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Transformations to Optimize the Superposition of Similar Structures

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Abstract

A simple, efficient and general method is described for finding the linear orthogonal transformation to superpose two similar structures given by sets of equivalent points, usually atomic position vectors. Formulae are also given for extracting the independent variables of rotation from the resulting transformation matrix. In addition, general transformations are derived, both in the case of proper rotation and in the case of rotatory inversion, to convert to a molecular frame of reference based on the superposition axis of symmetry.

Introduction

It often happens that two or more known structures are the same or similar but are arbitrarily placed with respect to one another. Important crystallographic examples include related molecular structures from different crystals, multiple copies of the same molecule in a single asymmetric unit, and similar substructures within a single molecule. Such situations are particularly common among biological macromolecules. For several reasons, it may be of interest to find the transformations that optimally superpose these structures. Most importantly, this facilitates a structural comparison. When the related structures are contiguous, the transforming operation can be an intrinsic molecular property and it might be desirable to transform the complete structure to a frame of reference based on the local symmetry operator.

Several different procedures have been described for finding the linear orthogonal transformation to superpose two structures that can be described by sets of equivalent points, usually atomic position vectors (Cox, 1967; McLachlan, 1972; Rao & Rossmann, 1973; Nyburg, 1974; Kabsch, 1976; Ferro & Hermans, 1977). Perhaps still other methods have been used in the specific applications for which procedures have not been elaborated. Transformation to a molecular reference frame based on local symmetry operators has also been made in specific applications, but no general procedures for finding these transformations have been described.

The purpose of this note is to describe a particularly simple and general method for superposing similar structures and to derive, from the parameters of this transformation, the transformation to convert to a local molecular frame of reference. The method for superposition developed here is most closely related to that of Rao & Rossmann (1973). Both that method and this one start by finding the general linear transformation that brings equivalent points in the two structures into least-squares superposition. These two methods differ in the means by which the transformation is then constrained to be an orthogonal transformation, *i.e.* one which moves the structure as a rigid body. In the method of Rao & Rossmann approximate Eulerian angles are estimated from certain elements of the general transformation matrix, these are then adjusted to a best fit to all of the matrix elements, and finally the Eulerian angles are refined by a procedure like that of Cox (1967). In the present method orthogonality constraints are imposed directly through the device of Lagrange multipliers. In this respect the method for superposition suggested here is like that given by Kabsch (1976) and belatedly noticed by this author. Kabsch's solution of the superposition problem is superior in that it requires no iteration.

Least-squares superposition

Suppose that two similar structures, denoted A and B, that have in common N equivalent points (usually atomic positions) are to be superposed. Suppose also that these structures have already been referred to rectangular Cartesian reference frames of uniform physical scale (*e.g.* ångström units). Then the position vector, $\mathbf{x}_{B,k}$, of the kth point in structure B can be related to the position vector, $\mathbf{x}_{A,k}$, of the equivalent point in structure A by a linear transformation:

$$\mathbf{x}_{A,k} \simeq \mathbf{x}''_{B,k} = \mathbf{R}\mathbf{x}_{B,k} + \mathbf{t}, \qquad (1)$$

where $\mathbf{R}$ is a 3×3 matrix with elements r_{ij} and $\mathbf{t}$ is a translation vector with elements ($t_1 = t_x$, $t_2 = t_y$, $t_3 = t_z$). The optimal parameters for this general linear transformation will be those that minimize the weighted sum of squares of discrepancies between equivalent points in the superposed structures,

$$\phi = \sum_{k=1}^{N} w_k(\mathbf{x}_{A,k} - \mathbf{x}''_{B,k})^2. \tag{2}$$

This poses a linear least-squares problem that can be solved directly and uniquely from the set of twelve normal equations generated by the minimization conditions that $\partial\phi/\partial r_{ij} = 0$ and $\partial\phi/\partial t_i = 0$ for all i and j.

