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On the isotropic temperature factor equivalent to a given anisotropic temperature factor.†

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In view of the current trend toward routine determination of anisotropic temperature factors in crystal structure analyses, it seems worthwhile to define an isotropic temperature factor which we shall call *equivalent* to the anisotropic components. There are a number of situations where such a definition may be convenient. If anisotropic temperature factors have been determined and the deviations from isotropy do not appear to be significant or seem physically unrealistic, it would seem wise to include in the report of such an investigation the values of the equivalent isotropic B's. Furthermore, a more rapid comparison can be made between the temperature factors for different projections of the same structure or for different structures if the equivalent B's are given. In the author's experience, occasion has also arisen to change from anisotropic refinement to isotropic refinement when it appears that the data is not sufficient to determine meaningful anisotropic values. Provision can be made to include such a change automatically during the course of a least-squares refinement by an electronic computer.

Matrix notation provides a concise and elegant presentation of the desired results. We define the following matrices (the primes denote transposes):

$$\mathbf{X}' \equiv (x_1 x_2 x_3)\ , \tag{1}$$

a vector with components referred to the cell axes

$$\mathbf{A}' \equiv (\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3)\ . \tag{2}$$

The vector in direct space defined by $\mathbf{X}'$ is then given by

$$\mathbf{X}'\mathbf{A} \equiv x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3\ . \tag{3}$$

Further

$$\mathbf{S}' \equiv (2\pi h\ 2\pi k\ 2\pi l) \tag{4}$$

is a vector with components along the reciprocal axes $\mathbf{A}^*$ with $\mathbf{A}^*$ defined by

$$\mathbf{A}^*\mathbf{A}' \equiv I\ . \tag{5}$$ ‡

It may be shown (Busing & Levy, 1958) that

$$(\mathbf{A}\mathbf{A}')^{-1} = \mathbf{A}^*\mathbf{A}^{*\prime}, \tag{6}$$

a result which will be used below.

It has been shown (Cochran, 1954)§ that if the thermal motion of an atom is described by

$$p(\mathbf{X}) = |\mathbf{M}|^{1/2}\pi^{-3/2}\exp\left(-\mathbf{X}'\mathbf{M}\mathbf{X}\right) \tag{7}$$

then the scattering factor must be multiplied by

$$t(\mathbf{S}) = \exp\left[-\mathbf{S}'\mathbf{B}\mathbf{S}\right] \tag{8}$$

with the *temperature factor* matrix $\mathbf{B}$ defined by†

$$\mathbf{B} \equiv \tfrac{1}{4}\mathbf{M}^{-1}. \tag{9}$$

It may be shown (Waser, 1955) by a transformation to orthogonal axes and integration that the mean value of r^2 is given by

$$\langle r^2\rangle \equiv \langle \mathbf{X}'\mathbf{A}\mathbf{A}'\mathbf{X}\rangle = 2Tr(\mathbf{B}\mathbf{A}\mathbf{A}')\ . \tag{10}$$

But this may be shown to be equivalent to

$$\langle r^2\rangle = 2\mathbf{A}'\mathbf{B}\mathbf{A}\ . \tag{10a}$$

Now for isotropy of thermal motion we know that

$$t(\mathbf{S}) = \exp\left[-B\sin^2\theta/\lambda^2\right] \tag{11}$$

$$= \exp\left[-\frac{B}{16\pi^2}\mathbf{S}'(\mathbf{A}\mathbf{A}')^{-1}\mathbf{S}\right] \tag{11a}$$

i.e.

$$\mathbf{B}_{\text{isotropic}} = \frac{B}{16\pi^2}(\mathbf{A}\mathbf{A}')^{-1}\ . \tag{12}$$

Given an anisotropic thermal motion, we define the *equivalent* isotropic motion as that which gives rise to the same value of $\overline{r^2}$ (the same value of the energy in the first vibrational state). Thus we may write

$$\frac{B}{16\pi^2}\mathbf{A}'(\mathbf{A}\mathbf{A}')^{-1}\mathbf{A} = \mathbf{A}'\mathbf{B}\mathbf{A}\ , \tag{13}$$

or, noting that $\mathbf{A}'(\mathbf{A}\mathbf{A}')^{-1}\mathbf{A} = 3$,

$$B = \frac{16\pi^2}{3}\mathbf{A}'\mathbf{B}\mathbf{A}\ . \tag{14}$$

Frequent practice among crystallographers is to refine the components of a matrix $\mathbf{b}$ such that

$$\mathbf{H}'\mathbf{b}\mathbf{H} \equiv \mathbf{S}'\mathbf{B}\mathbf{S} \tag{15}$$

with

$$\mathbf{H}' \equiv (hkl)\ . \tag{16}$$

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‡ The use of the 3×1 matrices $\mathbf{A}$ and $\mathbf{A}^*$ to describe the vector triples in direct and reciprocal space, implicit in the discussion of section 2·5 of the *International Tables* (1952), is extremely convenient in a variety of circumstances, and, in the author's opinion should be more generally used in discussions of this type. In performing operations involving these matrices, one need only remember that $\mathbf{a}_i\mathbf{a}_j$ is to be interpreted as $\mathbf{a}_i\cdot\mathbf{a}_j$, and hence that multiplications involving more than two of these matrices do not in general obey the associative law of multiplication. For example, $(\mathbf{A}\mathbf{A}')(\mathbf{A}\mathbf{A}')$ is not equivalent to $\mathbf{A}(\mathbf{A}'\mathbf{A})\mathbf{A}'$.

