** relative to the fixed point, is a vector and is linear in **r**, and therefore can be expressed as **D** · **r**, with **D** the rotational displacement tensor. The problem is to express **D** in terms of the angle $\lambda \equiv |\lambda|$ and axis-direction λ/λ of the rotation, to add to **D** · **r** any translation **t** of the fixed point to get the total displacement **u** of the point of interest, and to evaluate the components $U_{ij} \equiv u_i u_j$ of its vibration tensor by averaging over all aspects of the motion, both λ and **t** being regarded as functions of the time and/or the lattice position.

In a rigid molecule, then, the instantaneous rotational displacement of an atom originally at **r** relative to an arbitrary, molecule-fixed origin is given by

$$\mathbf{D} \cdot \mathbf{r} = \lambda \times \mathbf{r} (\sin \lambda) / \lambda + [(\mathbf{r} \cdot \lambda) \lambda - \lambda^2 \mathbf{r}] (1 - \cos \lambda) / \lambda^2, \quad (1)$$

where $\lambda \equiv |\lambda|$ is the angle of rotation about an axis through the origin and parallel to λ : the first term on the right is a component of **D** · **r** perpendicular to both λ and **r** (Fig. 1) and the second – with $\mathbf{r} \cdot \lambda \lambda - \lambda^2 \mathbf{r}$ identical to $\lambda \times (\lambda \times \mathbf{r})$ – is the remaining component, in the plane of λ and **r**, perpendicular to λ , and small compared with the first if λ is small. If equal orthogonal

(ordinary Cartesian) axes are assumed and the transpose λ' of λ is expressed as $\lambda' \equiv (\alpha, \beta, \gamma) \equiv (\lambda_1, \lambda_2, \lambda_3)$, the rotational tensor becomes

$$\begin{aligned} \mathbf{D} &= \begin{pmatrix} 0 & -\gamma & \beta \\ \gamma & 0 & -\alpha \\ -\beta & \alpha & 0 \end{pmatrix} (\sin \lambda) / \lambda \\ &+ \begin{pmatrix} \alpha^2 - \lambda^2 & \alpha\beta & \alpha\gamma \\ \alpha\beta & \beta^2 - \lambda^2 & \beta\gamma \\ \alpha\gamma & \beta\gamma & \gamma^2 - \lambda^2 \end{pmatrix} (1 - \cos \lambda) / \lambda^2 \\ &= \begin{pmatrix} 0 & -\gamma & \beta \\ \gamma & 0 & -\alpha \\ -\beta & \alpha & 0 \end{pmatrix} \\ &+ \left(\frac{1}{2}\right) \begin{pmatrix} -\beta^2 - \gamma^2 & \alpha\beta & \alpha\gamma \\ \alpha\beta & -\alpha^2 - \gamma^2 & \beta\gamma \\ \alpha\gamma & \beta\gamma & -\alpha^2 - \beta^2 \end{pmatrix} + O(\lambda^3). \quad (2) \end{aligned}$$

Here the remainder term, $O(\lambda^3)$, is of the order of λ^3 for $\lambda \rightarrow 0$.

It is useful to write **D** in ordinary tensor notation, so that **D** · **r** is given by $(\mathbf{D} \cdot \mathbf{r})_i = D_{ij} r_j$:

$$\begin{aligned} D_{ij} &= -e_{ijk} \lambda_k (\sin \lambda) / \lambda + (\lambda_i \lambda_j - \lambda^2 \delta_{ij}) (1 - \cos \lambda) / \lambda^2 \quad (3) \\ &= -e_{ijk} \lambda_k + \left(\frac{1}{2}\right) (\lambda_i \lambda_j - \lambda^2 \delta_{ij}) + O(\lambda^3). \quad (3a) \end{aligned}$$

Here the summation convention is assumed, as it will be in most of this paper (capitalized subscripts will be used when it is to be suppressed); e_{ijk} is the permutation symbol, equal to +1 for i, j, k a cyclic permutation of 1, 2, 3, to -1 for i, j, k a non-cyclic permutation of 1, 2, 3, and to zero otherwise; δ_{ij} is zero except for $i=j$, for which it is +1; and **D**, **e**, λ , λ^2 , δ , and all the quantities derived from them below are ordinary Cartesian tensors [see e.g. Temple (1960), or Goldstein (1950), p. 146] – they transform like proper tensors if only rotations of Cartesian axis systems are allowed. Equation (2) can also be written in a form suited equally to the usual crystallographic axes and reciprocal axes;

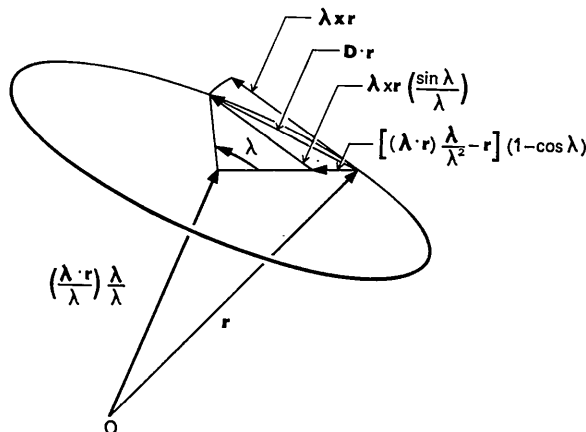


Fig. 1. Illustration of the terms in equation (1).

* Many symbols and conventions are used here; for convenience, they are summarized in an Appendix.

the results are not used here, but are stated at the end of the Appendix.

If the molecule is also translated the vector distance \mathbf{t} , the total displacement of the atom at \mathbf{r} is simply

$$\mathbf{u} = \mathbf{D} \cdot \mathbf{r} + \mathbf{t}. \quad (4)$$

In any case, the desired mean-square displacements $U_{ij} = u_i u_j$ are then obtained easily enough by forming the respective products and taking the appropriate time-and-lattice averages. The result is

$$U_{ij} = \overline{D_{ik} D_{jl} r_k r_l} + (\overline{D_{ik} t_j} + \overline{D_{jk} t_i}) r_k + t_i t_j \quad (5)$$

$$= A_{ijkl} r_k r_l + B_{ijk} r_k + t_i t_j + 0(\epsilon^3) \quad (6)$$

with $A_{ijkl} = A_{jikl}$, $\lambda_i = 0(\epsilon)$, and $t_i = 0(\epsilon)$, and with \mathbf{A} and \mathbf{B} as shown in Table 1.*

In quadratic approximation, then, the U_{ij} depend on the average tensors $\mathbf{L} \equiv \overline{\lambda \lambda}$, $\mathbf{S} \equiv \overline{\lambda \mathbf{t}}$, and $\mathbf{T} \equiv \overline{\mathbf{t} \mathbf{t}}$, all defined here in diadic notation ($T_{ij} \equiv \overline{t_i t_j}$, etc.; in matrix notation \mathbf{T} would be $\mathbf{T} \equiv \overline{\mathbf{t} \mathbf{t}'}$) and with \mathbf{L} the same as Cruickshank's ω , as illustrated in Table 1; \mathbf{S} is the new feature of the present treatment. (In view of the time-and-lattice averaging, the trace of \mathbf{S} is subject to the Schwartz inequality $\text{Tr}(\mathbf{S}) \leq [\text{Tr}(\mathbf{L})\text{Tr}(\mathbf{T})]^{1/2}$). In practice, it will often be best to determine \mathbf{U} for each atom of the molecule, particularly when non-rigid-body vi-

brations may also be important (e.g. Lonsdale, 1961), rather than to follow Pawley's (1964, 1966) scheme of refining only the molecular rigid-body parameters in the primary least-squares refinement of the fit of the structure factors. Thus, following Cruickshank's (1956a) analysis, a least-squares fit of the U_{ij} corresponding to the individual atomic anisotropic temperature factors with those calculated from the rigid-body approximation is made, including however the unsymmetrical tensor \mathbf{S} as well as the symmetrical tensors \mathbf{L} and \mathbf{T} . (The U_{ij} must be the Cartesian components of the \mathbf{U} , unless the general tensor formulation indicated at the end of the Appendix is used.) The observation equations are then based on the above expression for U_{ij} rearranged to the form

$$U_{ij} = G_{ijkl} L_{kl} + H_{ijkl} S_{kl} + T_{ij}. \quad (7)$$

Table 2 gives \mathbf{G} and \mathbf{H} in terms of the atomic coordinates $x(\equiv r_1)$, $y(\equiv r_2)$, and $z(\equiv r_3)$. Inclusion of \mathbf{S} adds eight additional parameters, $\text{Tr}(\mathbf{S}) \equiv S_{ii}$ being indeterminate because only the differences $S_{II} - S_{JJ}$ (no summation) are significant for \mathbf{U} , as can be seen in Table 1 (only the differences occur) and in Table 2 (the coefficients of S_{II} , H_{ijII} , are equal and opposite in pairs). The resulting normal equations, not shown here, are formed exactly in parallel with Cruickshank's (1956a), the necessary derivatives being

$$\begin{aligned} \partial U_{ij} / \partial T_{mn} &= \delta_{im} \delta_{jn}, \\ \partial U_{ij} / \partial L_{mn} &= G_{ijmn}, \quad \text{and} \quad \partial U_{ij} / \partial S_{mn} = H_{ijmn}. \end{aligned}$$

The normal equations are linear in the eight determinable components of \mathbf{S} and the twelve independent components of \mathbf{L} and \mathbf{T} ; these equations (which can be

* One can also go directly from $(\lambda \times \mathbf{r})_i = e_{ijk} \lambda_j r_k$:
 $u_i = e_{imk} \lambda_m r_k + t_i$, and
 $U_{ij} = u_i u_j = e_{imk} e_{jnl} \lambda_m \lambda_n r_k r_l$
 $+ e_{imk} \lambda_n t_j r_k + e_{jnl} \lambda_m t_i r_k + t_i t_j$, corresponding to
 $A_{ijkl} = e_{imk} e_{jnl} L_{mn}$ and
 $B_{ijk} = e_{imk} S_{nj} + e_{jnk} S_{ni}$.

