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Transformations of Variance-Covariance Tensors

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The variances and covariances of atomic coordinates are elements of second-rank contravariant tensors. The effects of transformations of axes, symmetry operations, and shifts of origin have been determined. Formulas have been derived for calculating the variances and covariances of bond lengths and angles. The principal axes of variance–covariance ellipsoids have been determined, and a method has been obtained for calculating the minimum variance weighted mean of correlated variables.

Introduction

The variance of a function f of a set of atomic parameters x^i is given by

$$\sigma^2(f)=\Sigma\frac{\partial f}{\partial x^i}\frac{\partial f}{\partial x^j}\operatorname{cov}(x^i,x^j) \qquad (1)$$

where the summation is over all parameters included in f. The quantity $\operatorname{cov}(x^i, x^j)$ is the covariance of x^i and x^j if these are different parameters; it is the variance of x^i if $i=j$. This equation is strictly valid for linear functions, but it is still useful for slowly varying non-linear functions (Arley & Buch, 1950). The v.c. (variance-covariance) matrix can be obtained from the least-squares inverse matrix (Hamilton, 1964).

If f is a function of crystallographically equivalent atoms, certain parameters will be linearly related to others, and the corresponding covariances will be non-zero. The covariances between the parameters of a single atom may also be non-zero; this will be the case if symmetry imposes a relationship between the parameters, but it is also true of an atom in a general position in an oblique coordinate system (Templeton, 1959). Even crystallographically independent parameters in an orthogonal system may not be statistically independent, and the covariances will not be exactly zero.

If f is a scalar function, the derivatives in (1) with respect to contravariant vector components are the covariant* components of a vector. The invariance of $\sigma^2(f)$ with respect to linear transformation is proof that the v.c. matrix of the atomic coordinates is a second-rank contravariant tensor (*International Tables for X-ray Crystallography*, 1959). That is, v.c. matrices transform in the same way as products of coordinates.

Among the functions of crystallographic interest are bond lengths and bond angles. Frequently, the parameters used in computing these distances and angles are not those obtained directly in the structure determination, for which the complete v.c. matrix is presumed known, but are generated from these parameters by application of certain symmetry operators of the space group. The variance of f may be computed from the original v.c. matrix if the derivatives in (1) are evaluated with respect to the original parameters (Busing, Martin & Levy, 1964). Alternatively, the derivatives can be evaluated with respect to the transformed coordinates; in this case the transformed v.c. matrix must be used. These transformations are among the topics discussed in this paper.

A generalization of (1) is

$$\operatorname{cov}(f_k,f_l)=\Sigma\frac{\partial f_k}{\partial x^i}\frac{\partial f_l}{\partial x^j}\operatorname{cov}(x^i,x^j) \qquad (2)$$

where the summation is over all parameters x^i and x^j included in the functions f_k and f_l. The transformation properties of v.c. matrices are implicit in this formula. In matrix notation

$$\mathbf{F}=\mathbf{D}\,\mathbf{V}\,\bar{\mathbf{D}} \qquad (3)$$

where $\operatorname{cov}(f_k,f_l)$ is the klth element of $\mathbf{F}$, $\partial f_i/\partial x^j$ is the ijth element of $\mathbf{D}$, $\mathbf{V}$ is the v.c. matrix of the parameters, and $\bar{\mathbf{D}}$ is the transpose of $\mathbf{D}$.

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* *Covariance* is both a differential geometry term which describes transformation properties and a statistical term for a measure of correlation. The intended meaning will be apparent from the context.