§ Cochran discusses the relationship between the isotropic and anisotropic temperature factors, and, specifically, introduces a *distorted reciprocal lattice* for aid in graphical determination of the anisotropic temperature factor once the components of thermal vibration are known.

† Equations (8) and (9) follow from (7) provided that the scattering center and hence $f(\mathbf{S})$ are spherically symmetrical in the absence of thermal motion.

It follows that

$$\mathbf{b} = 4\pi^2\mathbf{B} \tag{17}$$

and that

$$B = \tfrac{4}{3}\mathbf{A}'\mathbf{b}\mathbf{A} = \tfrac{4}{3}\sum_i\sum_j b_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j)\ . \tag{18}$$

If some of the components of the **b** matrix are unknown, for example, if refinement is carried out in two dimensions only, one may still obtain an equivalent isotropic temperature factor by assuming that the unknown components of the anisotropic matrix and the isotropic matrix are identical, i.e., we may set

$$b_{ij} = \frac{B}{4}(\mathbf{AA}')^{-1}_{ij} \tag{19}$$

$$= \frac{B}{4}(\mathbf{A}^*\mathbf{A}^{*\prime})_{ij} \tag{19a}$$

by virtue of (6).

Suppose we have refined an [001] projection; we may write

$$\mathbf{b} = \begin{pmatrix} b_{11} & b_{12} & \frac{B}{4}a^*c^*\cos\beta^* \\ b_{12} & b_{22} & \frac{B}{4}b^*c^*\cos\alpha^* \\ \frac{B}{4}a^*c^*\cos\beta^* & \frac{B}{4}b^*c^*\cos\alpha^* & \frac{B}{4}c^{*2} \end{pmatrix} \tag{20}$$

and applying (18), we find after some manipulation that the equivalent isotropic temperature factor is

$$B = \frac{4}{1+(cc^*)^2}\left[a^2b_{11}+ab\cos\gamma(2b_{12})+b^2b_{22}\right]\ . \tag{21}$$

It should be pointed out that the equivalent isotropic temperature factor defined here is not necessarily that which would minimize the least-squares error. This could be found only by taking into account the least-squares error matrix for the individual components.

References

Busing, W. R. & Levy, H. (1958). *Acta Cryst.* **11**, 450.

Cochran, W. (1954). *Acta Cryst.* **7**, 503.

International Tables for X-ray Crystallography (1952), p. 15. Birmingham: Kynoch Press.

Waser, J. (1955). *Acta Cryst.* **8**, 731.

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A general method for determining film-to-film scaling constants.

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In a recent short communication, Kraut (1958) has proposed a systematic method of scaling a set of mutually intersecting reciprocal lattice planes obtained using zero-level precession camera photographs. The purpose of this paper is to propose an alternative method applicable where not all planes are mutually intersecting, as when upper level photographs are used.

Kraut's method may be briefly summarized as follows: If k_i is the desired scaling constant for reciprocal lattice plane i or film i, and if r_{ij} is the average value of the reciprocal-point-by-point ratio between reflections occurring on films i and j, or $r_{ij} = \langle I_{j(hkl)}/I_{i(hkl)}\rangle$, then the desired constant for film i is given by:

$$k_i = \left[\prod_{j=1}^{n}\frac{r_{ij}r_{jn}}{r_{ji}r_{nj}}\right]^{1/2n} \tag{1}$$

where n is the total number of planes and k_n is arbitrarily chosen to be unity. The criterion leading to this equation is the minimization of the following function with respect to all $\log k_j$'s

$$F(k_i, r_{ij}) = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\log\frac{k_i}{k_j} - \log r_{ij}\right)^2 . \tag{2}$$

This approach is inapplicable to upper level photographs, in which case there are planes which do not intersect, for here r_{ij} and r_{ji} are indeterminate quantities. It is not correct simply to omit such terms from the product, for this implicitly assumes that $r_{ij}/r_{ji} = 1$, which could be true only if the scaling constants for the two planes were identical.

In the process of obtaining data for a Fourier synthesis of myoglobin with 2 Å resolution we collect twenty-two sets of zero and upper level precession photographs, of the type h, n, l ($n = 0$ to 6), h, k, n ($n = 0$ to 6), and $h, k, k-n$ ($n = 0$ to 7). We have found the following to be a convenient method of scaling these films so as to make the maximum possible use of film intersection. Define J_{ij} as the sum of all reflections on film i which are common to film j, and J_{ji} as a similar sum on film j. Because of reciprocal-space symmetry these may lie on more than one row. If i and j do not intersect, then $J_{ij} = J_{ji} = 0$, but both may be considered formally as present. Define k_j as the desired scaling constant for film j. If there were no experimental errors then the 'residual' for one pair of planes would be zero when proper scaling constants were used: $e_{ij} = k_iJ_{ij}-k_jJ_{ji} = 0$. This is never realized, but the best set of k's will be that minimizing the sum of squares of residuals, the sum being taken over all pairs of intersecting films. From a formal viewpoint the sum may be taken over all possible combinations of planes with the above stipulation about J values of non-intersecting planes.

$$E = \sum_{i=1}^{n}\sum_{j=1}^{n}(k_iJ_{ij}-k_jJ_{ji})^2\ . \tag{3}$$

Differentiation with respect to a particular k_i yields:

$$\sum_{j=1}^{n}(k_iJ_{ij}^2-k_jJ_{ji}J_{ij}) = 0\ . \tag{4}$$

For convenience, J_{ii} may be defined as zero, since the terms with $j = i$ cancel.

Changing to a more convenient nomenclature, let: