reciprocal axes. Hence for special positions the restrictions which are valid for the components of **b** are equally valid for the components of **U** referred to either crystal or reciprocal axes. .

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On the refinement of thermal rigid-body vibration tensors.

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Cruickshank (1956) – here referred to as CK – was the first to propose a procedure for the refinement of rigid-body vibration tensors. These are obtained in a least-squares procedure, in which the vibration tensors of the individual atoms are used as data. These tensors in turn have been obtained from a normal refinement with diffraction data. Recently Pawley (1964) – here referred to as PA – described a least-squares method for refining rigid-body tensors by making direct use of diffraction data. The question arises whether or not the two approaches yield the same results. It turns out that this is true only under certain conditions, which will be determined in this paper. This provides a theoretical foundation for the setting of weights in CK's determination of rigid-body tensors.

For n atoms in the molecule assumed to be rigid, CK equation (2·3) may be written in matrix notation as

$$\mathbf{U}=\mathbf{R}\mathbf{T}\,, \tag{1}$$

where **U** represents the $6n$ components of the n atomic tensors, **T** the 12 components of CK's molecular tensors **T** and $\boldsymbol{\omega}$. **R** is a $6n\times 12$-matrix with the coefficients of CK (2·3). If the increments ε_U and ε_T of **U** and **T** are substituted in (1), then CK's normal equations (2·5) may be written as

$$\overline{\mathbf{R}}\mathbf{P}\mathbf{R}\varepsilon_T=\overline{\mathbf{R}}\mathbf{P}\varepsilon_U{}^{\text{obs}}\,. \tag{2}$$

P is a $6n\times 6n$ weighting matrix, $\overline{\mathbf{R}}$ the transpose of **R**. Let

$$\mathbf{M}\varepsilon_U{}^{\text{obs}}=\mathbf{N} \tag{3}$$

be the normal equations for determining $\varepsilon_U{}^{\text{obs}}$, then PA's approach can be shown to have the normal equations

$$\overline{\mathbf{R}}\mathbf{M}\mathbf{R}\varepsilon_T=\overline{\mathbf{R}}\mathbf{N}\,. \tag{4}$$

If we now introduce $\varepsilon_U{}^{\text{obs}}=\mathbf{M}^{-1}\mathbf{N}$ in (2), comparison of (2) and (4) shows that these equations are equivalent only if $\mathbf{P}=\mathbf{M}$. Thus CK's and PA's approaches are equivalent, if **M** of the last cycle of structure-factor refinement is chosen to be the weighting matrix. **M** is proportional to the inverse of the covariance matrix of the thermal parameters of the individual atoms, which in turn is obtained from the covariance matrix of the intensity data. Hence the use of **M** as weighting matrix is in accordance with the Gaussian law of setting weights.

The use of **M** as weighting matrix greatly increases the amount of computation necessary in CK's determination of rigid-body tensors. Furthermore, **M** is usually not available, because structure-factor refinement is usually carried out with respect to atomic vibration tensors, which are referred to the reciprocal axes of the crystal system rather than to the molecular axes. Thus we shall now derive a simple but sufficient approximation **Q** which may be used instead of **M** in all practical work.

At first we assume that the Cartesian coordinate system of the molecule coincides in direction with the (orthogonal) crystal system. The results obtained with this assumption will be generalized below. The elements of **M** are

$$M^r_{st}=\Sigma w\,\frac{\partial|F|}{\partial U^r_s}\,\frac{\partial|F|}{\partial U^r_t}\,, \tag{5}$$

w being the weights of the experimental data, F the structure factor. r denotes the atom, $s,\ t=1\ldots6$ the independent components of $\mathbf{U}^r$. We now use unitary form factors $\hat{f}$ for all atoms, given by $f_r=\hat{f}Z_r$, where Z_r is the number of electrons in the rth atom. Let G_r be the geometrical structure-factor term, and $V_s=S_iS_k$ with subscript $s=s(i,k)$ for the elements of $\mathbf{U}^r$ in the sequence 11, 22, 33, 12, 13, 23, and let S_i be the ith component in reciprocal space (in Å^{-1}) of the reflexion considered, then

$$M^r_{st}\simeq 4\pi^4Z^2_r\Sigma w\hat{f}^2\exp\left(-2\overline{\mathbf{h}}\boldsymbol{\beta}_r\mathbf{h}\right)G^2_rV_sV_t\,. \tag{6}$$

h is a 3×1-column matrix of the Miller indices, $\boldsymbol{\beta}_r$ the anisotropic parameter matrix. If one of the indices s or t is >3, a factor of 2 enters on the right-hand side of (6) owing to the symmetry of $\mathbf{U}^r$. For $s>3$, $t>3$ the factor is 4. These factors will be introduced into the final result. We now assume that the data have been obtained with equal quality in each spherical shell of the reciprocal space and that their number is infinite in a finite region. Furthermore, the temperature factor is assumed to be isotropic. Also some mean value G^2_{sh} of G^2_r, assumed to be the same for each atom, is constant for integration over the shell. (These approximations have also been used by Scheringer (1965) to derive an approximate matrix for positional parameters.) With these approximations the factors $4\pi^4$, w, $\hat{f}^2$, $\exp\left(-2\overline{\mathbf{h}}\boldsymbol{\beta}_r\mathbf{h}\right)$ and