Table 1. The arrays* A and B

ij	kl	A_{ijkl}						B_{ijk}		
		11	22	33	23	31	12	k	1	2
11	0	$\overline{\gamma^2}$	$\overline{\beta^2}$	$-2\overline{\beta\gamma}$	0	0	0	0	$-2\overline{\gamma a}$	$2\overline{\beta a}$
22	$\overline{\gamma^2}$	0	$\overline{\alpha^2}$	0	$-2\overline{\alpha\gamma}$	0	0	$2\overline{\gamma b}$	0	$-2\overline{\alpha b}$
33	$\overline{\beta^2}$	$\overline{\alpha^2}$	0	0	0	$-2\overline{\alpha\beta}$	0	$-2\overline{\beta c}$	$2\overline{\alpha c}$	0
23	$-\overline{\beta\gamma}$	0	0	$-\overline{\alpha^2}$	$\overline{\alpha\beta}$	$\overline{\alpha\gamma}$	$\overline{\gamma c} - \overline{\beta b}$	$\overline{\alpha b}$	$\overline{\alpha a} - \overline{\gamma c}$	$-\overline{\alpha c}$
31	0	$-\overline{\alpha\gamma}$	0	$\overline{\alpha\beta}$	$-\overline{\beta^2}$	$\overline{\beta\gamma}$	$-\overline{\beta a}$	$\overline{\alpha a} - \overline{\gamma c}$	$\overline{\beta c}$	$-\overline{\beta b} - \overline{\alpha a}$
12	0	0	$-\overline{\alpha\beta}$	$\overline{\alpha\gamma}$	$\overline{\beta\gamma}$	$-\overline{\gamma^2}$	$\overline{\gamma a}$	$-\overline{\gamma b}$		

* The components of λ and \mathbf{t} have been represented here as unsubscripted quantities: $\alpha \equiv \lambda_1$, $\beta \equiv \lambda_2$, $\gamma \equiv \lambda_3$; $a \equiv t_1$, $b \equiv t_2$, $c \equiv t_3$.
 $A_{ijkl} = \overline{D_{ik} D_{jl}} + \overline{D_{ji} D_{lk}}$ for $l = k + 1 \pmod{3}$, $A_{ijkl} = 0$ for $l = k + 2 \pmod{3}$, $A_{ijkk} = \overline{D_{ik} D_{jk}}$.

Table 2. The arrays* G and H

ij	kl	G_{ijkl}						H_{ijkl}							
		11	22	33	23	31	12	11	22	33	23	31	12	32	13
11	0	z^2	y^2	$-2yz$	0	0	0	0	0	0	$-2y$	0	0	0	$2z$
22	z^2	0	x^2	0	$-2xz$	0	0	0	0	0	0	$-2z$	$2x$	0	0
33	y^2	x^2	0	0	0	$-2xy$	0	0	0	$-2x$	0	0	0	$2y$	0
23	$-yz$	0	0	$-x^2$	xy	xz	0	$-x$	x	0	0	y	0	$-z$	0
31	0	$-xz$	0	xy	$-y^2$	yz	y	0	$-y$	z	0	0	0	0	$-x$
12	0	0	$-xy$	xz	yz	$-z^2$	$-z$	z	0	0	x	0	$-y$	0	0

* $G_{ijkl} = 0$ for $l = k + 2 \pmod{3}$.

formed with any desired weights or even a full weight matrix for all the U_{ij} of all the atoms) are in general readily solvable, although there will sometimes be limitations like the singularity mentioned by Cruickshank for circular planar molecules. We shall not discuss such cases of insufficient data, except to note that Cruickshank's singularity occurs also whenever all the atoms of a planar molecule lie along *any* quadratic curve. We shall however discuss the average motions implied by **L**, **S**, and **T**, and consider the restrictions that follow if the molecule occupies a symmetrical site; some results of the application of the analysis are given later.

Interpretation of **L**, **S**, and **T**

The formulation of **U** in terms of **L**, **S**, and **T** is valid no matter what arbitrary origin of coordinates and orientation of coordinate axes happen to be used, but the matter is rendered more perspicuous by referring the symmetric tensors **U**, **L**, $(\mathbf{S} + \mathbf{S}')/2$, and **T** to their respective principal axes and regarding $(\mathbf{S} - \mathbf{S}')/2$, the antisymmetric part of **S**, as a vector by thinking explicitly of $e_{ijk}S_{jk}/2$ instead of $(\mathbf{S} - \mathbf{S}')_{jk}/2$ [this ubiquitous but rather delicate point is discussed very clearly in unusually great detail by Goldstein (1950) p. 124 ff]. However, a shift in origin of coordinates intermixes **S** and **T**, leaving **U** and **L** unchanged, so that something has to be done to remove the arbitrary element and thus make possible meaningful comparison and discussion of different experimental results. A suitable device is to choose the origin that makes **S** symmetric and, it also happens (as shown below), minimizes $\text{Tr}(\mathbf{T}) \equiv T_{ii}$, which of course is itself invariant to rotations of the coordinate axes. In terms of the principal axes of **L**, **T**, and the now symmetric **S**, the 21 original components of **L**, **S**, and **T** are accounted for as 3 rotational amplitudes, 3 translational amplitudes, 3 screw correlations (only two of them determinable), 9 angles of orientation of the principal-axis systems, and the 3 coordinates of the new origin. This is a succinct description of the motion insofar as it is defined by **L**, **S**, and **T**. However, it involves the actual averages over all manner of instantaneous translations and rotations, and it may be desired to find instead a simpler picture, equivalent for the quadratic approximation to **U**, in terms of a small number of independently distributed simple motions. In particular, it may be desired to eliminate as far as possible the explicit attention to rotation-translation correlation. This could be done by translating to the same new origin described above (which symmetrizes **S**), rotating the remaining **S** to principal axes, and defining three corresponding screw motions (two of them determinate) of pitch *times* mean-square angular amplitude chosen to account for the additive contribution to **U** of the remaining **S**. The respective rotational and translational consequences of these screw motions can then be subtracted from **L** and **T**, and the remainders of these tensors rotated to principal axes. This equivalent motion would thus con-

sist of 9 statistically independent motions – 3 rotations and 3 screw rotations, all about the same origin, and 3 translations. Unfortunately, this picture is no less arbitrary than the original **L**, **S**, and **T**: although the origin is fixed, the pitches of the three screw rotations are not.

A different description, detailed at the end of this section, is preferable. It is easier to picture because it reduces the equivalent average motion to the sum of 6 independently distributed instantaneous motions – 3 screw librations about non-intersecting axes and 3 translations – and it involves the required 21 parameters: 6 amplitudes, 6 angles of orientation, 6 coordinates of axis displacement, and 3 screw pitches, of which one has to be chosen arbitrarily.

As mentioned above, Hirshfeld *et al.* (1963), Pawley (1963), and Cruickshank *et al.* (1964) have attempted to find effective rotational centers for molecules in sites of low symmetry,* correctly rejecting the possible inference from Cruickshank's (1956*a*) discussion that the (known) center of mass would always be the effective center of rotation. We are not aware of any previous treatment of the crystallographic problem in which it was recognized that the effective axes of libration might not intersect, or that the general motion is helical rather than simply rotational, but C.K. Johnson and H.A. Levy have brought to our attention Brenner's completely independent analysis of a superficially quite different problem [latest paper: *Coupling between the Translational and Rotational Brownian Motions of Rigid Particles of Arbitrary Shape*, Brenner (1967)]. It is remarkably similar to this one in many details, and some readers of the present treatment have enjoyed following both in parallel.

It is hardly necessary to detail the rotations to principal axes, for which we have used standard matrix operations, because all follow the pattern of replacing **r** by $\Omega\mathbf{r}$ and **U** by $\Omega\mathbf{U}\Omega'$, with Ω an orthogonal matrix. However, the systematic shift in origin and the displacements of nonintersecting axes merit explicit attention. The calculations run as follows.

* The problem of achieving a least-squares fit of **L**, **S**, and **T** to the **U**'s is linear, whereas the incomplete one ignoring **S** but including an unknown center, as formulated by Hirshfeld *et al.* and Pawley, is not. The two problems therefore have an essential difference in structure; nonetheless, failing to appreciate the full bearing of this clue, we tried to find a constraint on the complete problem that would lead to the Hirshfeld-Pawley result by a linear calculation. As ought to have been anticipated, the tantalizing prospect of achieving this in the least-squares calculation simply by applying the linear constraint that **S** be antisymmetric and then making its three remaining components vanish by adjusting the three components of the origin vector is illusory: although the symmetric and antisymmetric parts of **S** transform independently under rotations of axes, they do not do so under shifts of origin, and the scheme fails, leading to a certain non-zero symmetric **S** where zero **S** is desired. Altogether, it is clearly both better and easier to determine **L**, **S**, and **T** fully, imposing only such constraints as follow from site symmetry.