The transformation matrix, $\mathbf{R}$, found in the minimization of ϕ will not necessarily correspond to a rigid-body rotation. Indeed, Diamond (1976) has shown how such a matrix can be factored into the product, $\mathbf{R} = \mathbf{AT}$ of a pure rotation and a pure strain. The transformation $\mathbf{T} = (\tilde{\mathbf{R}}\mathbf{R})^{1/2}$ is a symmetric matrix (six independent elements) representing the strain, and the transformation $\mathbf{A} = \mathbf{RT}^{-1}$ is an orthogonal matrix (three independent elements) representing the rotation that brings into coincidence the principal axes of strain in the two structures. Clearly, if the structures are to be moved as rigid bodies, $\mathbf{R}$ itself must be an orthogonal transformation matrix. The elements of such a matrix are the direction cosines of one rectangular Cartesian reference frame with respect to another. Consequently, the necessary and sufficient conditions that $\mathbf{R}$ should represent an orthogonal transformation (Dresden, 1930) are that

$$\begin{aligned}
g_1 &= r_{11}^2 + r_{12}^2 + r_{13}^2 - 1 = 0,\\
g_2 &= r_{21}^2 + r_{22}^2 + r_{23}^2 - 1 = 0,\\
g_3 &= r_{31}^2 + r_{32}^2 + r_{33}^2 - 1 = 0,\\
g_4 &= r_{21}r_{31} + r_{22}r_{32} + r_{23}r_{33} = 0,\\
g_5 &= r_{31}r_{11} + r_{32}r_{12} + r_{33}r_{13} = 0,\\
g_6 &= r_{11}r_{21} = r_{12}r_{22} + r_{13}r_{23} = 0.
\end{aligned} \tag{3}$$

The desired linear transformation can be constrained to meet the orthogonality conditions through the introduction of Lagrange multipliers, λ_l, and subsequent minimization of the auxiliary function,

$$\Phi = \phi + \sum_{l=1}^{6} \lambda_l g_l, \tag{4}$$

with respect to all parameters including the Lagrange multipliers. Inasmuch as the constraining conditions are quadratic, this minimization is not a straightforward linear least-squares problem. Kabsch has given an elegant eigenvalue solution special to this problem. Alternatively, equations (3) can be linearized by a Taylor series expansion about approximate values for the matrix elements r_{ij} and equation (1) can also be expressed as a first-order Taylor expansion. The initial parameters for these expansions derive from the unconstrained minimization of ϕ. Parameter shifts tending to minimize ϕ and, thereby, to impose the constraints are then found by solving the resulting set of eighteen normal equations: $\partial\Phi/\partial\delta r_{ij} = 0$, $\partial\Phi/\partial\delta t_i = 0$ and $\partial\Phi/\partial\lambda_l = 0$ for all allowed i, j and l. The process is then iterated until convergence is reached.

Rotation-angle representation

Although all nine elements of an orthogonal transformation matrix are, in general, unique, the number of independent parameters is reduced to three by the constraints. In many instances it will be desirable to express this matrix in terms of the independent parameters. In fact, there are many such representations. Superficially, these are of two classes depending upon the sign of the determinant of the transformation matrix. If $|\mathbf{R}| = +1$, $\mathbf{R}$ corresponds to a proper rotation of coordinates; whereas if $|\mathbf{R}| = -1$, $\mathbf{R}$ corresponds to an improper rotation or rotatory inversion. However, as is discussed below, a rotatory inversion matrix is the negative of a proper rotation matrix, $\mathbf{R} = -\mathbf{Q}$, so that representations in terms of rotation angles suffice for both cases.

Two especially useful representations of rotational transformations are those in terms of Eulerian angles or in terms of a single rotation about an axis specified by spherical polar coordinates. Rossmann & Blow (1962) have described now widely used conventions for both types of representations. They have tabulated the rotation matrix elements in terms of the Eulerian angles $(\theta_1,\theta_2,\theta_3)$ and in terms of the spherical polar angles (φ,ψ,χ). By equating these elements with the values determined from the minimization of Φ, equation (4), it is possible to extract rotation angles that are the independent variables of an arbitrary orthogonal transformation matrix.

In the general case, Eulerian angles in the Rossmann & Blow convention can be evaluated according to

$$\begin{aligned}
\theta_1 &= \tan^{-1}[r_{31}/-r_{32}],\\
\theta_3 &= \tan^{-1}[r_{13}/r_{23}],\\
\theta_2 &= \tan^{-1}[(r_{13}/\sin\theta_3)/r_{33}]\\
&= \tan^{-1}[(r_{23}/\cos\theta_3)/r_{33}].
\end{aligned} \tag{5}$$

In the special case that $r_{33} = \pm 1$, $r_{13} = r_{31} = r_{23} = r_{32} = 0$ and the Eulerian angles are indeterminate from equations (5). In this case

$$\begin{aligned}
\theta_1 + \theta_3 &= \tan^{-1}(r_{12}/r_{11}),\\
\theta_2 &= \cos^{-1}(r_{33});
\end{aligned} \tag{6}$$

θ_1 and θ_3 are redundant so that all combinations giving the specified sum, $\theta_1 + \theta_3$, are equivalent.

The equations for the extraction of spherical polar angles. in the Rossman & Blow convention are, in the general case,

$$\begin{aligned}
\varphi &= \tan^{-1}\{(r_{21}-r_{12})/(r_{23}-r_{32})\},\\
\psi &= \tan^{-1}\{[(r_{21}-r_{12})/\sin\varphi]/(r_{31}-r_{13})\}\\
&= \tan^{-1}\{[(r_{23}-r_{32})/\cos\varphi]/(r_{31}-r_{13})\},\\
\chi &= \tan^{-1}\{[(r_{31}-r_{13})/\cos\psi]/(r_{11}+r_{22}+r_{33}-1)\}\\
&= \tan^{-1}\{[(r_{21}-r_{12}/\sin\psi\sin\varphi]/(r_{11}+r_{22}+r_{33}-1)\}\\
&= \tan^{-1}\{[(r_{23}-r_{32}/\sin\psi\cos\varphi]/(r_{11}+r_{22}+r_{33}-1)\}.
\end{aligned} \tag{7}$$

The alternative expressions for ψ and χ must be considered in order to guard against singularities when φ or ψ are at cardinal values. These equations also break down in the special case that $r_{12} = r_{21}$, $r_{23} = r_{32}$ and $r_{13} = r_{31}$. Several situations arise depending upon whether neither, either or both of r_{12} and r_{23} are equal to zero. If neither r_{12} nor r_{23} is zero, then

$$\begin{aligned}
\varphi &= \tan^{-1}[-r_{23}/r_{12}],\\
\psi &= \tan^{-1}[(r_{31}/\sin\varphi)/-r_{12}]\\
&= \tan^{-1}[(r_{31}/\cos\varphi)/r_{23}],\\
\chi &= \pi.
\end{aligned} \tag{8}$$

If either but not both of r_{12} and r_{23} is zero, then

$$\psi = \tan^{-1}[(r_{12}-r_{23})/(r_{22}+1)], \tag{9}$$

and φ and χ are as specified by equations (8). If both r_{12} and r_{23} are zero when $r_{13} = r_{31}$, then r_{13} is necessarily also zero. Since only the case of $|\mathbf{R}| = +1$ is considered here, this situation has four special possibilities: (φ,ψ,χ) are $(\pi/2,\pi/2,\pi)$, $(0,0,\pi)$, $(0,\pi/2,\pi)$ or $(0,0,0)$ according as (r_{11},r_{22},r_{33}) are $(1,-1,-1)$, $(-1,1,-1)$, $(-1,-1,1)$ or $(1,1,1)$. A final special case occurs when $r_{12} = r_{21}$, $r_{23} = r_{32}$ and $r_{13} \neq r_{31}$ which happens only at $r_{12} = r_{23} = 0$ and $r_{13} = -r_{31}$. Then (φ,ψ,χ) are $[0,0,\tan^{-1}(r_{31}/r_{11})]$.

In the case of rotatory inversion, *i.e.* $|\mathbf{R}| = -1$, rotation-angle representations for $\mathbf{Q} = -\mathbf{R}$ can be found by substituting the elements of $\mathbf{Q}$ into equations (5)–(9).

Molecular reference frames

When similar structures are contiguous, as in oligomeric molecules or in single molecules possessing repeated substructures, the transformations to superpose these structures are aspects of an intrinsic molecular symmetry. This symmetry may only be approximate and a rotation need not be rational, *e.g.* the symmetry operator may be an arbitrary screw axis. Whatever may be the intramolecular symmetry it can be advantageous to transform the entire structure to a new reference frame based on the molecular axis (or axes) of symmetry. In this way the inherent symmetry properties are expressed free of orientational factors and illustrations can readily be prepared to display the symmetry.

The orthogonal transformation is sought which brings the points $\mathbf{x}$ of a given molecule in an arbitrary rectangular reference frame XYZ into the points $\mathbf{x}'$ in a new frame $X'Y'Z'$ based on the molecular symmetry relating substructure B of the molecule to substructure A. A convenient Cartesian system will have Z' coincident with the symmetry axis, X' perpendicular to Z' and in the direction of a given point $\mathbf{x}_p$, and Y' mutually perpendicular to X' and Z' and directed so as to form a right-handed system. The required transformation is

$$\mathbf{x}' = \mathbf{S}(\mathbf{x}-\mathbf{u}), \tag{10}$$

where $\mathbf{u}(u_x,u_y,u_z)$ locates the new molecular origin in the old reference frame and $\mathbf{S}(s_{ij})$ rotates the XYZ system into correspondence with $X'Y'Z'$. Two different situations arise depending upon whether structures A and B are related by proper or improper rotation. In either case the transformation parameters, $\mathbf{R}$ and $\mathbf{t}$, relating A and B and the coordinates of a single non-axial point $\mathbf{x}_p$ (the centroid of structure B is a convenient choice), suffice to determine $\mathbf{S}$ and $\mathbf{u}$.

Proper rotation

Matrix $\mathbf{S}$ is composed of the direction cosines of $X'Y'$ and Z' with respect to XYZ. The vector $\boldsymbol{\zeta}(\zeta_x,\zeta_y,\zeta_z)$ of direction cosines for Z', the symmetry axis, is known from the spherical polar angles, φ and ψ, locating this axis. These angles are determined from $\mathbf{R}$ by equations (7)–(9). Thus,

$$\begin{aligned}
s_{31} &= \zeta_x = \cos\varphi\sin\psi,\\
s_{32} &= \zeta_y = \cos\psi,\\
s_{33} &= \zeta_z = -\sin\varphi\sin\psi.
\end{aligned} \tag{11}$$

Any rotational transformation can be described as a screw operation. The rotation angle, χ, about the screw axis specified by φ and ψ and the translation, t_χ, along this axis are the intrinsic parameters of this operation. The screw translation is given by the projection, $\mathbf{t}.\boldsymbol{\zeta}$, of $\mathbf{t}$ onto the symmetry axis, $\boldsymbol{\zeta}$. Thus,

$$t_\chi = \cos\varphi\sin\psi\, t_x + \cos\psi\, t_y - \sin\varphi\sin\psi\, t_z. \tag{12}$$

The origin of the molecular reference frame can be located at the intersection of the symmetry axis with the plane normal to this axis which passes through the point $\mathbf{x}_p$. The line which constitutes the symmetry axis can be defined by considering the effect of the superposing transformation on a point on the axis.

Such a point remains axial but is translated along the axis by t_χ. Thus the equations of the symmetry axis are

$$\mathbf{x} + t_\chi \boldsymbol{\zeta} = \mathbf{R}\mathbf{x} + \mathbf{t}$$

$$(\mathbf{R} - \mathbf{I})\mathbf{x} = t_\chi \boldsymbol{\zeta} + \mathbf{t}. \qquad (13)$$

[Notice that although these constitute three equations in three variables (x,y,z), the system is underdetermined since $(\mathbf{R} - \mathbf{I})$ is of rank 2, $|\mathbf{R} - \mathbf{I}| = 0$.] The family of planes perpendicular to the symmetry axis is given by $\boldsymbol{\zeta}.\mathbf{x} = p$. The particular plane passing through the point $\mathbf{x}_p$ is specified by evaluating p for that point. Since $\mathbf{u}$ must also lie on this plane, its equation together with any two of the three equations given by (13) serve to define the origin point. For example, $\mathbf{u}$ can be found by solving this system of linear equations:

$$\begin{pmatrix} r_{11} - 1 & r_{12} & r_{13} \\ r_{21} & r_{22} - 1 & r_{23} \\ \zeta_x & \zeta_y & \zeta_z \end{pmatrix} \begin{bmatrix} u_x \\ u_y \\ u_z \end{bmatrix} = \begin{bmatrix} t_\chi \zeta_x - t_x \\ t_\chi \zeta_y - t_y \\ \zeta_x x_p + \zeta_y y_p + \zeta_z z_p \end{bmatrix}. \qquad (14)$$

