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## Rigid-body vibrations in non-orthogonal systems.

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Cruickshank's (1956*b*) treatment of molecular rigid-body vibrations has been extended by Pawley (1964) to permit the direct least-squares refinement of the molecular translation and libration tensors **T** and **ω** from the diffraction data without prior evaluation of the atomic vibration tensors **U**. Pawley's equations, while applicable to any crystal system, require that **T** and **ω** be referred to orthogonal coordinate axes. Transformation to such an axial system may often be instructive for the interpretation of the results but its introduction in the refinement equations seems needlessly cumbersome. The relevant considerations are most conveniently stated in tensor notation (see, *e.g.* Patterson, 1959).

The symmetric tensor **U** specifying an atom's harmonic vibration amplitudes manifests itself in diffraction measurements by way of the temperature factor

$$q(\mathbf{s}) = \exp -2\pi^2 s_i U^{ij} s_j \tag{1}$$

(Cruickshank, 1956*a*), where $\mathbf{s} = [s_1\ s_2\ s_3]$ is the reciprocal-lattice vector. Since **s** is generally defined by its covariant components $h, k, l$ with respect to the crystal axes $\mathbf{a}_i$ measurement of $q(\mathbf{s})$ naturally leads to a determination of the contravariant components $U^{ij}$ of **U** in this same axial system. In Cruickshank's notation these are $(1+\delta_{ij})b_{ij}/4\pi^2$. Cruickshank, however, implicitly introduces a set of dimensionless (though not generally unit-length) axes

$$\alpha_k = \mathbf{a}_i A^i_k ,$$

where $\mathbf{a}_i$ are the crystal axes and $[A^i_k]$ is the diagonal matrix

$$[A^i_k] = \begin{bmatrix} a^* & 0 & 0 \\ 0 & b^* & 0 \\ 0 & 0 & c^* \end{bmatrix} .$$

These axes $\alpha_k$ are reciprocal to the unit reciprocal vectors $\hat{\mathbf{a}}^i = \hat{\mathbf{a}}^*, \hat{\mathbf{b}}^*, \hat{\mathbf{c}}^*$. It is in this coordinate system that the vibration tensor has the contravariant components designated by Cruickshank (1956*a*) as $U_{ij}$ (but in tensor notation properly written $U^{ij}$). This axial system has the virtue of giving the mean square vibration amplitude in the direction of a unit vector $\hat{\mathbf{l}}$ the simple expression

$$\overline{u^2}_{\hat{\mathbf{l}}} = l_i U^{ij} l_j ,$$

where $l_i$ are the covariant components of $\hat{\mathbf{l}}$, *i.e.*

$$\hat{\mathbf{l}} = l_i \hat{\mathbf{a}}^i .$$

In particular, the diagonal components $U^{ii}$ are just the mean square displacements parallel to the reciprocal axes $\mathbf{a}^i$. In this coordinate system the reciprocal-lattice coordinates $s_i$ appearing in (1) are

$$s_i = ha^*, kb^*, lc^* .$$

For a rigid molecule undergoing small harmonic translational and librational oscillations, Cruickshank (1956*b*) has given the relation between the atomic vibration tensors **U** and the molecular tensors **T** and **ω** when all are referred to an orthonormal coordinate system. His equations (2,3) have the matrix formulation

$$[U] = [T] + [R]\ [\omega]\ [\tilde{R}] , \tag{2}$$

in which, for an atom at position $\mathbf{r} = [\lambda\,\mu\,\nu]$ relative to the center of molecular libration, $[R]$ is the antisymmetric matrix

$$[R] = \begin{bmatrix} 0 & -\nu & \mu \\ \nu & 0 & -\lambda \\ -\mu & \lambda & 0 \end{bmatrix} .$$