Shift of origin to symmetrize S and minimize Tr(T)

We require that \mathbf{u} and λ (and therefore \mathbf{U} and \mathbf{L}) be invariant to shifting the origin by the vector \mathbf{q} , so that the old origin-to-atom vector \mathbf{r} and the new one \mathbf{r}^0 are related by

$$\mathbf{r} = \mathbf{r}^0 + \mathbf{q}.$$

The condition on λ is direct ($\lambda^0 = \lambda$) but the condition on \mathbf{u} induces the transformation $\mathbf{t} \rightarrow \mathbf{t}^0$ which in turn induces those for $\mathbf{S} \rightarrow \mathbf{S}^0$ and $\mathbf{T} \rightarrow \mathbf{T}^0$. Keeping only linear terms in λ and using the abbreviated dot notation $\mathbf{e} : \mathbf{r}\lambda = \mathbf{r} \times \lambda$ analogous to the $\mathbf{D} \cdot \mathbf{r}$ of (1), we then have

$$\mathbf{u} = -\mathbf{e} : \mathbf{r}\lambda + \mathbf{t} = -\mathbf{e} : (\mathbf{r}^0 + \mathbf{q})\lambda + \mathbf{t} = \mathbf{u}^0 = -\mathbf{e} : \mathbf{r}^0\lambda + \mathbf{t}^0. \quad (8)$$

The abbreviated notation (e.g. Drew, 1961; Goldstein, 1950, p.148) is illustrated by the following parallel, equivalent ways of writing $\lambda \times \mathbf{r}$:

$$\begin{aligned} \lambda \times \mathbf{r} &\equiv \mathbf{e} : \lambda \mathbf{r} \equiv \mathbf{r} \cdot \mathbf{e} \cdot \lambda \equiv \lambda \mathbf{r} : \mathbf{e} \equiv -\mathbf{e} : \mathbf{r}\lambda \equiv -\lambda \cdot \mathbf{e} \cdot \mathbf{r} \\ &\equiv -\mathbf{r}\lambda : \mathbf{e} \end{aligned}$$

$$\begin{aligned} (\lambda \times \mathbf{r})_i &\equiv e_{ijk} \lambda_j r_k \equiv r_k e_{kij} \lambda_j \equiv \lambda_j r_k e_{jki} \equiv -e_{ikj} r_k \lambda_j \\ &\equiv -\lambda_j e_{jik} r_k \equiv -r_k \lambda_j e_{kji}, \end{aligned}$$

the minus signs arising by virtue of the antisymmetry $e_{ijk} = -e_{ikj}$ of \mathbf{e} . The notation is compact and suggestive, and can always be checked by writing in the implied indices; it is further described in the Appendix. Comparison of the last two members of (8) gives

$$\mathbf{t}^0 = \mathbf{t} - \mathbf{e} : \mathbf{q}\lambda = \mathbf{t} + \lambda \mathbf{q} : \mathbf{e}. \quad (9)$$

By adjoining λ in (9) and averaging we then obtain

$$\mathbf{S}^0 = \mathbf{S} + \mathbf{L}\mathbf{q} : \mathbf{e}, \quad (10)$$

with

$$(\mathbf{L}\mathbf{q} : \mathbf{e})_{il} = L_{ij} q_k e_{jkl}.$$

From (9) we also obtain \mathbf{T}^0 :

$$\begin{aligned} \mathbf{T}^0 &\equiv \overline{\mathbf{t}^0 \mathbf{t}^0} = \overline{(\mathbf{t} - \mathbf{e} : \mathbf{q}\lambda)(\mathbf{t} + \lambda \mathbf{q} : \mathbf{e})} \\ &= \mathbf{T} - \mathbf{e} : \mathbf{q}\mathbf{S} - (\mathbf{e} : \mathbf{q}\mathbf{S})' - \mathbf{e} : \mathbf{q}\mathbf{L}\mathbf{q} : \mathbf{e}, \quad (11) \end{aligned}$$

the transposed term $(\mathbf{e} : \mathbf{q}\mathbf{S})'$ arising from

$$\begin{aligned} \overline{(\mathbf{t}\lambda \mathbf{q} : \mathbf{e})}_{ij} &= \overline{t_i \lambda_k q_l e_{kij}} \equiv \\ S_{kij} q_l e_{kij} &= -e_{jik} q_l S_{kij} = -(\mathbf{e} : \mathbf{q}\mathbf{S})_{ji}. \end{aligned}$$

The expression for \mathbf{U} ,

$$\mathbf{U} = \mathbf{T} - \mathbf{e} : \mathbf{r}\mathbf{S} - (\mathbf{e} : \mathbf{r}\mathbf{S})' - \mathbf{e} : \mathbf{r}\mathbf{L}\mathbf{r} : \mathbf{e}, \quad (11a)$$

is analogous in structure to that for \mathbf{T}^0 given in (11); it is of course equivalent to (7).

From (10) and $(\mathbf{e} : \mathbf{S})_i = S_{jk} - S_{kj}$, $k-j=j-i=1 \pmod{3}$, the condition that \mathbf{S}^0 be symmetric, $\mathbf{S}^0 - \mathbf{S}^0' = 0$, is then

$$\mathbf{e} : \mathbf{S}^0 = \mathbf{e} : \mathbf{S} + \mathbf{e} : (\mathbf{L}\mathbf{q} : \mathbf{e}) = 0, \quad (12)$$

and the same condition arises on requiring that $\text{Tr}(\mathbf{T}^0) \equiv T_{ii}^0 \equiv \mathbf{T}^0 : \delta$ be an extremum with respect to arbitrary variations of \mathbf{q} . This follows on summing the diagonal elements of (11) to obtain

$$\mathbf{T}^0 : \delta = \mathbf{T} : \delta - 2\mathbf{q} : \mathbf{e} : \mathbf{S} - \mathbf{q} : \mathbf{e} : (\mathbf{L}\mathbf{q} : \mathbf{e}) \quad (13)$$

and taking the standard variation, here symbolized by Δ to avoid confusion with δ ,

$$-\Delta \mathbf{T}^0 : \delta = 0 = 2\Delta \mathbf{q} : \mathbf{e} : \mathbf{S} + 2\Delta \mathbf{q} : \mathbf{e} : (\mathbf{L}\mathbf{q} : \mathbf{e}),$$

the factor 2 in the second term on the right arising from the symmetry ($\mathbf{L} = \mathbf{L}'$) and quadratic character of $\mathbf{e} : \mathbf{q}\mathbf{L}\mathbf{q} : \mathbf{e}$. The desired result is then obtained by solving

$$\mathbf{e} : \mathbf{S} = -\mathbf{e} : (\mathbf{L}\mathbf{q} : \mathbf{e}) = (\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \mathbf{q}, \quad (14)$$

which is identical with (12).*

The solution of (14) is

$$\mathbf{q} = (\mathbf{L} : \delta\delta - \mathbf{L})^{-1} \cdot \mathbf{e} : \mathbf{S}, \quad (15)$$

which in terms of the principal axes of \mathbf{L} reduces to

$$\begin{aligned} q_I &= (S_{JK} - S_{KJ}) / (L_{JJ} + L_{KK}), \\ K &= J+1 = I+2 \pmod{3}. \quad (16) \end{aligned}$$

The extreme trace is seen to be a minimum by substituting from (14) and (16) into (13) to give

$$\mathbf{T}^0 : \delta = \mathbf{T} : \delta - \mathbf{q} : \mathbf{e} : \mathbf{S} = \mathbf{T} : \delta - \sum_I (S_{JK} - S_{KJ})^2 / (L_{JJ} + L_{KK}),$$

again in the \mathbf{L} axes with $K = J+1 = I+2 \pmod{3}$, all the terms in the sum being positive unless \mathbf{S} is symmetric, whereupon they vanish and $\mathbf{T} : \delta$ cannot be reduced further.

Non-intersecting rotation axes

The preferred reduction of the average motion is achieved by rotating to the principal axes of \mathbf{L} and shifting to three generally non-intersecting displaced axes of libration, each used for one of the principal directions of libration and chosen to eliminate the off-diagonal part of \mathbf{S} . The diagonal components of \mathbf{S} are then accounted for by regarding the eigenvalues of \mathbf{L} as representing independent rotations, each with a screw component. Finally, \mathbf{T} is appropriately reduced to keep \mathbf{U} invariant and is referred to its own principal axes. The picture is thus one of six independent simple motions. Labelled according to the principal axis of libration involved (Fig. 2), the shifts of axis ${}^J\mathbf{q}$ and new position vectors ${}^J\mathbf{R}$ are given by

$$\begin{aligned} {}^J q_I &= r_I - {}^J R_I = e_{IJK} S_{JK} / L_{JJ} \\ &\quad \text{(no summation, } I \neq J \neq K) \quad (17) \end{aligned}$$

in consequence of the conditions that the shifted off-diagonal terms of \mathbf{S} should vanish,

$${}^J S_{JK} = S_{JK} + (\mathbf{L}^J \mathbf{q} : \mathbf{e})_{JK} = 0, \quad K \neq J \text{ [see (10)]}.$$

(No values of ${}^J q_J$ are defined: the diagonal terms of \mathbf{S} as referred to the principal axes of \mathbf{L} are independent of shifts in origin and so cannot be removed.)