Magnitude of variance in a given direction

Let $\mathbf{V}$ be the 3×3 v.c. matrix of an atom [ijth element $=\operatorname{cov}(x^i, x^j)$]. The magnitude of $\mathbf{V}$ in the direction specified by the covariant vector components (h_1, h_2, h_3) of vector $\mathbf{h}$ is $\bar{\mathbf{h}}\,\mathbf{V}\,\mathbf{h}/h^2$, where h is the length of $\mathbf{h}$. If the vector is expressed in terms of the contravariant components (x^1, x^2, x^3) of vector $\mathbf{x}$ of length l, the magnitude is $\bar{\mathbf{x}}\,\mathbf{g}\,\mathbf{V}\,\mathbf{g}\,\mathbf{x}/l^2$, where $\mathbf{g}$ is the metric tensor with ijth element

$$g_{ij}=\mathbf{a}_i\,.\,\mathbf{a}_j\,. \tag{4}$$

Symmetry applied to one of a pair of atoms

Let $\mathbf{V}$ be the 6×6 v.c. matrix for atoms A and B. We can write

$$\mathbf{V}=\begin{pmatrix}\mathbf{V}_{AA} & \mathbf{V}_{AB}\\ \mathbf{V}_{BA} & \mathbf{V}_{BB}\end{pmatrix} \tag{5}$$

where $\mathbf{V}_{AA}$, $\mathbf{V}_{AB}$, $\mathbf{V}_{BA}$, $\mathbf{V}_{BB}$ are 3×3 matrices with ijth elements $\operatorname{cov}(x_A^i, x_A^j)$, $\operatorname{cov}(x_A^i, x_B^j)$, $\operatorname{cov}(x_B^i, x_A^j)$, $\operatorname{cov}(x_B^i, x_B^j)$, respectively. Let B' be generated from B by symmetry operator $\mathbf{S}$. That is,

$$\mathbf{x}_{B'}=\mathbf{S}\,\mathbf{x}_B\,. \tag{6}$$

Let

$$f^i=x_A^i,\ \text{for } i=1,2,3 \tag{7}$$

$$f^k=\sum_j S_j^i\,x_B^j,\ \text{for } k=4,5,6,\ i=k-3 \tag{8}$$

where S_j^i is the ijth element of $\mathbf{S}$. The 6×6 matrix $\mathbf{D}$ can be conveniently written

$$\mathbf{D}=\begin{pmatrix}\mathbf{I} & \mathbf{O}\\ \mathbf{O} & \mathbf{S}\end{pmatrix} \tag{9}$$

where $\mathbf{I}$ and $\mathbf{O}$ are, respectively, the unit matrix and the null matrix. When (5) and (9) are inserted in (3) the result is

$$\begin{pmatrix}\mathbf{V}_{AA} & \mathbf{V}_{AB'}\\ \mathbf{V}_{B'A} & \mathbf{V}_{B'B'}\end{pmatrix}=\begin{pmatrix}\mathbf{V}_{AA} & \mathbf{V}_{AB}\,\bar{\mathbf{S}}\\ \mathbf{S}\,\mathbf{V}_{BA} & \mathbf{S}\,\mathbf{V}_{BB}\,\bar{\mathbf{S}}\end{pmatrix}. \tag{10}$$

Symmetry applied to both atoms

If symmetry operator $\mathbf{S}$ is applied to both atoms A and B to give A' and B',

$$\mathbf{D}=\begin{pmatrix}\mathbf{S} & \mathbf{O}\\ \mathbf{O} & \mathbf{S}\end{pmatrix} \tag{11}$$

and

$$\begin{pmatrix}\mathbf{V}_{A'A'} & \mathbf{V}_{A'B'}\\ \mathbf{V}_{B'A'} & \mathbf{V}_{B'B'}\end{pmatrix}=\begin{pmatrix}\mathbf{S}\,\mathbf{V}_{AA}\,\bar{\mathbf{S}} & \mathbf{S}\,\mathbf{V}_{AB}\,\bar{\mathbf{S}}\\ \mathbf{S}\,\mathbf{V}_{BA}\,\bar{\mathbf{S}} & \mathbf{S}\,\mathbf{V}_{BB}\,\bar{\mathbf{S}}\end{pmatrix}. \tag{12}$$

