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**The anisotropic temperature factor in triclinic coordinates.** By JÜRG WASER, *Department of Chemistry, The Rice Institute, Houston, Texas, U.S.A.*

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The problem of finding the principal axes of the ellipsoid describing the anisotropic temperature factor in a system of oblique axes has been recently treated (Rollett & Davies, 1955) by first introducing a set of orthogonal axes. It is, however, simpler and more directly solved in the original system of axes, as will be shown in the following.

Consider the triclinic axes $\mathbf{a}_j$ with corresponding reciprocal axes $\mathbf{b}_j$. The anisotropic temperature factor of a given atom is of the form

$$\exp\left(-\sum_{ij} B_{ij}h_i h_j\right),$$

where the $h_i$ are the indices of a given reflection which has the reciprocal-lattice vector $\mathbf{h} = \sum_i h_i \mathbf{b}_i$ associated with it. The $B_{ij} = B_{ji}$ are the components of a symmetric tensor describing the temperature effect. More generally, in terms of a continuous reciprocal-space vector $\mathbf{q} = \sum_i q_i \mathbf{b}_i$, the temperature factor has the form

$$\exp\left(-\sum_{ij} B_{ij}q_i q_j\right).$$

Consider the surface, in reciprocal space, for which the temperature factor is constant,

$$\text{i.e.}\ \sum_{ij} B_{ij}q_i q_j = \text{const.} = B\,.$$

Owing to the physical nature of the tensor $B_{ij}$ the quadratic form is positive definite and this equation represents an ellipsoid. The problem of finding the principal axes of this ellipsoid is the same as that of finding vectors $\mathbf{q}$ for which $q^2 = \sum_j q_i q_j \mathbf{b}_i \cdot \mathbf{b}_j$ is stationary with the subsidiary condition

$$\sum_{ij} B_{ij}q_i q_j = B\,. \tag{1}$$

Thus, introducing the Lagrange multiplier $1/\lambda$, we have

$$\delta\left[\sum_{ij} (\mathbf{b}_i \cdot \mathbf{b}_j - B_{ij}/\lambda) q_i q_j\right] = 0\,,$$

whence

$$\sum_i (B_{ij} - \lambda \mathbf{b}_i \cdot \mathbf{b}_j) q_i = 0;\ \ j = 1, 2, 3\,. \tag{2}$$

These three linear homogeneous equations for the $q_i$ have non-trivial solutions only when the determinant of the coefficients vanishes:

$$\|B_{ij} - \lambda \mathbf{b}_i \cdot \mathbf{b}_j\| = 0\,. \tag{3}$$

This represents a cubic equation in $\lambda$ which has three real, positive solutions (since the quadratic form is positive definite) which we shall call $\lambda^{(r)}$, $r = 1, 2, 3$. For each $\lambda^{(r)}$, (1) and (2) determine a set $q_i^{(r)}$ and thus a vector $\mathbf{q}^{(r)}$ which points along a principal axis.

When $\mathbf{q}$ is set equal to $\mathbf{q}^{(r)}$ equations (1) and (2) yield $\lambda^{(r)}(q^{(r)})^2 = B$, so that the $r$'th principal axis has the length $q^{(r)} = (B/\lambda^{(r)})^{\frac{1}{2}}$. When all $\lambda^{(r)}$ are different from each other, the different $\mathbf{q}^{(r)}$ can be shown (by the use of (2)) to be perpendicular to each other. If two or three $\lambda^{(r)}$ are identical the corresponding $\mathbf{q}^{(r)}$ are not completely determined but can always be chosen mutually perpendicular (ellipsoid of revolution or sphere). We assume that the $\mathbf{q}^{(r)}$ have been chosen in this way so that

$$\mathbf{q}^{(r)} \cdot \mathbf{q}^{(r')} = \sum_{ij} q_i^{(r)} q_j^{(r')} \mathbf{b}_i \cdot \mathbf{b}_j = \delta_{rr'} B/\lambda^{(r)}\,, \tag{4}$$

and introduce a dimensionless cartesian coordinate system with axes parallel to the principal axes. The base vectors are:

$$\mathbf{e}_r = \sum_i (q_i^{(r)}/q^{(r)})\mathbf{b}_i;\ e_r = 1;\ r = 1, 2, 3\,.$$

Let $Q_j$ be the components of $\mathbf{q}$ in this system, $\mathbf{q} = \sum_j Q_j \mathbf{e}_j$. Since the $q_j$ transform with the inverse transposed transformation matrix of the $\mathbf{b}_i$,

$$q_i = \sum_j (q_i^{(j)}/q^{(j)}) Q_j\,.$$

In terms of the new coordinates $Q_j$ the quadratic form (1) becomes diagonalized,

$$\sum_{ij} B_{ij} q_i q_j = \sum_r \lambda^{(r)} Q_r^2\,.$$

The Fourier transform of $\exp\left(-\sum_r \lambda^{(r)} Q_r^2\right)$ is $\left[\prod_r (\pi/\lambda^{(r)})^{\frac{1}{2}}\right] \exp\left[-\sum_r (\pi^2/\lambda^{(r)}) X_r^2\right]$, where the $X_r$ are the components of the displacement $\mathbf{x}$ of the atom considered in the system extended by the $\mathbf{e}_r$. Along the axis $\mathbf{e}_r$ the mean square displacement is

$$\langle X_r^2 \rangle_{\text{ave.}} = \left[\prod_r (\pi/\lambda^{(r)})^{\frac{1}{2}}\right] \times \iiint X_r^2 \exp\left(-\sum_j \pi^2 X_j^2/\lambda^{(j)}\right) dX_1 dX_2 dX_3 = \lambda^{(r)}/2\pi^2$$

(see also Cochran, 1954). More generally, the mean square of the component of the displacement in an arbitrary direction characterized by direction cosines $\alpha_i$ is given by

$$\left\langle \left(\sum_i \alpha_i X_i\right)^2 \right\rangle_{\text{ave.}} = \sum_i \alpha_i^2 \lambda^{(i)}/2\pi^2\,.$$

This relationship is described by the ellipsoid $\sum_i x_i^2 \lambda^{(i)}/2\pi^2 = 1$ in the following way. Its principal axes have the lengths $(\lambda^{(r)}/2\pi^2)^{-\frac{1}{2}}$ and, more generally, the length of a radius vector in the direction characterized by cosines $\alpha_i$ is $\left(\sum_i \alpha_i^2 \lambda^{(i)}/2\pi^2\right)^{-\frac{1}{2}}$, which is the inverse of the root-mean-square displacement of the atom in this direction. On the other hand, the surface generated by a radius vector

$$\mathbf{r} = \left(\sum_j \alpha_j^2 \lambda^{(j)}/2\pi^2\right)^{\frac{1}{2}} \sum_i \alpha_i \mathbf{e}_i\,,$$

whose length is equal to the r.m.s. displacement in the direction $(\alpha_i)$, is of the fourth order.

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## References

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