We can convert equation (2) into a tensor equation, valid in any coordinate system, by writing, for example,

$$U^{ij} = T^{ij} + R^{ik}\omega_{kl}R^{jl} , \tag{3}$$

which contains the contravariant components of **U** and **T** and the covariant components of **ω**. To obtain $R^{ik}$ from the components of **r** we first introduce the metric tensor $G_{ij} = \mathbf{a}_i \,.\, \mathbf{a}_j$ (if we are working in the crystal axial system $\mathbf{a}_i$; otherwise the appropriate metric tensor is defined analogously). Letting $g$ represent the determinant of the matrix $[G_{ij}]$, we define

$$[R^{ij}] = g^{-\frac{1}{2}} \begin{vmatrix} 0 & -\lambda_3 & \lambda_2 \\ \lambda_3 & 0 & -\lambda_1 \\ -\lambda_2 & \lambda_1 & 0 \end{vmatrix} ;$$

in this expression $\lambda_k = \lambda^i G_{ik}$ are the covariant components of **r**, whose contravariant components are $\lambda^i = x^i - \xi^i$, where $x^i$ and $\xi^i$ are, respectively, the ordinary contravariant coordinates of the atom and of the libration center.

Equation (3) can be readily differentiated with respect to the rigid-body parameters $T^{ij}$, $\omega_{ij}$, and $\xi^i$ to permit the least-squares derivation of these parameters from the previously obtained atomic $U^{ij}$. (Note that for $k \neq l$ we must add the derivatives with respect to $\omega_{kl}$ and $\omega_{lk}$ since these are a single variable). Such a treatment, taking explicit account of the covariance matrix of the several components $U^{ij}$ of each atom, as estimated during the prior refinement of the structural parameters from the diffraction data, has been programmed in FORTRAN and successfully run on a Control Data Corporation 1604A computer.

As an alternative to this two-stage procedure, we can substitute equation (3) into (1) and this into the standard formula for the structure factor $F$, thereby obtaining an expression analogous to Pawley's equation (1) but lacking his transformation matrix $[A^{-1}]$ that converts from orthonormal to crystal axes. This expression,

$$F(\mathbf{s}) = c \sum_{\text{atom}} f \exp(2\pi i s_i x^i) \exp\left[-2\pi^2 s_i (T^{ij} + R^{ik}\omega_{kl}R^{jl}) s_j\right] ,$$

can be differentiated with respect to the rigid-body parameters, allowing these to be refined directly from the diffraction data. In fact this simply means evaluating derivatives of $F(\mathbf{s})$ with respect to the several $U^{ij}$ and from these, *via* multiplication by the derivatives of equation (3) and summation, obtaining the derivatives of $F(\mathbf{s})$ with respect to the rigid-body parameters. This one-stage procedure has been embodied in a FORTRAN least-squares program that allows some or all of the atoms in the asymmetric unit to be regarded as constituting one or more rigid units, while others may be allowed to vibrate independently. The T and ω tensors of the several rigid units are refined directly, as in Pawley's method, along with the usual coordinates, occupancy factors, *etc.* Experience suggests that this one-stage procedure may be highly advantageous, especially in rate of convergence, provided the molecules are sufficiently rigid and the $f$ curves used (for X-ray data) represent the stationary-atom electron densities to the required accuracy. When these conditions are not met, the two-stage procedure, or a comparison of the two, may help to reveal inadequacies of the model, due to internal vibrations, charge polarization, altered hybridization, *etc.*, more readily than extensive difference syntheses.