Covariances between vector components

Let $\mathbf{V}$ be the 9×9 v.c. matrix for the coordinates (x_A^1, x_A^2, x_A^3), (x_B^1, x_B^2, x_B^3), (x_C^1, x_C^2, x_C^3) of atoms A, B, C. As in (5) we can write $\mathbf{V}$ in terms of 3×3 matrices

$$\mathbf{V}=\begin{pmatrix}\mathbf{V}_{AA} & \mathbf{V}_{AB} & \mathbf{V}_{AC}\\ \mathbf{V}_{BA} & \mathbf{V}_{BB} & \mathbf{V}_{BC}\\ \mathbf{V}_{CA} & \mathbf{V}_{CB} & \mathbf{V}_{CC}\end{pmatrix}. \tag{13}$$

We choose the functions

$$\begin{aligned}u_1^i&=x_A^i-x_B^i\\ u_2^i&=x_B^i-x_C^i\\ u_3^i&=x_C^i-x_A^i\end{aligned} \tag{14}$$

so that u_j^i is the ith component of vector j. Then $\mathbf{D}$ is a 9×9 matrix given by

$$\mathbf{D}=\begin{pmatrix}\mathbf{I} & -\mathbf{I} & \mathbf{O}\\ \mathbf{O} & \mathbf{I} & -\mathbf{I}\\ -\mathbf{I} & \mathbf{O} & \mathbf{I}\end{pmatrix}. \tag{15}$$

Equation (3) now gives the 9×9 v.c. matrix for the components of the three vectors A–B, B–C, C–A. For example, the 3×3 v.c. matrix for the components of vector A–B is

$$\mathbf{V}_{AA}-\mathbf{V}_{BA}-\mathbf{V}_{AB}+\mathbf{V}_{BB}$$

with ijth element $\operatorname{cov}(u_1^i, u_1^j)$. The covariances between the components of A–B and B–C are given by

$$\mathbf{V}_{AB}-\mathbf{V}_{BB}-\mathbf{V}_{AC}+\mathbf{V}_{BC}$$

with ijth element $\operatorname{cov}(u_1^i, u_2^j)$; this is a special case of the expression $\mathbf{V}_{AC}-\mathbf{V}_{BC}-\mathbf{V}_{AD}+\mathbf{V}_{BD}$ for the covariances between the components of vectors A–B and C–D.

Transformations of axes

Let $\mathbf{T}$ be a matrix which transforms to a new set of axes

$$\mathbf{a}'=\mathbf{T}\,\mathbf{a}\,. \tag{16}$$

The covariant components h_i of a vector $\mathbf{h}$ also obey this transformation:

$$\mathbf{h}'=\mathbf{T}\,\mathbf{h}\,. \tag{17}$$

The magnitude of a variance–covariance tensor in the direction of the unit vector $\mathbf{h}$ must be invariant under transformation.

$$\bar{\mathbf{h}}'\,\mathbf{V}'\,\mathbf{h}'=\bar{\mathbf{h}}\,\mathbf{V}\,\mathbf{h} \tag{18}$$

$$\bar{\mathbf{h}}\,\bar{\mathbf{T}}\,\mathbf{V}'\,\mathbf{T}\,\mathbf{h}=\bar{\mathbf{h}}\,\mathbf{V}\,\mathbf{h}\,. \tag{19}$$

The transformed v.c. matrix is therefore

$$\mathbf{V}'=\bar{\mathbf{T}}^{-1}\,\mathbf{V}\,\mathbf{T}^{-1}\,. \tag{20}$$

Bond lengths between non-equivalent atoms

Given the 9×9 v.c. matrix for the coordinates of atoms A, B, and C (13), we want to calculate the 3×3 v.c. matrix for the three interatomic distances. If one or more of these atoms was generated by symmetry from the atoms actually involved in the structure determination, either (10) or (12) must first be used.

Some simplification can be achieved by applying (15) to (13) to obtain the v.c. matrix for the components u_i^j of the interatomic vectors $\mathbf{l}_i$, as described above. In terms of these components

$$\mathbf{l}_i=\Sigma_j u_i^j\,\mathbf{a}_j\,. \tag{21}$$

In matrix notation, $\mathbf{l}_i$ is a column vector with components u_i^j. The bond lengths l_1, l_2, l_3 are given by

$$l_i^2 = |\mathbf{l}_i|^2 = \Sigma_{jk} u_i^j u_i^k g_{jk} \,. \tag{22}$$

The desired result is obtained by using l_i in (3). If the v.c. matrix of the vector components is used, the appropriate matrix **D** is of dimension 3 × 9 with elements

$$D_{ij} = \mathbf{l}_i \,.\, \mathbf{a}_k / l_i \tag{23}$$

where $k = j - 3i + 3$ and $D_{ij} = 0$ unless k is 1, 2, or 3. The calculation gives

$$\sigma^2(l_1) = \bar{\mathbf{l}}_1\, \mathbf{g}\, (\mathbf{V}_{AA} - \mathbf{V}_{AB} - \mathbf{V}_{BA} + \mathbf{V}_{BB})\, \mathbf{g}\, \mathbf{l}_1 / l_1^2 \tag{24}$$

$$\begin{aligned} &\operatorname{cov}(l_1, l_2) = \\ &\quad = \bar{\mathbf{l}}_1\, \mathbf{g}\, (\mathbf{V}_{AB} - \mathbf{V}_{AC} - \mathbf{V}_{BB} + \mathbf{V}_{BC})\, \mathbf{g}\, \mathbf{l}_2 / l_1 l_2 \,. \end{aligned} \tag{25}$$

For the special case of uncorrelated atoms $\mathbf{V}_{AB} = \mathbf{V}_{BA} = \mathbf{O}$, and (24) is just the sum of the variances of A and B in the direction of the bond, in agreement with formula 5.2 of Cruickshank & Robertson (1953). However, our equation (25) does not agree with their formula 5.5 for the covariance of the lengths of two bonds with a common atom. Several numerical examples have been used to confirm (25); the result of Cruickshank & Robertson is correct if, in addition to the atoms being uncorrelated, the errors are isotropic.

Bond lengths when atoms are related by symmetry

We again consider the case of three atoms. However, atom B is now generated from atom A by symmetry matrix **S**, as in (6). The v.c. matrix is

$$\begin{aligned} &\begin{pmatrix} \mathbf{I} & \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \mathbf{S} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \mathbf{I} \end{pmatrix} \begin{pmatrix} \mathbf{V}_{AA} & \mathbf{V}_{AA} & \mathbf{V}_{AC} \\ \mathbf{V}_{AA} & \mathbf{V}_{AA} & \mathbf{V}_{AC} \\ \mathbf{V}_{CA} & \mathbf{V}_{CA} & \mathbf{V}_{CC} \end{pmatrix} \begin{pmatrix} \mathbf{I} & \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \bar{\mathbf{S}} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \mathbf{I} \end{pmatrix} \\ &\qquad = \begin{pmatrix} \mathbf{V}_{AA} & \mathbf{V}_{AA}\bar{\mathbf{S}} & \mathbf{V}_{AC} \\ \mathbf{S}\mathbf{V}_{AA} & \mathbf{S}\mathbf{V}_{AA}\bar{\mathbf{S}} & \mathbf{S}\mathbf{V}_{AC} \\ \mathbf{V}_{CA} & \mathbf{V}_{CA}\bar{\mathbf{S}} & \mathbf{V}_{CC} \end{pmatrix} . \end{aligned} \tag{26}$$