The direction cosines, $\boldsymbol{\xi}(\xi_x,\xi_y,\xi_z)$, of the X' axis with respect to XYZ can now be evaluated from the equations for the directed line passing from the point $\mathbf{u}$ to the point $\mathbf{x}_p$. Thus,

$$\begin{aligned} s_{11} &= \xi_x = (x_p - u_x)/d, \\ s_{12} &= \xi_y = (y_p - u_y)/d, \qquad (15) \\ s_{13} &= \xi_z = (z_p - u_z)/d, \end{aligned}$$

where

$$d = [(x_p - u_x)^2 + (y_p - u_y)^2 + (z_p - u_z)^2]^{1/2}.$$

The direction cosines, $\boldsymbol{\eta}(\eta_x,\eta_y,\eta_z)$, of Y' with respect to XYZ are completely specified by the direction cosines $\boldsymbol{\xi}$ and $\boldsymbol{\zeta}$ of the other two axes. This follows directly from the conditions (3) on orthogonal transformations and the need to preserve a right-handed system. The magnitudes of these direction cosines are determined by

$$\begin{aligned} |s_{21}| &= \eta_x = (1 - \xi_x^2 - \zeta_x^2)^{1/2}, \\ |s_{22}| &= \eta_y = (1 - \xi_y^2 - \zeta_y^2)^{1/2}, \qquad (16) \\ |s_{23}| &= \eta_z = (1 - \xi_z^2 - \zeta_z^2)^{1/2}, \end{aligned}$$

and the signs of these elements are determined by the conditions

$$\begin{aligned} \eta_x\eta_y &= -(\xi_x\xi_y + \zeta_x\zeta_y), \\ \eta_x\eta_z &= -(\xi_x\xi_z + \zeta_x\zeta_z), \qquad (17) \\ \eta_y\eta_z &= -(\xi_y\xi_z + \zeta_y\zeta_z), \\ |\mathbf{S}| &= +1. \end{aligned}$$

If the signs of the products $(\eta_x\eta_y,\ \eta_x\eta_z,\ \eta_y\eta_z)$ are (+,+,+), (+,−,−), (−,+,−) or (−,−,+) [other sign combinations are impossible], then the signs of the direction cosines themselves (η_x,η_y,η_z) must be either (+,+,+) or (−,−,−), (+,+,−) or (−,−,+), (+,−,+) or (−,+,−), or (−,+,+) or (+,−,−) respectively. In each case, only one of the two possibilities will satisfy the condition that $|\mathbf{S}| = +1$.

The transformation of superposition can now be described in the new coordinate frame in terms of the two fundamental parameters χ and t_χ. This transformation is given by $(\theta'_1,\theta'_2,\theta'_3) = (\chi,0,0)$ or $(\varphi',\psi',\chi') = (\pi/2,-\pi/2,\chi)$ and $(t_{x'},t_{y'},t_{z'}) = (0,0,t_\chi)$.

Rotatory inversion

The transformation of rotatory inversion ($|\mathbf{R}| = -1$) is a point symmetry operation rather than a screw-axis operation as in a rotational transformation. Both a rotation axis and an inversion center on that axis are involved, but there is no intrinsic translational component. It is obvious to identify the point of inversion with the origin $\mathbf{u}$ of the molecular reference frame. The transformation of superposition by rotatory inversion can equally well be represented by equation (1) with $\mathbf{R}$ constrained to be orthogonal or by

$$\mathbf{x}'' = \mathbf{Q}(\mathbf{u} - \mathbf{x}) + \mathbf{u}, \qquad (18)$$

wherein coordinates are first reflected through the inversion center $\mathbf{u}$ and then rotated by an orthogonal matrix $\mathbf{Q}$ ($|\mathbf{Q}| = +1$). Since, by definition, (1) and (18) are identical transformations,

$$\mathbf{R}\mathbf{x} + \mathbf{t} = -\mathbf{Q}\mathbf{x} + (\mathbf{Q} + \mathbf{I})\mathbf{u}. \qquad (19)$$

Upon equating components in (19) it follows that

$$\mathbf{Q} = -\mathbf{R}, \qquad (20)$$

as was noted above, and

$$\mathbf{u} = (\mathbf{I} - \mathbf{R})^{-1}\,\mathbf{t}. \qquad (21)$$

Equation (21) also follows directly from equation (1) on noticing that the center of inversion is unmoved by the transformation.

