

Direction of Molecular Symmetry Axis

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Abstract

A least-squares method is described for determining the orientation of a non-crystallographic symmetry axis in a general rectilinear coordinate system. In addition to the components of the symmetry axis, the calculation gives the coordinates of points from which the observed coordinates may be generated by application of the symmetry operator. A statistical test of the significance of the fit is described.

Introduction

A standard crystallographic computation determines the least-squares plane through a set of points. The principles of this computation were first derived by Schomaker, Waser, Marsh & Bergman (1959); an efficient matrix formulation of the process and a statistical analysis of the results have been given by Hamilton (1964).

A problem related to the least-squares-plane calculation is the determination of whether or not a set of points is related by a non-crystallographic symmetry operation. In this case, the points do not lie on the symmetry element, but may be considered to be generated by application of a proper or improper rotation operator to three coordinates $x^1(0)$, $x^2(0)$, $x^3(0)$. The operator may be represented as

$$x^i(k) = R_j^i(k) x^j(0), \quad (1)$$

where $R_j^i(k)$ is the element in row i and column j of the matrix representing symmetry operator k . Throughout this paper we follow the tensor conventions (Sands, 1982) that superscripts denote contravariant quantities, subscripts denote covariant quantities, and summation is implied over an index appearing once as a superscript and once as a subscript in a term. The indices in parentheses in (1) designate the particular symmetry operator; k runs from 1 to r , where r is the order of the rotation group, and we shall assign $k = 1$ to the identity operator.

Mathematical formulation

The coordinates $x^i(k)$ are estimates of the observed coordinates $x_{\text{obs}}^i(k)$, and the $x^j(0)$ may be regarded as

ideal or 'best' coordinates that will give the best fit between the observations and the values estimated by (1). The general expression for R_j^i for a rotation through angle θ about a unit vector \mathbf{u} is (Sands, 1982)

$$R_j^i = \pm [u^i u_j + (\delta_j^i - u^i u_j) \cos \theta + g^{ik} \varepsilon_{klj} u^l \sin \theta], \quad (2)$$

in which δ_j^i is the Kronecker delta, g^{ik} is an element of the reciprocal metric tensor, and ε_{klj} is an element of the permutation tensor. The plus sign in front of the brackets in (2) applies to a proper rotation and the minus sign applies to an improper rotation (an axis of rotatory inversion). The computation will require the derivatives of R_j^i with respect to the components of \mathbf{u} ; the refinement may be carried out on either the covariant or the contravariant components of \mathbf{u} , and the corresponding derivatives are

$$\frac{\partial R_j^i}{\partial u^m} = \pm [(\delta_m^i u_j + g_{mj} u^i)(1 - \cos \theta) + g_{ik} \varepsilon_{kmj} \sin \theta], \quad (3)$$

$$\frac{\partial R_j^i}{\partial u_m} = \pm [(g^{im} u_j + u^i \delta_j^m)(1 - \cos \theta) + g^{ik} g^{lm} \varepsilon_{klm} \sin \theta]. \quad (4)$$

We shall take the contravariant coordinates u^i as unknowns, but the problem may be reformulated easily in terms of the covariant u_i . The other unknown parameters to be determined by the method of least squares are the coordinates $x^i(0)$. The problem may be generalized to multiple independent sets of points, as might occur, for example, in a molecule such as 1,3,5-trichlorobenzene where there are four distinct atom types (two kinds of carbon, chlorine, and hydrogen); a convenient notation for such generalization is $x^i(0, j)$ where the j refers to atom type.

Another potential source of unknowns involves specification of the origin. Equivalent to including the coordinates of the origin as explicit parameters in the least-squares treatment is the simple process of subtracting from each $x^i(k)$ the weighted mean over all values of k of the coordinates $x_{\text{obs}}^i(k)$. Even points expected to lie on the rotation axis may be included in these weighted averages. The weighting should properly take into account correlations between coordinates, for

which a method of computation has been given by Sands (1966), although little useful information will be lost if a simple weighting by the reciprocal of the variances is used.