G^2_{sh} will form a constant C_{sh} for an infinitesimal spherical shell in reciprocal space. Then (6) becomes

$$M^r_{st} \simeq Z^2_r \int_{sphere} C_{sh} \int_{shell} V_s V_t \,. \tag{7}$$

$|S|$ is constant for a given shell, and we can write $S_i = |S| \cos \varphi$, $S_k = |S| \sin \varphi$ for an orthogonal coordinate system. Now integration of the various products $V_s V_t$ over the shell leads to the integrals

$$\int_0^{2\pi} \cos^p\varphi \sin^q\varphi \, d\varphi$$

with $p, q = 0, 1, 2, 3, 4$, and $p+q=4$, and to the integral with $p=q=1$. (The integrals are known in terms of Γ-functions.) These integrals are the same for each shell considered and are denoted by q_{st}. Then (7) becomes

$$M^r_{st} \simeq C Z^2_r q_{st} \,.$$

C represents the integral over all shells in reciprocal space and includes all constant factors which arise on integration over the shell. For an infinite number of data C approaches infinity, and so does M^r_{st}. For establishing the weighting matrix, however, only the ratio M^r_{st}/C will be needed. If we now consider all atoms ($r = 1 \ldots n$), the approximate matrix $\mathbf{Q}$ becomes a block-diagonal matrix because of non-squared geometrical terms. With the introduction of the factor of 4 the rth block is then

$$\mathbf{Q}^r = Z^2_r \begin{pmatrix} 3 & 1 & 1 & & & \\ 1 & 3 & 1 & & & \\ 1 & 1 & 3 & & & \\ & & & 4 & & \\ & & & & 4 & \\ & & & & & 4 \end{pmatrix} . \tag{8}$$

We now eliminate the initial restriction that the coordinate system of the molecule coincides with the crystal system, but still retain orthogonality. Then the reference system in the spherical shell is rotated, but as integration is carried out over the whole shell, the integrals remain unchanged. Hence (8) holds for any orthogonal system to which the $\mathbf{U}^r$-tensors are referred. Thus $\mathbf{Q}^r$ should be used as weighting matrix for the rth atom.

Equation (8) no longer holds when the $\mathbf{U}^r$-tensors refer to oblique crystal axes. We can derive (8) for this case by making use of the requirement that, with a non-orthogonal transformation w.r.t. unit axes $\mathbf{Q}$ and $\mathbf{M}$ have to be equally transformed. Let this transformation be

$$\mathbf{X}_C = \mathbf{A}\mathbf{X}_S$$

for the components of $\mathbf{X}$ in Å (C denotes the oblique, S the orthogonal (standard) crystal system); then $\mathbf{M}$ is transformed according to

$$\mathbf{M}_C = \overline{\mathbf{L}}^{-1} \mathbf{M}_S \mathbf{L}^{-1} \,, \tag{9}$$

where $\mathbf{L}$ is a 6×6 matrix derived from the 9×9 Kronecker-product $\mathbf{A} \times \mathbf{A}$. The elements of $\mathbf{L}$ are

$$L_{uv} = A_{il}A_{kl} \quad \text{for} \quad u = u(i,k),\ v = v(l,l)$$

and

$$L_{uv} = A_{il}A_{km} + A_{im}A_{kl} \quad \text{for} \quad v = v(l,m)$$

with $u, v = 1 \ldots 6$. $\mathbf{Q}_C$ is obtained from $\mathbf{Q}_S$ by substituting $\mathbf{Q}$ for $\mathbf{M}$ in (9).

If the appropriate weights are used in CK's method, CK's and PA's approaches are equivalent with respect to the use of diffraction data, and thus with respect to minimizing standard deviations. From the computational point of view PA's approach is certainly advantageous: the number of parameters to be refined and thus the number of normal equations to be set up is reduced to the minimum possible (see also Pawley, 1965). CK's approach, however, allows a number of tests to be made with the use of the atomic vibration tensors, of which PA's approach is inherently incapable.

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Unit-cell parameters and space group of molybdenyl(VI) acetylacetonate.

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The yellow crystals of molybdenyl(VI) acetylacetonate (Fernelius, Terada & Bryant, 1960) suitable for crystallographic measurements were obtained from an acetylacetone solution to which petroleum spirit had been added without mixing and left over several days at room temperature. The prism-shaped crystals have a great number of faces which are found by goniometric measurements to be related through a centre of symmetry. The smallest unit cell, found from oscillation and Weissenberg photographs taken with nickel-filtered Cu K radiation, has the dimensions

$$a = 8{\cdot}19 \pm 0{\cdot}02, \quad b = 12{\cdot}50 \pm 0{\cdot}02, \quad c = 12{\cdot}76 \pm 0{\cdot}02 \text{ Å};$$
$$\alpha = 104{\cdot}2 \pm 0{\cdot}2^\circ \quad \beta = 82{\cdot}3 \pm 0{\cdot}2^\circ \quad \gamma = 92{\cdot}4 \pm 0{\cdot}2^\circ$$

and contains four formula units of $MoO_2(C_5H_7O_2)_2$ ($\varrho_{calc} = 1{\cdot}71$ g.cm^{-3}, $\varrho_{obs} = 1{\cdot}79$ g.cm^{-3}). No conditions limiting possible reflexions were found. The goniometric measurements strongly indicated the pinacoidal class; the space group is $P\bar{1}$ (C^1_i, No.2).

We do not intend to proceed with the crystal-structure analysis of this compound. We are indebted to the Rudjer Bošković Institute, Zagreb for experimental facilities.

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