These foregoing considerations together with the formulae already presented for the case of proper rotation suffice to describe the transformation [equation (10)] to a molecular reference frame in the event of rotatory inversion. The origin point is defined by equation (21). As before the $\boldsymbol{\zeta}$ vector of direction cosines is given by equations (11) where the spherical polar angles are now extracted from $\mathbf{Q}$ rather than $\mathbf{R}$. However, now only the direction of the X' axis is specified by $\mathbf{x}_p$, the axis does not necessarily pass through this point. The direction cosines $\boldsymbol{\xi}$ of X' are those of a line passing through $\mathbf{x}_p$ from the point of intersection, $\mathbf{x}_a$, between the rotation axis and the plane normal to the axis which also passes through $\mathbf{x}_p$. The point $\mathbf{x}_a$ is given by

$$\mathbf{x}_a = \mathbf{u} + s\boldsymbol{\zeta}, \qquad (22)$$

where s can be determined by substituting (22) into the equation of the normal plane, $\mathbf{x}.\boldsymbol{\zeta} = p$, passing through the point $\mathbf{x}_p$. Thus, $(\mathbf{u} + s\boldsymbol{\zeta}).\boldsymbol{\zeta} = \mathbf{x}_p.\boldsymbol{\zeta}$ and

$$s = (x_p - u_x)\zeta_x + (y_p - u_y)\zeta_y + (z_p - u_z)\zeta_z. \quad (23)$$

The direction cosines, $\boldsymbol{\xi}$ for X', can now be computed from equations (15) by substituting the elements of $\mathbf{x}_a$ for those of $\mathbf{u}$. Given $\boldsymbol{\xi}$ and $\boldsymbol{\zeta}$, $\boldsymbol{\eta}$ can be computed as before from equations (16) and (17) to complete the specification of $\mathbf{S}$ in this case.

Implementation

The procedures described above have been implemented as a computer program written in Fortran. This program has been tested by superposing the two mononucleotide-binding units of the NAD-binding domain in lactate dehydrogenase (Rao & Rossmann, 1973). This superposition was made on α-carbon positions at unit weight and used the same coordinates and correspondences as described earlier (Hendrickson & Ward, 1977). The method used in this earlier fitting involved a crude search for approximate Eulerian angles followed by a non-linear least-squares refinement of the Eulerian angles and translation elements (Cox, 1967). Both that procedure and the final stage of the Rao & Rossmann procedure converged to four significant figures in the six transformation parameters after four cycles of refinement. The present method converged to exactly the same values after two cycles. The program has also been tested on a trimerization product of *C*,*C*-diphenyl-N^{α}-(4-chlorophenyl)-N^{β}-cyanazomethinimin (Flippen-Anderson, 1978). This molecule has three similar parts of 24 non-hydrogen atoms each. The results showed that one of the three pairs of substructures can be superposed by a proper rotation but that the other two pairs require rotatory inversions for superposition. Tests have also been run on a number of other problems.

The procedures presented here are completely general. Special symmetry causes no difficulty. Moreover, this method for superposition, unlike alternative methods, other than that of Kabsch (1976), handles rotatory inversion as readily as it does proper rotation. This superposition method is also very effective. Since only the constraining equations present non-linearities and these are only quadratic, convergence in the least-squares minimization is rapid and the process is quite free of false minima. As a result, the procedure is also robust to ill defined situations such as are presented by very dissimilar structures. The method is also computationally efficient. There are only ten unique elements in the normal matrix for the linear least-squares step and only 48 of the 144 elements are non-zero. These same elements carry over directly to the non-linear step; only the simple factors for the Lagrange multipliers change. However, the right-hand-side vector of the normal equations must be computed anew each cycle. Nonetheless, the process is fast: even with an unoptimized program, superpositions are computed on a TI-ASC at the rate of 2 ms per atom per cycle following an initial set-up of 5 ms per atom.

Additional conditions can readily be imposed on the transformations for superposition in special situations. For example, rotations can be constrained to be twofold ($\chi = \pi$) by fixing $r_{12} - r_{21} = 0$, $r_{13} - r_{31} = 0$ and $r_{23} - r_{32} = 0$. Proper rotational transformations (screw operations) can be constrained to be pure rotations by setting $t_{\chi} = 0$. Thus a pure diad is fixed by imposing all four of these constraints with added Lagrange multipliers in equation (4). Similarly, improper rotations can be avoided by introducing $|\mathbf{R}| = +1$ as an added constraint.