Corresponding to each observation we define

$$F(m) = R_j^i(k) x^j(0) \quad (5)$$

in which

$$m = i + 3(k - 1). \quad (6)$$

If there is more than one independent atom, $x^j(0)$ in (5) should be replaced by $x^j(0, l)$, and m becomes

$$m = i + 3(k - 1) + 3r(l - 1). \quad (7)$$

With this ordering of the observations,

$$\Delta F(m) = R_j^i(k) x^j(0) - x_{\text{obs}}^i(k), \quad (8)$$

where m takes on values from 1 to the number of observations n . If the number of parameters to be determined is p , the design matrix \mathbf{A} is an $n \times p$ matrix in which the elements in row m are the derivatives of $F(m)$ with respect to each of the parameters. Specifically,

$$A_{mq} = \frac{\partial F(m)}{\partial u^q} = x^j(0) \frac{\partial R_j^i(k)}{\partial u^q} \quad \text{if } q = 1, 2, \text{ or } 3, \quad (9)$$

$$A_{mq} = \frac{\partial F(m)}{\partial x^j(0)} = R_j^i(k) \quad \text{if } q > 3. \quad (10)$$

The elements of \mathbf{A} may be computed from an initial set of parameters. In the notation of Hamilton (1964), corrections to the parameters are given by the $p \times 1$ column matrix $\Delta \mathbf{X}$,

$$\Delta \mathbf{X} = (\bar{\mathbf{A}}\mathbf{W}\mathbf{A})^{-1} \bar{\mathbf{A}}\mathbf{W} \Delta \mathbf{F}, \quad (11)$$

in which $\bar{\mathbf{A}}$ is the transpose of \mathbf{A} , \mathbf{W} is an $n \times n$ weight matrix given by

$$\mathbf{W} = \mathbf{V}^{-1}, \quad (12)$$

where \mathbf{V} is the variance-covariance matrix of the coordinates ordered as in (6) or (7). The shifts produced by (11) should be subtracted from the initial $u^1, u^2, u^3, x^1(0), x^2(0), x^3(0)$. Since the problem is non-linear, the design matrix depends upon the parameters, and iteration generally will be required to converge to the set of parameters that minimizes the quantity $\Delta \bar{\mathbf{F}}\mathbf{W} \Delta \mathbf{F}$.

Equation (2) requires that \mathbf{u} be a unit vector. Hence, before iteration the corrected \mathbf{u} should be normalized. The problem might, in fact, be treated as a constrained least-squares calculation with the condition

$$g_{ij} u^i u^j = 1. \quad (13)$$

Infinitesimal shifts in the vector components must then obey

$$g_{ij} u^i du^j = 0. \quad (14)$$

The relationship is not so simple for finite shifts, so formal introduction of the constraint into the least-squares calculation does not obviate the necessity for renormalization of \mathbf{u} after each cycle.

Statistical significance of results

The variance-covariance matrix of the least-squares parameters may be obtained from

$$\mathbf{V} = \Delta \bar{\mathbf{F}}\mathbf{W} \Delta \mathbf{F} [\mathbf{B}^{-1} - \mathbf{B}^{-1} \mathbf{Q} \bar{\mathbf{Q}} \mathbf{B}^{-1} / (\bar{\mathbf{Q}} \mathbf{B}^{-1} \mathbf{Q})] \times (n - p + 1)^{-1}, \quad (15)$$

where \mathbf{B} is the $p \times p$ matrix

$$\mathbf{B} = \bar{\mathbf{A}}\mathbf{W}\mathbf{A}, \quad (16)$$

and \mathbf{Q} is the $p \times 1$ constraint matrix with elements

$$Q_j = g_{ij} u^i = u_j \quad \text{for } j = 1, 2, 3 \quad (17)$$

$$Q_j = 0 \quad \text{for } j > 3;$$

i.e. the constraint of (14) may be expressed as

$$Q_j du^j = 0. \quad (18)$$

The statistical significance of the results may be examined by means of a χ^2 test on $\Delta \bar{\mathbf{F}}\mathbf{W} \Delta \mathbf{F}$: if $\Delta \bar{\mathbf{F}}\mathbf{W} \Delta \mathbf{F}$ is less than χ^2 for $n - p + 1$ degrees of freedom and α , the deviations from the assumed symmetry are not significant at level α . Suitable tables of the χ^2 distribution are available in most statistical references (*e.g.* Hamilton, 1964).