The v.c. matrix of the vector components is obtained by using (26) and (15) in (3), and the v.c. matrix for the bond lengths is then derived by applying matrix **D** of (23). The results are

$$\sigma^2(l_1) = \bar{\mathbf{l}}_1\, \mathbf{g}\, (\mathbf{V}_{AA} - \mathbf{S}\mathbf{V}_{AA} - \mathbf{V}_{AA}\bar{\mathbf{S}} + \mathbf{S}\mathbf{V}_{AA}\bar{\mathbf{S}})\mathbf{g}\, \mathbf{l}_1 / l_1^2 \tag{27}$$

$$\sigma^2(l_2) = \bar{\mathbf{l}}_2\, \mathbf{g}\, (\mathbf{S}\mathbf{V}_{AA}\bar{\mathbf{S}} - \mathbf{V}_{AC}\bar{\mathbf{S}} - \mathbf{S}\mathbf{V}_{AC} + \mathbf{V}_{CC})\mathbf{g}\, \mathbf{l}_2 / l_2^2 \tag{28}$$

$$\sigma^2(l_3) = \bar{\mathbf{l}}_3\, \mathbf{g}\, (\mathbf{V}_{AA} - \mathbf{V}_{AC} - \mathbf{V}_{CA} + \mathbf{V}_{CC})\, \mathbf{g}\, \mathbf{l}_3 / l_3^2 \tag{29}$$

$$\begin{aligned} &\operatorname{cov}(l_1, l_2) \\ &\quad = \bar{\mathbf{l}}_1\, \mathbf{g}\, (\mathbf{V}_{AA}\bar{\mathbf{S}} - \mathbf{S}\mathbf{V}_{AA}\bar{\mathbf{S}} - \mathbf{V}_{AC} + \mathbf{S}\mathbf{V}_{AC})\, \mathbf{g}\, \mathbf{l}_2 / l_1 l_2 \end{aligned} \tag{30}$$

$$\begin{aligned} &\operatorname{cov}(l_1, l_3) \\ &\quad = \bar{\mathbf{l}}_1\, \mathbf{g}\, (-\mathbf{V}_{AA} + \mathbf{S}\mathbf{V}_{AA} + \mathbf{V}_{AC} - \mathbf{S}\mathbf{V}_{AC})\, \mathbf{g}\, \mathbf{l}_3 / l_1 l_3 \end{aligned} \tag{31}$$

$$\begin{aligned} &\operatorname{cov}(l_2, l_3) \\ &\quad = \bar{\mathbf{l}}_2\, \mathbf{g}\, (-\mathbf{S}\mathbf{V}_{AA} + \mathbf{V}_{CA} + \mathbf{S}\mathbf{V}_{AC} - \mathbf{V}_{CC})\, \mathbf{g}\, \mathbf{l}_3 / l_2 l_3 \,. \end{aligned} \tag{32}$$

For the special case of A and B related by a center of symmetry, (27) is equivalent to formula 5.3 of Cruickshank & Robertson (1953). However, (30) does not agree with their corresponding formula 5.6 unless the errors are isotropic.

Bond angles*

The angles α_1, α_2, α_3 at A, B, C, respectively, of the triangle ABC with edges $l_1 = AB$, $l_2 = BC$, $l_3 = CA$ are given by

$$\begin{aligned} \alpha_1 &= \cos^{-1} [(l_1^2 + l_3^2 - l_2^2)/2l_1 l_3] \\ \alpha_2 &= \cos^{-1} [(l_1^2 + l_2^2 - l_3^2)/2l_1 l_2] \\ \alpha_3 &= \cos^{-1} [(l_2^2 + l_3^2 - l_1^2)/2l_2 l_3] \,. \end{aligned} \tag{33}$$

The v.c. matrix for these angles is obtained from (3), where the elements of **V** are given by (27)–(32) and the ijth element of **D** is $\partial\alpha_i/\partial l_j$. The results are

$$\begin{aligned} &(l_1 l_3 \sin\alpha_1 / l_2)^2 \sigma^2(\alpha_1) \\ &\qquad = \cos^2\alpha_2 \sigma^2(l_1) - 2\cos\alpha_2 \operatorname{cov}(l_1, l_2) \\ &\qquad + 2\cos\alpha_2 \cos\alpha_3 \operatorname{cov}(l_1, l_3) + \sigma^2(l_2) \\ &\qquad - 2\cos\alpha_3 \operatorname{cov}(l_2, l_3) + \cos^2\alpha_3 \sigma^2(l_3) \end{aligned} \tag{34}$$