* The result $(\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \mathbf{q}$ can be calculated directly from the components. It also follows from the vector identity $\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{A} \cdot \mathbf{C} \mathbf{B} - \mathbf{A} \cdot \mathbf{B} \mathbf{C}$ and recourse to the average-dyad character of \mathbf{L} :

$$\begin{aligned} -\mathbf{e} : (\mathbf{L}\mathbf{q} : \mathbf{e}) &= -\mathbf{e} : (\lambda \lambda \times \mathbf{q}) = -\lambda \times (\lambda \times \mathbf{q}) = \lambda \cdot \lambda \mathbf{q} - \lambda \lambda \cdot \mathbf{q} \\ &= \lambda \lambda : \delta \mathbf{q} - \mathbf{L} \cdot \mathbf{q} = (\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \mathbf{q}. \end{aligned}$$

The U may then be rewritten as

$$U_{II} = {}^rT_{II} + L_{JJ} {}^J R_K^2 + L_{KK} {}^K R_J^2, \quad (18)$$

and

$$U_{IJ} = {}^rT_{IJ} - L_{KK} {}^K R_J {}^K R_I - S_{II} {}^I R_K + S_{JJ} {}^J R_K, \\ K=J+1=I+2 \pmod{3} \quad (19)$$

with

$${}^rT_{II} = T_{II} - \sum_{K \neq I} S_{KI}^2 / L_{KK} \quad (20a)$$

and

$${}^rT_{IJ} = T_{IJ} - \sum_K S_{KI} S_{KJ} / L_{KK}, \quad J \neq I, \quad (20b)$$

where, as for all expressions in this paragraph, the axes parallel to the eigenvectors of \mathbf{L} are implied. (Note that in ${}^r\mathbf{T}$ the trace and indeed the separate diagonal components of \mathbf{T} have been minimized with respect to the axis displacements – the terms in the decrements are always positive until the stage $S_{ij}=0$, $i \neq j$, is reached. Moreover, ${}^r\mathbf{T} : \delta$ is lower than the reduced $\mathbf{T} : \delta$ of the origin-shift method, which symmetrizes the off-diagonal part of \mathbf{S} but does not make it vanish.) Explicit reference to \mathbf{S} can then finally be removed by defining the screw pitches σ_I :

$$\sigma_I = S_{II} / L_{II}.$$

It remains to remark that the shifted axes are independent of the arbitrary initial origin, and that the indeterminacy of the trace of \mathbf{S} , $\mathbf{S} : \delta$, affects the reduced \mathbf{T} but obviously not the axis shifts [see (17)]. The uniqueness of the ${}^J R_I$ is shown by a short calculation suppressing the summation convention and recalling that $L_{IJ} \equiv 0$ holds in this axial system:

$$\mathbf{r} = \mathbf{r}^0 + \mathbf{q}; \quad {}^J R_I = r_I - e_{IJK} S_{JK} / L_{JJ}; \quad {}^J R_I^0 = r_I^0 - \\ e_{IJK} S_{JK}^0 / L_{JJ} = r_I - q_I - e_{IJK} (S_{JK} + L_{JJ} q_I e_{IJK}) / L_{JJ} = \\ {}^J R_I - q_I + q_I = {}^J R_I.$$

The effect of the indeterminacy of $\mathbf{S} : \delta$ on the reduced \mathbf{T} is evident from the presence of terms in S_{11} , S_{22} , and S_{33} in the expressions (20b) for ${}^rT_{ij}$, \mathbf{T} being well determined to begin with; these terms are compensated in the expressions (19) for the U_{ij} by the terms linear in ${}^I R_k$, so that the U_{ij} are indeed unaffected by the indeterminacy of $\mathbf{S} : \delta$. However, this indeterminacy must be removed, by imposing a systematic restraint, so that the reduced \mathbf{T} will not itself be indeterminate. The recommended constraint is $\mathbf{S} : \delta = 0$ because it is affected by neither the translations nor the rotations of coordinates employed in the solution and so can safely be imposed at the very beginning in the least-squares fit. These properties can be shown at once from (10), noting again that in the \mathbf{L} -axial system $L_{ij} \equiv 0$ ($i \neq j$) so the second term on the right side of (10) vanishes for S_{11} (etc.) and that $\mathbf{S} : \delta$ is invariant to rotation of axes. The constraint $\mathbf{S} : \delta = 0$ is free of the possible ambiguity of assignment that might afflict such a constraint as, say, $S_{33} = 0$ (in the \mathbf{L} -axial system with $L_{11} \geq L_{22} \geq L_{33}$) when there is symmetry-imposed degeneracy or accidental near-degeneracy of the eigenvalues of \mathbf{L} .

Consequences of site symmetry

We now require of $\mathbf{L} \equiv \overline{\lambda\lambda}$, $\mathbf{S} \equiv \overline{\lambda t}$, and $\mathbf{T} \equiv \overline{t t}$ (as well as \overline{u} , \overline{t} , and $\overline{\lambda}$, which will also be of interest) that they be invariant to the operations of site symmetry. The familiar case of a quadratic form then applies to \mathbf{L} and \mathbf{T} , but \mathbf{S} is somewhat different because λ is an axial (or pseudo-) vector: if \mathbf{P} and \mathbf{Q} are the matrices representing the transformation of a vector and a pseudo-vector by an operation of site symmetry, $\mathbf{t} \rightarrow \hat{\mathbf{t}} \equiv \mathbf{P}\mathbf{t}$, $\lambda \rightarrow \hat{\lambda} \equiv \mathbf{Q}\lambda$, \mathbf{Q} is the same as \mathbf{P} for a proper rotation but is equal to $-\mathbf{P}$ for an improper rotation. One then has $\hat{\mathbf{S}} \equiv \overline{\mathbf{Q}\lambda(\mathbf{P}\mathbf{t})} \equiv \mathbf{Q}\mathbf{S}\mathbf{P}' = \mathbf{S}$, which leads to the requirements summarized in Table 3 for the crystallographic elements of point symmetry and in Table 4 for the crystallographic point groups. [Some of the information in Table 4 can be found in Table 26 of Nye (1957).] For an n -fold rotation, the transformation goes

$$\mathbf{P} = \begin{pmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad c = \cos 2\pi/n, \quad s = \sin 2\pi/n,$$

$$\hat{\mathbf{S}} = \begin{pmatrix} c\lambda_1 - s\lambda_2 & & \\ s\lambda_1 + c\lambda_2 & & \\ & & \lambda_3 \end{pmatrix} \begin{pmatrix} ct_1 - st_2 & & \\ st_1 + ct_2 & & \\ & & t_3 \end{pmatrix}'$$

$$= \begin{pmatrix} c^2 S_{11} + s^2 S_{22} - sc(S_{12} + S_{21}) & & \\ c^2 S_{21} - s^2 S_{12} + sc(S_{11} - S_{22}) & & \\ & c S_{31} - s S_{32} & \\ c^2 S_{12} - s^2 S_{21} + sc(S_{11} - S_{22}) & c S_{13} - s S_{23} & \\ c^2 S_{22} + s^2 S_{11} + sc(S_{12} + S_{21}) & c S_{23} + s S_{13} & \\ & c S_{32} + s S_{31} & S_{33} \end{pmatrix},$$

and for an n -fold rotatory inversion the sign of $\hat{\mathbf{S}}$ is changed, whereupon all the results follow by straightforward but somewhat tedious calculation.

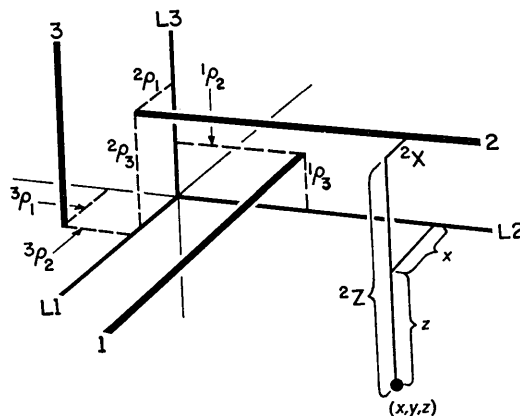


Fig. 2. The three non-intersecting axes parallel to the principal axes of \mathbf{L} . The displacement of each axis (J) parallel to another axis (I) is shown as ${}^J \rho_I$. The X and Z coordinates relative to axis 2 are shown for a point (x, y, z) .

Table 3. Requirements imposed by the several symmetry elements*

Element	$\bar{\lambda}$	\bar{u}, \bar{t}, S_a	S_s	S
1	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 13 \\ 12 & 22 & 23 \\ 13 & 23 & 33 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{pmatrix}$
2	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 21 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$
3, 4, 6	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ -12 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$
$\bar{1}$	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$	0	0	0
$\bar{2}=\bar{h}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 13 \\ 0 & 0 & 23 \\ 13 & 23 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 13 \\ 0 & 0 & 23 \\ 31 & 32 & 0 \end{pmatrix}$
$\bar{3}=\bar{3} \times i$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	0	0	0
$\bar{4}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	0	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & -11 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & -11 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
$\bar{6}=\bar{3} \times \bar{h}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	0	0	0
2, horizontal, along axis 1	$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 22 & 23 \\ 0 & 23 & 33 \end{pmatrix}$	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 22 & 23 \\ 0 & 32 & 33 \end{pmatrix}$
m, vertical ⊥ axis 1	$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 2 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 0 & 12 & 13 \\ 12 & 0 & 0 \\ 13 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 12 & 13 \\ 21 & 0 & 0 \\ 31 & 0 & 0 \end{pmatrix}$
3, cubic orientation†	$\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 12 \\ 12 & 11 & 12 \\ 12 & 12 & 11 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 13 \\ 13 & 11 & 12 \\ 12 & 13 & 11 \end{pmatrix}$

* For tensor components referred to a Cartesian coordinate system with axis 3 parallel to the indicated symmetry axis. Non-zero entries imply non-vanishing components, and identical non-zero entries, in any array, reflect symmetry requirements: S_{ij} , for example, is indicated by ij , $-S_{ij}$ by $-ij$, etc. The arbitrary requirement $\text{Tr}(S)=0$ is not imposed here. The results quoted here and in Table 4 for $\bar{\lambda}$ and \bar{t} are representative of time-averaged (or lattice-averaged) axial and polar vectors respectively.

$$\dagger P=Q = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}; \quad \bar{S} = \begin{pmatrix} \lambda_2 \\ \lambda_3 \\ \lambda_1 \end{pmatrix} \quad \begin{pmatrix} t_2 \\ t_3 \\ t_1 \end{pmatrix} = \begin{pmatrix} 22 & 23 & 21 \\ 32 & 33 & 31 \\ 12 & 13 & 11 \end{pmatrix}.$$

 Table 4. Site-symmetry requirements imposed by the crystallographic point groups^(a)

Point group	$\bar{u}, \bar{t}, \bar{S}_a$	U, L, T	$\bar{\lambda}$	S	Comments ^(b)
C_1-1	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 13 \\ 12 & 22 & 23 \\ 13 & 23 & 33 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{pmatrix}$	The general case considered at length in the foregoing discussion.
$C_i-\bar{1}$	0	$\begin{pmatrix} 11 & 12 & 13 \\ 12 & 22 & 23 \\ 13 & 23 & 33 \end{pmatrix}$	$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$	0	Corresponds to Cruickshank's treatment.
C_2-2	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 21 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	Each axis can have a helical component. S_{12} and $S_{21} \rightarrow 0$ by transformation to axes at different heights, still intersecting 2. Third axis along 2.

Table 4 (cont.)

Point group	$\bar{u} \bar{t}, \bar{S}_a$	U, L, T	$\bar{\lambda}$	S	Comments ^(b)
$C_s - m$	$\begin{pmatrix} 1 \\ 2 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 13 \\ 0 & 0 & 23 \\ 31 & 32 & 0 \end{pmatrix}$	No helical components. S_{13} etc. $\rightarrow 0$ by displacing two axes in the plane and the intersection of the third with the plane.
$C_{2h} - 2/m$	0	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	0	
$D_2 - 222$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	Unequal helicals intersecting at origin of D_2 .
$C_{2v} - mm2$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	$\begin{pmatrix} 0 & 12 & 0 \\ 21 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	Two axes normal to the two-fold axis, not at same level.
$D_{2h} - mmm$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	0	
$C_4 - 4, C_3 - 3, C_6 - 6$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ -12 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$ ^(c)	Two axes normal to symmetry axis at same level, with equal helicals.
$S_4 - \bar{4}$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & -11 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ ^(d)	Two equal and opposite helicals, equally and oppositely displaced along $\bar{4}$.
$C_{4h} - 4/m, C_{3i} - \bar{3}, C_{3h} - \bar{6}, C_{6h} - 6/m$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	0	
$D_4 - 422, D_3 - 32, D_6 - 622$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$ ^(c)	Two equal helicals through origin.
$C_{4v} - 4mm, C_{3v} - 3m, C_{6v} - 6mm$	$\begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}$	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	$\begin{pmatrix} 0 & 12 & 0 \\ -12 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ ^(c)	No helicals; axes normal to axis 3 at same level.
$D_{2d} - \bar{4}2m$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & -11 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ ^{(d),(e)}	Equal and opposite helicals normal to $\bar{4}$ through origin.
$D_{4h} - (4/m)mm, D_{3d} - \bar{3}m, D_{6h} - (6/m)mm$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	0	0	
$T - 23, O - 432$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 11 \end{pmatrix}$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 11 \end{pmatrix}$ ^(c)	
$T_h - m3, T_d - \bar{4}3m, O_h - m3m$	0	$\begin{pmatrix} 11 & 0 & 0 \\ 0 & 11 & 0 \\ 0 & 0 & 11 \end{pmatrix}$	0	0	

(a) For settings with principal symmetry axis along axis 3 and secondary axis (if any) along axis 1 of a Cartesian coordinate system. In general, the description will vary with other orientations. The convention of Table 3 is used for indicating tensor components. The arbitrary requirement $\text{Tr}(\mathbf{S})=0$ is not imposed here.

(b) The axes referred to in these comments are the displaced axes of effective uncorrelated screw rotation [equation (17) and Fig. 2]. In so far as is required by symmetry these axes conform in direction to the Cartesian system specified in the preceding footnote and are numbered accordingly, rather than in the order of their eigenvalues.

(c) Invariant to rotation about the principal axis. The cases $\mathbf{S}=0$ and $\mathbf{S}=S_{11}\delta$ are of course invariant to every proper rotation.

(d) \mathbf{S} varies with azimuthal orientation of the coordinate system as follows, with θ the angle of rotation from an arbitrary starting orientation and θ_0 the angle of rotation away from the principal azimuth defined by $S_{11}={}_0S_{11}$ and $S_{12}=0$.

$$\hat{S}_{11} = S_{11} \cos 2\theta - S_{12} \sin 2\theta = {}_0S_{11} \cos 2\theta_0$$

$$\hat{S}_{12} = S_{12} \cos 2\theta + S_{11} \sin 2\theta = {}_0S_{11} \sin 2\theta_0.$$

Note that at various orientations this can make either the helical components or the displacements of the axes vanish.

(e) Here $\theta=0, 45^\circ, 90^\circ$, etc. are the only natural values to consider.

It is perhaps easier simply to consider each component of \mathbf{S} as a pair of physical entities – a circular current loop \odot corresponding to λ_i and an ordinary vector for t_j – and to visualize how it is affected by the symmetry operations. Because this still requires calculation for a three- or six-fold rotation, it is helpful to note that, like any second-rank tensor, \mathbf{S} may be written as the sum of a symmetric part (\mathbf{S}_s) and an antisymmetric part (\mathbf{S}_a); \mathbf{S}_s transforms like an ordinary quadratic form under proper rotations, while \mathbf{S}_a is equivalent to $(\overline{\lambda \times \mathbf{t}})/2$, which is indeed a true vector displacement with components $(\overline{\lambda \times \mathbf{t}})_i/2 = (S_{jk} - S_{kj})/2 = (\mathbf{S}_a)_{jk} \equiv (\lambda_j t_k - \lambda_k t_j)/2$, (i, j, k cyclic). This vector can be interpreted as the average displacement of \mathbf{t} that would follow from the correlated rotation λ if the rotation were about the lattice-fixed initial origin of coordinates. Expressed in terms of its principal axes, \mathbf{S}_s consists of three principal screw correlations $\lambda_I t_I$ and has some rather surprising possibilities for symmetry because of the special character of λ and the absence of any requirement that the eigenvalues all have the same sign.

Errors in bond lengths

Cruickshank (1956*b*, 1961) has treated an important consequence of rigid-body libration, namely that bond lengths will appear foreshortened. Because his derivation presumes that *the* center of libration is known, it at first seemed that his foreshortening correction might be significantly altered by our recognition of the role of \mathbf{S} , for example in terms of three non-intersecting axes rather than a single center. In fact, however, the non-intersecting axes are irrelevant, and Cruickshank's result is essentially correct when applied to *intramolecular* distances, although it is not always (or even usually) applicable to atomic positions.

Busing & Levy (1964) have thoroughly discussed the general effect of thermal motion on bond lengths estimated from diffraction measurements, emphasizing that the joint distribution of the motions of the atoms must be known or assumed if proper corrections are to be made. Rigid-body motion is a specific case for which the joint distribution is well defined. It is worth noting that incautious use of Cruickshank's procedure for correcting position parameters of atoms may lead to erroneous conclusions about *intermolecular* distances, *e.g.* from a rigid-body atom to an atom which is not part of the rigid body. The distance between the 'corrected' positions of such a pair of atoms may be either larger or smaller than the average distance between them, whereas the distance between the average positions is never more and usually is less than the average distance. As Busing & Levy strongly emphasized, this latter difference between the *mean distance* and the *distance between mean positions* depends altogether on the joint distribution of atomic motions, which is not of course generally known. To re-emphasize: in extreme cases, the 'corrected' distance can even

be the maximum (highly unlikely) or the minimum (almost as unlikely) instantaneous separation of the atoms, with no precise *a priori* relationship to the properly averaged separation, whereas the uncorrected distance (the distance between average positions) is never greater than the true average distance and is indeed smaller unless the perpendicular motions of the two atoms are completely correlated (*i.e.* in phase) and of the same amplitude.