Example

A good example for illustrating the method of computation is afforded by the chromate oxygen atoms in sodium chromate tetrahydrate (Ruben, Olovsson, Zalkin & Templeton, 1973), in which the oxygen tetrahedron is appreciably distorted from regularity by, presumably, hydrogen bonding and packing effects. The crystals are monoclinic with $a = 6.186$, $b = 11.165$, $c = 12.20$ Å, $\beta = 104.95^\circ$. Table 1 lists the reported coordinates of the atoms in a chromate ion. For each calculation the weight matrix was the diagonal matrix with elements $1/\sigma_i^2$, where σ_i is the standard deviation given in parentheses in Table 1.

Table 1. *Coordinates of chromate atoms in Na₂CrO₄·4H₂O*

	x^1	x^2	x^3
Cr	0.2644 (2)	0.4003 (9)	0.2400 (9)
O(1)	0.3750 (8)	0.4286 (5)	0.3734 (4)
O(2)	0.3392 (8)	0.2641 (4)	0.2122 (4)
O(3)	0.3473 (8)	0.4939 (5)	0.1596 (4)
O(4)	-0.0146 (7)	0.4086 (5)	0.2137 (4)

Estimated standard deviations of the last digit are given in parentheses.

Table 2. *Fit of threefold axis to O(1)–O(2)–O(3)*

	Observed coordinates			Calculated coordinates		
	x^1	x^2	x^3	x^1	x^2	x^3
O(1)	0.0212	0.0538	0.1250	0.0197	0.0357	0.1252
O(2)	-0.0146	-0.1107	-0.0362	-0.0170	-0.1341	-0.0349
O(3)	-0.0065	0.1191	-0.0888	-0.0070	0.0985	-0.0907

Table 3. *Fit of 3 and $\bar{4}$ symmetry operators to chromate oxygen atoms*

Symmetry	Atoms	u^1	u^2	u^3	$\Delta\bar{F}W\Delta F$
3	O(1)–O(2)–O(3)	0.1667	-0.0037	0.0158	3.19×10^3
3	O(1)–O(2)–O(4)	0.0571	0.0605	-0.0461	1.47×10^3
3	O(1)–O(3)–O(4)	-0.0436	0.0828	0.0171	1.76×10^3
3	O(2)–O(3)–O(4)	0.0687	0.0213	0.0811	3.62×10^3
$\bar{4}$	O(1)–O(2)–O(4)–O(3)	-0.0850	0.0203	0.0570	81.4
$\bar{4}$	O(1)–O(3)–O(2)–O(4)	0.0829	-0.0516	0.0641	5.50×10^3
$\bar{4}$	O(1)–O(2)–O(3)–O(4)	-0.1011	-0.0654	-0.0393	4.89×10^3

Table 2 shows the result of the computation for a threefold axis relating the coordinates of atoms O(1), O(2), and O(3). The coordinates were shifted by subtracting the weighted means of the coordinates of these three atoms. The severe distortions from tetrahedral symmetry led to substantially poorer fits if the origin specification was based upon all five atoms of the anion, so only the atoms related by the particular symmetry operation were included in each case. For O(1)–O(2)–O(3) the best symmetry axis was found to be in the crystal direction [0.1667, -0.0037, 0.0158], which is at an angle of 0.8° with the Cr–O(4) direction.

Table 3 shows the derived unit vector and the degree of fit for each of the 3 and $\bar{4}$ symmetry axes that would relate the oxygen atoms in an anion of perfect tetrahedral symmetry. The order of listing the atoms in the $\bar{4}$ rows of Table 3 is the order in which successive applications of the $\bar{4}$ operator would generate the atoms. With seven degrees of freedom the probability that $\Delta\bar{F}W\Delta F$ be as high as 81.4 by chance is about 1×10^{-9} , so the probability is vanishingly small in each

case that the deviations from the assumed symmetry are not real; that is, it is virtually certain that the distortions are real.

The numerical calculations reveal that convergence occurs even if the initial choice of \mathbf{u} is far removed from the correct orientation. In one case, an incorrect vector was rotated 180° in the course of several iterations. Convergence of such extreme situations is not reliable, but the computation invariably converged if \mathbf{u} started within 60° of its final orientation.

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