$$\begin{aligned} &l_1^2 \sin\alpha_1 \sin\alpha_2 \operatorname{cov}(\alpha_1, \alpha_2) = \cos\alpha_1 \cos\alpha_2 \sigma^2(l_1) \\ &+ (\cos\alpha_2 \cos\alpha_3 - \cos\alpha_1) \operatorname{cov}(l_1, l_2) \\ &+ (\cos\alpha_1 \cos\alpha_3 - \cos\alpha_2) \operatorname{cov}(l_1, l_3) - \cos\alpha_3 \sigma^2(l_2) \\ &+ (1 + \cos^2\alpha_3) \operatorname{cov}(l_2, l_3) - \cos\alpha_3 \sigma^2(l_3) \,. \end{aligned} \tag{35}$$

When the atoms are independent equation (34) is equivalent to Cruickshank & Robertson's formula 5.4.

Covariances of bond angles with bond lengths

Using the nomenclature of the previous section, the covariances of α_1 with the bond lengths may be derived by letting **D** of (3) be the 4 × 3 matrix based on the derivatives of the functions α_1, l_1, l_2, l_3 with respect to l_1, l_2, l_3. Thus,

$$\begin{aligned} &(l_1 l_3 \sin\alpha_1 / l_2) \operatorname{cov}(\alpha_1, l_1) \\ &= -\cos\alpha_2 \sigma^2(l_1) + \operatorname{cov}(l_1, l_2) - \cos\alpha_3 \operatorname{cov}(l_1, l_3) \end{aligned} \tag{36}$$

$$\begin{aligned} &(l_1 l_3 \sin\alpha_1 / l_2) \operatorname{cov}(\alpha_1, l_2) \\ &= -\cos\alpha_2 \operatorname{cov}(l_1, l_2) + \sigma^2(l_2) - \cos\alpha_3 \operatorname{cov}(l_2, l_3). \end{aligned} \tag{37}$$

Equation (36) does not agree with the corresponding formula (5.7) of Cruickshank & Robertson (1953).

Shift of origin

It was pointed out by Templeton (1959, 1960) that the coordinate variances and covariances yielded by least-squares will depend upon which atom is kept fixed. The nature of this dependence may be deduced from our transformation equations. To illustrate, let us ex-

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* See Darlow (1960) for a different derivation of the errors in bond angles.

amine the change in the coordinate v.c. matrix (13) which ensues if the origin is shifted to atom A. The new coordinates of the three atoms are 0, $x^i_B - x^i_A$, and $x^i_C - x^i_A$. The transformation matrix is

$$\mathbf{D} = \begin{pmatrix} \mathbf{O} & \mathbf{O} & \mathbf{O} \\ -\mathbf{I} & \mathbf{I} & \mathbf{O} \\ -\mathbf{I} & \mathbf{O} & \mathbf{I} \end{pmatrix} \tag{38}$$

and application of (3) gives

$$\begin{aligned} \mathbf{V}'_{AA} &= \mathbf{V}'_{AB} = \mathbf{V}'_{AC} = \mathbf{V}'_{BA} = \mathbf{V}'_{CA} = \mathbf{O} \\ \mathbf{V}'_{BB} &= \mathbf{V}_{AA} - \mathbf{V}_{BA} - \mathbf{V}_{AB} + \mathbf{V}_{BB} \\ \mathbf{V}'_{BC} &= \mathbf{V}_{AA} - \mathbf{V}_{BA} - \mathbf{V}_{AC} + \mathbf{V}_{BC} \\ \mathbf{V}'_{CB} &= \mathbf{V}_{AA} - \mathbf{V}_{CA} - \mathbf{V}_{AB} + \mathbf{V}_{CB} \\ \mathbf{V}'_{CC} &= \mathbf{V}_{AA} - \mathbf{V}_{CA} - \mathbf{V}_{AC} + \mathbf{V}_{CC}\,. \end{aligned} \tag{39}$$

All bond length and bond angle variances and covariances must of course be invariant under this transformation. The invariance of the v.c. matrix of the vector components results from the relation

$$\mathbf{D}_1 \mathbf{D}_2 = \mathbf{D}_1 \tag{40}$$

where $\mathbf{D}_1$ is given by (15) and $\mathbf{D}_2$ is given by (38). Translation by a vector with zero error will obviously not change $\mathbf{V}$.