Estimates of errors in the twelve elements of the linear transformation can be found from the inverse of the normal matrix upon minimization of equation (4). However, it is the errors in the independent variables that are of interest. Errors in rotation angles could be evaluated by an analysis of the propagation of errors in matrix elements through the angle extraction formulae (5)–(9). Alternatively, these errors could be determined directly from the inverse of a final normal matrix based on refinement against the actual variables of interest.

As noted above, the Kabsch (1976) method for superposition is conceptually superior to that given here and to all others in that it requires no iteration. However, in typical applications there would be little if any practical advantage as convergence is very rapid in this iterative procedure. Moreover, the present method has the advantage of being more amenable to the imposition of added constraints. For example, it would not be possible to constrain to a pure diad by the Kabsch method since such a constraint is not quadratic and is a function of translation as well as rotation. Of course, the equations given here for finding rotation-angle representations and for transforming to a molecular frame of reference apply equally well to the results of a Kabsch superposition. Notice, though, that the preliminary translations to centroids of the vector sets that are required in the Kabsch method must be taken into account in applying these transformations to a molecular reference frame.

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X-ray Diffraction by Small Crystals

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Abstract

A general method of calculating the intensity of X-ray diffraction from small crystalline particles whose boundary is defined by a shape function is discussed. The intensity formula which is generally given by a double sum over the reciprocal-lattice points is simplified into the form of a single sum, using 'the random-shift treatment' which assumes that the position of the boundary relative to the crystal lattice varies at random from crystal to crystal. By the use of Fourier theorems, the intensity formulas are also converted into a single sum over the direct lattice. Although the electron distribution in the particle has been defined in various ways by the shape function, a more reasonable expression of the electron density appropriate to small crystals is introduced. The intensity formulas derived on the basis of the new form of the electron density are compared with other intensity formulas which have so far been proposed.

1. Introduction

The effect of the external shape and the size of a crystal on X-ray diffraction intensity was first dealt with by Laue (1936) for a parallelepiped crystal having N_i unit cells along the $\mathbf{a}_i$ axis ($i = 1, 2, 3$), for which the diffraction intensity is expressed as

$$I^L(\mathbf{b}) = |F(\mathbf{b})|^2 G(\mathbf{b}), \tag{1}$$

with

$$F(\mathbf{b}) = \sum_{\alpha} f_{\alpha}(\mathbf{b}) \exp(2\pi i \mathbf{b}\mathbf{r}_{\alpha}), \tag{2}$$

$$G(\mathbf{b}) = \frac{\sin^2 \pi N_1 \xi}{\sin^2 \pi\xi} \frac{\sin^2 \pi N_2 \eta}{\sin^2 \pi\eta} \frac{\sin^2 \pi N_3 \zeta}{\sin^2 \pi\zeta}, \tag{3}$$

where $F(\mathbf{b})$ is the structure factor, $G(\mathbf{b})$ the Laue function, $f_{\alpha}(\mathbf{b})$ the atomic scattering factor of the αth atom located at $\mathbf{r}_{\alpha} = x_{\alpha}\mathbf{a}_1 + y_{\alpha}\mathbf{a}_2 + z_{\alpha}\mathbf{a}_3$ and $\mathbf{b}$ the scattering vector expressed as $\mathbf{b} = \xi\mathbf{a}_1^* + \eta\mathbf{a}_2^* + \zeta\mathbf{a}_3^*$, $\mathbf{a}_i^*$ being the reciprocal vectors.

In order to treat small crystals of arbitrary shapes, Patterson (1939) and Ewald (1940) introduced the shape function $s(\mathbf{r})$ defined by

$$s(\mathbf{r}) = \begin{cases} 1 & \text{inside the crystal boundary} \\ 0 & \text{outside the crystal boundary} \end{cases} \tag{4}$$

and expressed the electron density in a small crystal as

$$\rho_e(\mathbf{r}) = \rho_{\infty}(\mathbf{r})s(\mathbf{r}), \tag{5}$$

where $\rho_{\infty}(\mathbf{r})$ is the electron density of a perfectly periodic infinite crystal. As a Fourier transform of $\rho_e(\mathbf{r})$, the amplitude of X-rays diffracted by the crystal is given as

$$A_e(\mathbf{b}) = (1/v) \sum_{\mathbf{h}} F(\mathbf{h})S(\mathbf{b} - \mathbf{h}) \tag{6}$$

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