For the estimation of corrections to intramolecular distances, we have not used the position of the maximum of a Fourier peak, as Cruickshank did, but have instead considered only the average position of an atom, $\bar{\mathbf{p}} = \mathbf{r} + \bar{\mathbf{u}}$, which could be measured from an isolated Fourier peak and in many cases may be more nearly what follows from a least-squares refinement. The consideration is an approximation of which the accuracy must be assessed and depends both on the rigid-body assumption and on assignments of origin for rotation and translation. For some sites, as shown in Tables 3 and 4, symmetry requires the vanishing of $\bar{\lambda}$ and $\bar{\mathbf{t}}$, or some of their components, and for these coordinates it is obvious enough to take the average, namely zero, as the origin of measurement in the discussion. It is perhaps not so obvious that the general conditions $\bar{\lambda} = 0$ and $\bar{\mathbf{t}} = 0$ are in fact appropriate, but they seem to be and they lead simply enough to an evaluation of $\bar{\mathbf{p}}$ in terms of the average rotational tensor $\bar{\mathbf{D}}$, which is known in useful approximation from \mathbf{L} as derived from the observed \mathbf{U} 's. Specifying that λ and \mathbf{t} are of the order of an infinitesimal ε , *i.e.* $0(\varepsilon)$, we recall expressions for the instantaneous displacement, \mathbf{u} , and instantaneous position, \mathbf{p} , relative to a lattice-fixed origin in the forms

$$\mathbf{p} = \mathbf{r} + \mathbf{u} = \mathbf{r} + \mathbf{t} + \mathbf{D} \cdot \mathbf{r}, \text{ with} \\ \mathbf{D} = -\mathbf{e} \cdot \lambda + \frac{1}{2}(\lambda\lambda - \lambda\lambda : \delta\delta) + 0(\varepsilon^3). \quad [(3a) \text{ restated}]$$

The conditions $\bar{\mathbf{t}} = \bar{\lambda} = 0$ then lead directly to

$$\mathbf{r} = \bar{\mathbf{p}} - \bar{\mathbf{t}} - \bar{\mathbf{D}} \cdot \mathbf{r} = \bar{\mathbf{p}} + \frac{1}{2}(\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \mathbf{r} + 0(\varepsilon^3).$$

The \mathbf{L} used here is based on the observed \mathbf{U} 's by means of

$$\mathbf{U} = \mathbf{T} - \mathbf{e} : \bar{\mathbf{p}}\mathbf{S} - (\mathbf{e} : \bar{\mathbf{p}}\mathbf{S})' - \mathbf{e} : \bar{\mathbf{p}}\mathbf{L}\bar{\mathbf{p}} : \mathbf{e} + 0(\varepsilon^3),$$

in which the explicit error term, $0(\varepsilon^3)$, is of lower order than either of the errors $0(\varepsilon^4)$ implied by the use of $\bar{\mathbf{p}}$ instead of \mathbf{r} , as required by (11*a*) [terms of second order in ε everywhere multiply $\bar{\mathbf{p}} - \mathbf{r} = 0(\varepsilon^2)$] or the errors $\bar{\mathbf{D}} \cdot (\bar{\mathbf{p}} - \mathbf{r}) = 0(\varepsilon^4)$ induced by writing $\bar{\mathbf{p}}$ for \mathbf{r} in $\bar{\mathbf{D}} \cdot \mathbf{r}$. The result for \mathbf{r} accordingly also holds in the form

$$\mathbf{r} = \bar{\mathbf{p}} + \frac{1}{2}(\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \bar{\mathbf{p}} + 0(\varepsilon^3).$$

Subtracting, and writing $\mathbf{r}(j) - \mathbf{r}(i) = \mathbf{r}(ij)$, *etc.*, then gives

$$\mathbf{r}(ij) = \bar{\mathbf{p}}(ij) + \frac{1}{2}(\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \bar{\mathbf{p}}(ij) + 0(\varepsilon^3) \quad (21)$$

for the interatomic vector relating atoms i and j in the rigid molecule at the reference orientation $\lambda = 0$.

Consequently, to the accuracy of this result, the intramolecular interatomic distance is

$$|\mathbf{r}(ij)| \equiv |\overline{\mathbf{r}(ij)}| = |\overline{\mathbf{p}(ij)}| + \frac{1}{2} \overline{\mathbf{p}(ij)} \cdot (\mathbf{L} : \delta\delta - \mathbf{L}) \cdot \overline{\mathbf{p}(ij)} / |\overline{\mathbf{p}(ij)}|. \quad (22)$$

It is as if the molecule had shrunk independently in each of the three principal directions of \mathbf{L} , in terms of which $(\mathbf{L} : \delta\delta - \mathbf{L})_{kl}$ of course vanishes for $k \neq l$. For example, the shrinkage in the first direction is $\overline{\mathbf{p}}_{11}(ij)(L_{22} + L_{33})/2$. To restore the actual dimensions corrections therefore have to be made in accordance with (21) to every coordinate of every atom. Any corrected intramolecular distance can then be calculated directly or it can be evaluated by (22), by finding the component, along the interatomic vector, of each principal coordinate correction and adding these to the original distance. When the correction term of the equation which Busing & Levy (1964) give under the heading *Molecular Libration* is written (and summed) for the three principal axes of \mathbf{L} , the result is equivalent to (22).

It should be noted from (22) that the average change in an intramolecular distance depends only on $\mathbf{L} \equiv \overline{\lambda\lambda}$ and is independent of any question of axes or center of rotation. It becomes somewhat simpler after transformation to the principal axes of \mathbf{L} , whereupon Cruickshank's (1956*b*) picture of the foreshortening would again be seen to be directly applicable, but this is not required. His result for the foreshortening [Cruickshank, 1956*b*, equation (11)],

$$\frac{1}{2r} \left(\frac{s^2}{1+s^2/q^2} + \frac{t^2}{1+t^2/q^2} \right),$$

or his more general expression [Cruickshank, 1961, equation (10)], agrees with ours to the second order in small quantities (our λ_i^2 , and his s^2 and t^2) for large enough q in the cases with a well defined center of rotation and for the special orientations of coordinates to which the cited equation applies. Moreover, the denominators $(1+s^2/q^2)$ and $(1+t^2/q^2)$ clearly have the proper qualitative effect in reducing the shift of the Fourier maximum when the fundamental peak dispersion, q , is no longer large compared with s and t , and a center of rotation is defined by symmetry, but it is not clear whether corresponding general expressions can be found or whether the implied accuracy to orders higher than second is realizable. The changes in intramolecular distances derived here are at any rate only good to the second order.

For the average distance between two atoms in different molecules this formulation has nothing to say unless the cross-correlations of translation and libration between the two molecules are known. If it can be assumed that these cross-correlations vanish, it is best at the present level of approximation to calculate the average distance from the average interatomic vector and the two \mathbf{U} 's without regard to the rigid-body assumption. This gives

$$|\overline{\mathbf{p}}|^2 \dagger = |\overline{\mathbf{p}}|^2 + \frac{1}{2} \mathbf{U} : \delta / |\overline{\mathbf{p}}| + 0(\epsilon^3) \quad (23)$$

and

$$|\overline{\mathbf{p}}| = |\overline{\mathbf{p}}| + \frac{1}{2} \mathbf{U} : \delta / |\overline{\mathbf{p}}| - \frac{1}{2} \overline{\mathbf{p}} \cdot \mathbf{U} \cdot \overline{\mathbf{p}} / |\overline{\mathbf{p}}|^3 + 0(\epsilon^3), \quad (24)$$

where \mathbf{p} and \mathbf{U} are here to be interpreted as the vector $\mathbf{p}(j) - \mathbf{p}(i)$ from one atom to the other and the sum $\mathbf{U}(i) + \mathbf{U}(j)$ of their displacement tensors. Equation (23) is equivalent to the result for non-correlated motion given by Busing & Levy (1964).

Examples

The analysis described here has been programmed in FORTRAN IV and applied to a variety of data on an IBM 7094 computer. The program is available from the ACA library (No. 1). Our results on five molecules in four different structures include a comparison (Table 5) of Cruickshank's method and the present one for the two independent molecules of cyclopropanecarboxamide (CPCA) in the asymmetric unit of the monoclinic crystals of this extensively hydrogen-bonded substance (Long, Maddox & Trueblood, 1968); verification of independence of origin (Table 6), with data from the analysis of the structure of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (MMC) (Goldstein & Trueblood, 1967); and a comparison of the present method with that of Hirshfeld, Sandler & Schmidt (1963) for two fairly rigid hydrocarbon molecules (their analysis involved location of an assumed center of libration by an iterative least-squares process involving non-linear equations, as discussed above). Table 8 gives data on the origins defined by equations (16) and (17) and on the effective screw translations in the four crystal structures. Our present concern is to show the general features of the present treatment as compared with the earlier ones – the improvement in the fit of the \mathbf{U} 's, the lack of dependence of the derived motional parameters on the initial assumed origin, the sorts of variation in librational and translational tensors to be expected when one ignores the cross-tensor \mathbf{S} , and the magnitudes of typical displacements of the non-intersecting axes and the screw translations implied by the present treatment. Further discussion of possible interpretations of the relation of the individual results to the structural features of the corresponding crystals will be presented elsewhere.