Atoms in special positions

The coordinates of atoms in special positions are either constants or they are linearly related to each other. In the former case the corresponding variances and covariances are zero. If linear relationships exist between the coordinates, a matrix $\mathbf{D}$ can be derived, and conditions on the components of $\mathbf{V}$ can be obtained by the invariance

$$\mathbf{V} = \mathbf{D}\,\mathbf{V}\,\bar{\mathbf{D}}\,. \tag{41}$$

An atom at $(x, 2x, z)$ of space group $P\bar{6}m2$, for example, gives

$$\mathbf{D} = \begin{pmatrix} 1 & 0 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

and the elements of $\mathbf{V}$ obey

$$V_{12} = 2V_{11},\ V_{22} = 4V_{11},\ V_{23} = 2V_{13}\,.$$

Principal axes of variance-covariance ellipsoid

A consequence of the extremum property of the principal axes of an ellipsoid is that the principal axes of a second-rank tensor are invariant in direction under operation by the tensor. When $\mathbf{V}$ is a contravariant tensor

$$\Sigma_j\, V^{ij} v_j = \lambda v^i\,, \tag{42}$$

where v_j and v^i are, respectively, covariant and contravariant components of $\mathbf{v}$. Since

$$v_j = \Sigma_k\, g_{jk} v^k \tag{43a}$$

$$v^i = \Sigma_l\, g^{il} v_l\,, \tag{43b}$$

where the elements g^{il} are given by the matrix reciprocal to (4), we have

$$\sum_{j,k} V^{ij} g_{jk} v^k = \lambda v^i \tag{44a}$$

$$\sum_j V^{ij} v_j = \lambda \sum_l g^{il} v_l\,. \tag{44b}$$

The condition for non-trivial solutions leads to the alternative secular equations

$$\|V^{ij} g_{jk} - \lambda \delta^i_k\| = 0 \tag{45a}$$

$$\|V^{ij} - \lambda g^{ij}\| = 0\,. \tag{45b}$$

Equation (45*b*) was obtained by Waser (1955) for the principal axes of anisotropic temperature factors, and (45*a*) was derived as an alternate solution by Busing & Levy (1958). The result is of course applicable to any second-rank contravariant tensor.

Weighted mean of correlated variables

The weighted mean of a set of variables l_i is given by

$$l = (\Sigma\, w_i l_i)/\Sigma\, w_i\,. \tag{46}$$

Whatever the choice of weights w_i, the variance of l must be computed by (1), which becomes

$$(\Sigma\, w_i)^2 \sigma^2(l) = \sum_{i,j} w_i w_j V_{ij}\,, \tag{47}$$

where V_{ij} is the ijth element of the v.c. matrix of the variables. If the l_i, for example, are chemically equivalent but crystallographically distinct bond lengths involving a common atom, the covariances may be quite large.

The set of weights which lead to the minimum $\sigma^2(l)$ may be obtained by differentiating (47) with respect to a particular w_k and setting $d\sigma^2(l)/dw_k = 0$. This leads to

$$\sigma^2(l)\, \Sigma\, w_i = \sum_i w_i V_{ik} \tag{48}$$

or

$$\Big(\sum_{i,j} w_i w_j V_{ij}\Big)\Big/\Sigma\, w_i = \sum_i w_i V_{ik}\,. \tag{49}$$

An equation of the form of (49) can be written for each k. These are equivalent to

$$\mathbf{v} = \mathbf{V}\,\mathbf{w}\,, \tag{50}$$

where the components of $\mathbf{w}$ are the w_i. Since the left side of (49) does not depend on k, the components of $\mathbf{v}$ satisfy $v_i = v_j$ for all i and j. Only relative weights are needed in (46) and (47), so it is convenient to set $v_i = 1$ for all i. The weights are given by

$$\mathbf{w} = \mathbf{V}^{-1}\,\mathbf{v}\,. \tag{51}$$

The weighted mean may then be obtained from (46), and its variance is readily calculated by (48).