The tensor formulation is also useful for evaluation of the libration corrections to the atomic coordinates. Assuming for simplicity that our refinement procedure has located the centroids of the atomic peaks rather than their maxima (either assumption is an approximation requiring justification in particular circumstances), we may, for the present argument, disregard the factor $D(a\varphi)$ in Cruickshank's (1961) equation (6) and obtain from his equations (10) the matrix equation for the coordinate shifts, in an orthonormal system,

$$-[\varepsilon_\lambda \varepsilon_\mu \varepsilon_\nu] = \tfrac{1}{2}\{t[\lambda\mu\nu] - [\lambda\mu\nu][\omega]\}\ ,$$

where $t$ is the trace of $[\omega]$. The tensor analog of this equation, valid in any coordinate system, gives the corrected atomic coordinates

$$\lambda^k - \varepsilon^k = (1 + \tfrac{1}{2}t)\lambda^k - \tfrac{1}{2}\lambda^i\omega_i^k\ .$$

Here, $\lambda^k$ are the uncorrected coordinates, measured from the center of libration; the mixed covariant-contravariant components of ω may be evaluated as

$$\omega_i^k = \omega_{ij}G^{jk}\ ,$$

where the matrix $[G^{jk}]$ is inverse to $[G_{ij}]$; and the trace

$$t = \sum_i \omega_i{}^i$$

is invariant under all coordinate transformations.

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# The anisotropic temperature factor of atoms in special positions.

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In this paper a table of symmetry restrictions on anisotropic temperature factor parameters for all special positions of the 230 space groups is presented. The text explains the table and describes the computer program which was used to derive it. The relationships between the various restricted forms are displayed diagrammatically. No recommendations for the method of programming these restrictions in least-squares refinement are included.

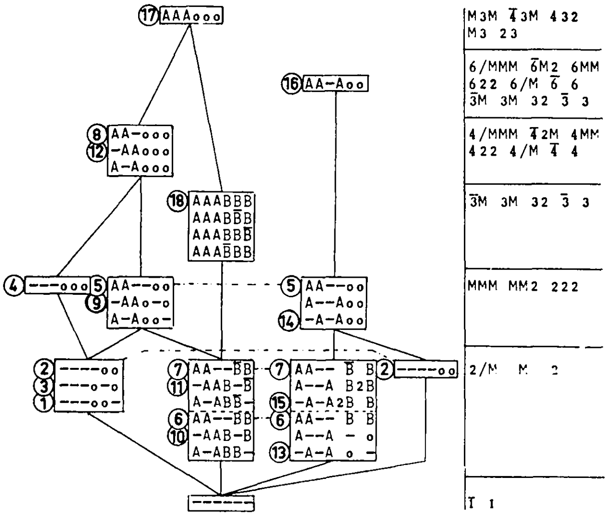

Fig. 1. Symmetry-imposed $\beta$-restrictions for all special positions.

The anisotropic atomic temperature factor may be defined as $\exp\,[-(\sum_{i=1}^{3}\sum_{j=1}^{3} h_ih_j\beta_{ij})]$. The $\beta_{ij}$ are the 9 contravariant components of a symmetric second-order tensor (Levy, 1956), while $h_i$ is the $i$th index of a reflexion $hkl$. Terms with $i \neq j$ may be combined two by two: $h_ih_j\beta_{ij} + h_jh_i\beta_{ji} = 2h_ih_j\beta_{ij}$,

Table 1. *The* 18 *β-restrictions that occur when only the first atom of an equivalent set given by Vol.*I *of* International Tables *is considered*

| I | B11 | B22 | B33 | 2B12 | 2B23 | 2B13 |
|---|---|---|---|---|---|---|
| 1 | | | | o | o | |
| 2 | | | | | o | o |
| 3 | | | | o | | o |
| 4 | | | | o | o | o |
| 5 | A | A | | | o | o |
| 6 | A | A | | | B | B |
| 7 | A | A | | | −B | B |
| 8 | A | A | | o | o | o |
| 9 | | A | A | o | | o |
| 10 | | A | A | B | | B |
| 11 | | A | A | −B | | B |
| 12 | | A | A | o | o | o |
| 13 | | A | | A | o | |
| 14 | | A | | A | o | o |
| 15 | | A | | A | 2B | B |
| 16 | A | A | | A | o | o |
| 17 | A | A | A | o | o | o |
| 18 | A | A | A | B | B | B |