The r.m.s. deviation of the observed U_{ij} from those calculated with the rigid-body parameters (corrected appropriately for the number of degrees of freedom) is given for each of the calculations reported in Tables 5, 6, and 7; it is evident that this parameter is smaller by a factor of two or more when the present method is used instead of Cruickshank's original method, and is also significantly smaller when the present method is compared with that of Hirshfeld *et al.* The data in Table 6 confirm that this measure of the fit of the model is independent of the origin chosen, even in such an extreme case. Our computer program does not yet include explicit provision for weighting the observational equations on the basis of the e.s.d.'s of the B_{ij} and we

do not yet have a proper error matrix for the components of **L**, **S**, and **T**, the axis displacements, *etc.*

The calculations reported for CPCA in Table 5 illustrate the sorts of deviations in the magnitudes and directions of the principal axes of **L** and **T** that may arise when Cruickshank's method is used and the origin is assumed to be at the center of mass. Since librational corrections to the apparent molecular geometry depend on **L**, the large errors possible in it can be particularly troublesome.

The values of **L** and **T** calculated by Cruickshank's method are markedly dependent on the origin chosen, as others (especially Pawley, 1963) have noted before. Both the magnitudes and directions of the principal

axes of the apparent **L** vary greatly (see the upper part of Table 6) when the origin is assumed to be far from the molecule. As is entirely reasonable, libration about the axis parallel to the 'vector of displacement' of the origin is then all that remains significant, since any appreciable needed rotation about any direction normal to this vector would be accompanied by a greatly exaggerated and unallowable translation of the molecule. (In the present method, **S** and **T** together compensate for this translational aspect of libration about a distant assumed origin.) Thus, the direction of the axis of maximum apparent libration reported in Table 6 shifted 74° to a position only 6° from the vector of displacement when Cruickshank's method was used,

Table 5. Comparison of some results for cyclopropanecarboxamide* in terms of the eigenvalues and eigenvectors of **L** and **T**

	Molecule A			Molecule B		
	Cr†	S & T†	Angular deviation‡	Cr†	S & T†	Angular deviation‡
$[\Sigma(\Delta U_{ij})^2/(n-s)]^\ddagger$	0.0088 Å ²	0.0020 Å ²		0.0101 Å ²	0.0030 Å ²	
L	51(°) ²	93(°) ²	39°	69(°) ²	92(°) ²	43°
	36	27	35	40	26	43
	17	14	45	9	14	3
T	0.046 Å ²	0.045 Å ²	49°	0.053 Å ²	0.053 Å ²	8°
	0.044	0.038	44	0.045	0.037	16
	0.036	0.031	37	0.032	0.032	13

* Two independent molecules in *P2₁/c* (Long, Maddox & Trueblood, 1968); for each molecule, the initial origin assumed in each calculation was at the center of mass.

† Cr means Cruickshank's (1956a) method was used; S & T means the present method was used. The **T** given for the latter is the *reduced* **T** of equation (20).

‡ Angular deviation of the directions of corresponding principal axes for the tensors determined by the two different methods.

Table 6. Effect of large displacement of initial origin on eigenvalues and eigenvectors for 1-methylamino-7-methylimino-1,3,5-cycloheptatriene*

	Initial origin at centroid	Initial origin 8.25 Å from centroid†	Angular deviation‡
Cruickshank's method			
L	16(°) ²	11(°) ²	74°
	14	1	22
	9	0	70
T	0.055 Å ²	0.065 Å ²	23°
	0.050	0.059	24
	0.041	0.032	14
$[\Sigma(\Delta U_{ij})^2/(n-s)]^\ddagger$	0.0058 Å ²	0.0109 Å ²	
Present method‡			
L	18(°) ²	18(°) ²	0°
	12	12	0
	10	10	0
T	0.054 Å ²	0.414 Å ²	67°
	0.049	0.276	77
	0.042	0.051	76
$[\Sigma(\Delta U_{ij})^2/(n-s)]^\ddagger$	0.0028 Å ²	0.0028 Å ²	

* One independent molecule in *Iba2* (Goldstein & Trueblood, 1967).

† The displacement was along the vector with direction cosines 0.656, 0.542, 0.526, just 6° from the direction of maximum libration as calculated by Cruickshank's method for the displaced origin, and only 2° from the direction of the minimum eigenvalue of the *unreduced* **T** calculated by the present method. See text.

‡ The **T** given is *unreduced*; the reduced **T** [equation (20)] was the same for each initial assumed origin, and had eigenvalues of 0.052, 0.048, and 0.042 Å². Its axes deviated an average of 5° from those calculated with the centroid origin by Cruickshank's method, and an average of 8° from those calculated with the centroid origin by the present method.

§ Angular deviation of the directions of corresponding principal axes for the tensors determined relative to the two different origins.

and the other two librational motions essentially vanished. T changed also, but considerably less. This is of course an exaggerated example, but it serves to illustrate the advantages of the present method of calculation. As the lower part of Table 6 shows, when L is properly calculated it is completely independent of the origin assumed initially, as are the reduced T of equation (20), the corresponding reduced S , the various quantities of Table 8, and (most important of all) the goodness of fit (Table 6). On the other hand, the unreduced T and S necessarily depend on the choice of origin, as indicated in the earlier discussion. For example (Table 6), two of the eigenvalues of T become very large when the origin is moved far away, and correspond to directions approximately normal to the vector of displacement; the third eigenvalue, more or less parallel to the vector of displacement (deviating by 2° in this example) remains small. The explanation is simple: because L (as well as the instantaneous motions

of which it is in principle composed) is independent of the origin, large values of S and T , corresponding to large translations of the origin strongly correlated with the rotations, are necessary to keep the atomic displacements reasonable by compensating for the translational (librational) aspect of the rotations. It is this strong dependence of S and T on initial choice of origin that makes desirable some sort of canonical reduction of S and T by means of a shift to a uniquely defined origin.

For the examples in Table 7, Hirshfeld's origin-refinement method did not yield good values for the libration tensor. Both the magnitudes and directions of the principal axes (and hence of any molecular geometry corrections dependent on them) vary appreciably from those obtained by the present method for benzo[*c*]phenanthrene, which is presumably a fairly rigid molecule and hence appropriate for the present analysis, perhaps more appropriate than cyclopropanecarbox-

Table 7. Some results for benzo[*c*]phenanthrene (BPh) and 1,12-dimethylbenzo[*c*]phenanthrene (DMBPh)*

	BPh			DMBPh		
	Present method	HSS	Angular deviation	Present method	HSS	Angular deviation
L	17.4(°) ² 7.4 5.2	12.7(°) ² 6.8 1.6	39° 83 85	5.3(°) ² 1.5 1.3	5.4(°) ² -0.3 1.4	11° 11 (0)
T	0.041 Å ² 0.032 0.025	0.040 Å ² 0.033 0.026	7° 13 13	0.0102 Å ² 0.0086 0.0076	0.0105 Å ² 0.0078 0.0083	2° (0) 2
$[\Sigma(AU_{ij})^2/(n-s)]^\ddagger$	0.0030 Å ²	0.0058 Å ²		0.0021 Å ²	0.0024 Å ² †	

* Eigenvalues and deviations of eigenvectors as in Table 5. BPh has one independent molecule in $P2_12_12_1$; DMBPh lies on a twofold axis (parallel to L_3 and T_2) in $Pban$. These hydrocarbons were studied by Hirshfeld, Sandler & Schmidt (1963) (HSS), whose results were obtained by refining a 'center of libration' (see also Table 8). The dimethyl derivative was analyzed at about 80°K. The T given for the present method is the reduced T of equation (20).

† The fit of the dimethyl compound by HSS omitted the two methyl groups because they appeared to give wide discrepancies; our analysis included all atoms, and the fit was not significantly worse for the methyls than for some of the other atoms.

Table 8. Symmetrizing origins, coordinates of displaced axes, and effective screw translations* (Å)

	CPCA Molecule A	CPCA Molecule B	MMC	BPh†	DMBPh†
Q_1	-0.70	-0.72	0.38	0.88 (0.87)	0
Q_2	0.28	-0.25	0.33	-0.15 (-0.37)	0
Q_3	0.11	0.07	-0.12	0.36 (1.13)	0.43 (0.72)
2Q_1	-0.50	-0.80	0.42	0.78	0
3Q_1	-1.07	-0.59	0.33	1.03	0
1Q_2	0.33	-0.23	0.52	-0.10	0
3Q_2	-0.05	-0.35	-0.04	-0.33	0
1Q_3	0.14	-0.02	0.08	0.13	0.82
2Q_3	0.02	0.35	-0.42	0.92	-0.91
$\sigma_1(L_{11})^\ddagger$	-0.022	-0.036	0.005	0.051	0.021
$\sigma_2(L_{22})^\ddagger$	0.028	0.025	0.002	-0.066	0.011
$\sigma_3(L_{33})^\ddagger$	0.018	0.057	-0.009	-0.014	-0.054

* See equations (16) and (17) and Fig. 2. The molecules are those of Tables 5, 6, and 7. Coordinates are expressed relative to the center of mass (for MMC, the centroid) parallel to the principal axes of L . The effective screw translation is, as indicated, the screw pitch times the r.m.s. libration amplitude about the corresponding axis.

† The values in parentheses are those given by Hirshfeld, Sandler & Schmidt for their effective center of libration, transformed to the present axial system.

amide (which may have appreciable internal libration about the bond to the amide group). Hirshfeld's results for the 1,12-dimethyl derivative show smaller deviations, in part because the molecule lies in a special position (on a twofold axis), but they include a negative eigenvalue of the libration tensor that is eliminated in the present analysis. On the other hand, his \mathbf{T} values agree quite well with ours.