When the variables are uncorrelated, (51) gives weights inversely proportional to the corresponding variances.

For the case of just two correlated variables

$$1/w_i = \sigma^2(l_i) - \operatorname{cov}(l_1, l_2)\ . \qquad (52)$$

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A Description of Various Rotation Function Programs

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Various closely related programs for the calculation of the rotation function are described. The latter explores systematically the amount of overlap between two differently oriented Patterson syntheses, and can be used to relate similar molecules or structures in the same or different crystals. The calculations require only the intensities rather than the Patterson sections. It is shown that (i) neglecting all but 10% of the largest intensities for one of the structures and (ii) construction of a table of the transform G, of the spherical volume within which the Patterson functions are being compared, sampled in a $5\times5\times5$ grid within the reciprocal unit cell, gives considerable improvement in computing time without excess loss of accuracy. The effect of premature truncation or coarseness of the G table is discussed, together with other considerations which are important in the successful application of this technique.

1. Introduction

We shall describe the flow diagram of various closely related programs for the calculation of the rotation function (Rossmann & Blow, 1962) (RB). Even with existing fast computers the time involved in exploring the three rotation angles at reasonable intervals is formidable and a number of techniques are here presented which significantly improve the speed of the computations. We also discuss strategic considerations required in the application of these techniques to various types of problem.

The rotation function is defined (RB) as

$$R = \int_U P_2(\mathbf{x}_2)\ .\ P_1(\mathbf{x}_1)\, d\mathbf{x}_1\ . \qquad (1)$$

It measures the degree of coincidence when the Patterson function P_1 is rotated on the Patterson function P_2. Any point $\mathbf{x}_1$ in P_1 is related to any other point $\mathbf{x}_2$ in P_2 through the rotation matrix [C] by the relationship

$$\mathbf{x}_2 = [\mathbf{C}]\mathbf{x}_1\ .$$

The above integral (1) can be shown (RB) to reduce to the double summation

$$R = \sum_{\mathbf{p}} |F_{\mathbf{p}}|^2 \{\sum_{\mathbf{h}} |F_{\mathbf{h}}|^2\, G_{\mathbf{h},\mathbf{h}'}\} \qquad (2)$$

where $|F_{\mathbf{p}}|$ and $|F_{\mathbf{h}}|$ are the structure amplitudes corresponding to the Patterson functions P_2 and P_1 respectively. $G_{\mathbf{h},\mathbf{h}'}$ is an interference function whose magnitude depends on the reciprocal lattice vectors $\mathbf{h}$ and $\mathbf{h}'$ as well as the volume U within which the integral (1) is evaluated. The non-integral reciprocal lattice vector $\mathbf{h}'$ is given by

$$\mathbf{h}' = \mathbf{p}[\mathbf{C}]\ .$$

The rotation function is particularly useful for the following problems:

(*a*) To determine the relative orientation of identical or similar rigid chemical groups in two different crystals. P_1 and P_2 must then represent the Patterson functions of the two crystals.

(*b*) To determine the orientation of a known rigid group in a molecular crystal. Here P_1 is the Patterson function of the unknown crystal, while P_2 is the Patterson function calculated from a model of rigid group in a known orientation.

(*c*) To determine the relative orientation of identical or similar groups of molecules within the same crystallographic asymmetric unit. Now P_1 and P_2 both represent the same Patterson function of the unknown crystal.

In all cases the integration is performed over the volume U equal to the volume around the origin of the Patter-