In Table 8, the coordinates of the origin that symmetrizes \mathbf{S} for each molecule [equation (16)] and the coordinates of the displaced (non-intersecting) axes [equation (17) and Fig.2] in the preferred alternative description of the motion have been expressed as displacements from the centers of mass (or, for MMC, the centroid) of the molecules. These displacements approach 1 Å for each of the independent molecules of CPCA and, gratifyingly, for each molecule, the displacement is toward the amide group. In this structure each molecule is involved in four hydrogen bonds; interestingly, the \mathbf{L} tensors are closely similar for the two molecules, and the axis of maximum libration for each is approximately parallel to a N-H...O hydrogen bond from the molecule to a neighbor (of the other type).

The displacements of the non-intersecting axes from one another, illustrated in Fig.2, may be calculated (for axes I and J) by taking the differences (${}^I Q_K - {}^J Q_K$) in Table 8. They vary from 0.09 to 1.73 Å, the latter value being for the only non-intersecting pair of axes (C_2 , Table 4) in 1,12-dimethylbenzo[*c*]phenanthrene. The upper lines of Table 8 permit also a comparison of the position of the origin that symmetrizes \mathbf{S} with the origin found by Hirshfeld; for each of the four coordinates not fixed by symmetry, the displacement from the center of mass has the same sign for each method of analysis, and indeed some of the magnitudes are quite similar too, although of course no exact correspondence is to be expected.

Table 8 also lists for each of the molecules what we have termed the effective screw translations, *i.e.* the products of the screw pitches σ_i with the r.m.s. amplitudes of libration about the corresponding axes. These values are appreciably smaller for MMC, for which (among these molecules) the Cruickshank treatment is more nearly applicable. However, it must be remembered that the individual screw pitches (and hence these effective screw translations) are arbitrary because the trace of \mathbf{S} is arbitrary; the values we have given here correspond to our choice of the constraint $\text{Tr}(\mathbf{S})=0$.

The development of this analysis was greatly facilitated by the computer tests made possible by the generous cooperation of the U.C.L.A. Computing Facility and the Union Carbide Computing Center in New York. The computing program used is an extensive modification of one based on Cruickshank's treatment that was originally written by P.K. Gantzel and C.L. Coulter. Robert Long assisted us in the computer tests. The illustrations were prepared by Maryellin Reinecke.

Appendix

Most of our symbols and conventions are listed here; a few have been omitted which appear only once and are defined in the text as they occur. Explanations of many of the symbols and conventions are given in the text; they are referred to here by citing the equation nearest to the appropriate discussion or definition.

Conventions

Transformation matrices are in plain roman.

Vectors are in **boldface**, generally lower case (exception ${}^J\mathbf{R}$).

Tensors of second and higher rank are in **BOLD-FACE**, generally upper case (exceptions δ, \mathbf{e}). For tensors of rank 2 boldface has usually been retained also for the *matrix* of the tensor, as in (2), for $\text{Tr}(\mathbf{S})$, *etc.*

Summation is assumed for *repeated lower case* indices, (3a).

Double scalar products, signified by \cdot , are used in the sense originally defined by Gibbs (Drew, 1961), *e.g.*,

$$\mathbf{a}\mathbf{b} : \mathbf{c}\mathbf{d} \equiv a_i b_j c_i d_j \text{ and } (\mathbf{a}\mathbf{b} : \mathbf{c}\mathbf{d})_{im} \equiv a_i b_j c_j d_{km}, \quad (8)$$

These products are by no means always associative; hence the parentheses in (12), for example. The Gibbs rule for multiple scalar products is simply to affix as many dummy indices on each side of the sign ($\cdot, \cdot, \cdot, \cdot$, *etc.*) as there are dots in it, skipping no positions except by reason of a prior assignment (and parenthesis), and ordering the dummy indices in the same left-to-right sequence on each side. In the alternative common ('nesting') convention, the ordering of the dummy indices is opposed on the two sides of the sign, right-to-left on the left and left-to-right on the right. This convention could just as well have been used here and might have offered some extra convenience.

Superscripts

' indicates transpose, thus: $A_{jk} = A'_{kj}$, (3).

0 indicates the value after shift to new origin, *e.g.* \mathbf{T}^0 , (8).

r indicates 'reduced' quantity, *e.g.* ${}^r\mathbf{T}$, (20).

\wedge indicates the value after the transformation implied in the context, *e.g.* $\hat{\mathbf{S}}$.

Symbols for quantities

α, β, γ See λ below.

a, b, c See \mathbf{t} below.

\mathbf{A} See (6).

\mathbf{B} See (6).

\mathbf{D} See (1), (2), (3).

δ The unit tensor of second rank (δ_{ij} is the Kronecker delta), (3a).

Δ Indicates small variation in a quantity in (14); ΔU_{ij} in Tables 5, 6, and 7 means the difference of the experimentally derived U_{ij} and those calculated from rigid-body parameters.

- e** The Cartesian permutation tensor, with components e_{ijk} , (3a).
- ε See $0(\varepsilon^n)$ below.
- G** See (7).
- H** See (7).
- $i, j, k, l, m; I, J, K$: Indices, usually used to designate different mutually orthogonal directions.
- L** The libration tensor (Cruickshank's ω).
- λ The general rotation vector (1) of magnitude λ , with components represented as $\lambda_1, \lambda_2, \lambda_3$ or, in (2) and Table 1 only, α, β, γ .
- $0(\varepsilon^n)$ means terms of the order of ε^n as ε approaches zero, (2), (21).
- p** Instantaneous position vector of an atom.
- P, Q** Transformation matrices.
- r** The position vector of an atom relative to an arbitrary molecule-fixed origin, with components represented as r_1, r_2, r_3 or x, y, z , (1), (7).
- g** An origin-shift vector, (8).
- ${}^J Q_I$ Displacement of axis J parallel to axis I ; see (17) and Fig. 2.
- ${}^J R$ New position vector of an atom after the axis shifts in the displaced-axes description, with components represented as ${}^J R_I$ or ${}^J X, {}^J Y, {}^J Z$. See (17) and Fig. 2.
- S** The tensor of correlation of translation and rotation, (6).
- S_a, S_s The antisymmetric and symmetric parts of S ; see the section on site symmetry.
- ${}^J S_{JK}$ is the value of S_{JK} after the displacement of axis J , and equals zero if (17) is used.
- σ_I The screw pitch along axis I , defined shortly after (20).
- T** The translation tensor, (6).
- ${}^r T$ The reduced translation tensor of (20).
- t** The general translation vector (6), with components represented as t_1, t_2, t_3 or, in Table 1 only, a, b, c .
- $\text{Tr}(\mathbf{X}) \equiv X_{ii} \equiv \mathbf{X} : \delta$, the trace (sum of diagonal elements) of \mathbf{X} .
- U** The mean-square displacement tensor for an atom.
- u** The instantaneous displacement of an atom (as a consequence of molecular motion).
- x, y, z See **r** above.
- X, Y, Z See ${}^J R$ above.

Use of general axes

The formal analysis looks almost the same if the usual crystallographic axes \mathbf{a}_i and reciprocal axes \mathbf{a}^i are used instead of ordinary Cartesians: one only maintains the general tensorial distinction between contravariant and covariant components, which is unnecessary in Cartesian tensor algebra, and replaces e_{ijk} by $\varepsilon_{ijk} = e_{ijk}/g$ and $\varepsilon^{ijk} = e_{ijk}/g$, where g is the determinant of the matrix of covariant components $g_{ij} \equiv \mathbf{a}_i \cdot \mathbf{a}_j$ of the metric tensor; cf. e.g. Block (1962), McConnell (1957), or Spain (1956). However, in order to write observation

equations, the \mathbf{U} 's, which have ordinarily been obtained as contravariant components in the Debye temperature factor $\exp(-M) = \exp(-2\pi^2 \mathbf{U} : \mathbf{h}\mathbf{h}) \equiv \exp(-2\pi^2 U^{ij} h_i h_j)$, would have to be re-expressed in covariant components by means of $U_{ij} = g_{ik} g_{jl} U^{kl}$ or $\lambda, \mathbf{r}, \mathbf{L}, \mathbf{S}$, and \mathbf{T} would have to be expressed in covariant rather than contravariant components or the simple representation of the permutation tensor as ε^{ijk} or ε_{ijk} would have to be replaced in the calculation by the more complicated $\varepsilon_{jk}^i = g_{jl} g_{km} \varepsilon^{ilm} = g^{il} \varepsilon_{ijk}$. At the same time the eigenvalue and eigenvector subroutines would also become more complicated, corresponding for example to the equations

$$\mathbf{L} \cdot \mathbf{x} = l\mathbf{x}$$

with components

$$L_{ij} x^j = l g_{ij} x^j,$$

and

$$|L_{ij} - l g_{ij}| = 0,$$

instead of the Cartesian

$$\mathbf{L} \cdot \mathbf{x} = l\mathbf{x}, \quad L_{ij} x_j = l x_j \quad \text{and} \quad |L_{ij} - l \delta_{ij}| = 0.$$

Equation (22) for the foreshortening correction still holds if \mathbf{p} and \mathbf{L} are appropriately expressed, in contravariant and covariant components respectively (or *vice versa*), but again it is not clear that it isn't better just to use Cartesian coordinates.

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