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3.1. Distances, angles, and their standard uncertainties

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3.1.1. Introduction

A crystal structure analysis provides information from which it is possible to compute distances between atoms, angles between interatomic vectors, and the uncertainties in these quantities. In Cartesian coordinate systems, these geometric computations require the Pythagorean theorem and elementary trigonometry. The natural coordinate systems of crystals, though, are determined by symmetry, and only in special cases are the basis vectors (or coordinate axes) of these systems constrained to be of equal lengths or mutually perpendicular.

It is possible, of course, to transform the positional parameters of the atoms to a Cartesian system and perform the subsequent calculations with the transformed coordinates. Along with the coordinates, the transformations must be applied to anisotropic thermal factors, variance–covariance matrices and other important quantities. Moreover, leaving the natural coordinate system of the crystal sacrifices the simplified relationships imposed by translational and point symmetry; for example, if an atom has fractional coordinates x^1, x^2, x^3, an equivalent atom will be at $1 + x^1$, x^2, x^3, *etc.*

Fortunately, formulation of the calculations in generalized rectilinear coordinate systems is straightforward, and readily adapted to computer languages (Section 3.1.12 illustrates the use of Fortran for such calculations). The techniques for these computations are those of tensor analysis, which provides a compact and elegant notation. While an effort will be made to be self-sufficient in this chapter, some proficiency in vector algebra is assumed, and the reader not familiar with the basics of tensor analysis should refer to Chapter 1.1 and Sands (1982*a*).

3.1.2. Scalar product

The scalar product of vectors **u** and **v** is defined as

$$\mathbf{u} \cdot \mathbf{v} = uv \cos\varphi, \tag{3.1.2.1}$$

where u and v are the lengths of the vectors and φ is the angle between them. In terms of components,

$$\mathbf{u} \cdot \mathbf{v} = (u^i \mathbf{a}_i) \cdot (v^j \mathbf{a}_j) \tag{3.1.2.2}$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j \mathbf{a}_i \cdot \mathbf{a}_j \tag{3.1.2.3}$$

$$\mathbf{u} \cdot \mathbf{v} = u^i v^j g_{ij}. \tag{3.1.2.4}$$

In all equations in this chapter, the convention is followed that summation is implied over an index that is repeated once as a subscript and once as a superscript in an expression; thus, the right-hand side of (3.1.2.4) implies the sum of nine terms

$$u^1 v^1 g_{11} + u^1 v^2 g_{12} + \ldots + u^3 v^3 g_{33}.$$

The g_{ij} in (3.1.2.4) are the components of the metric tensor [see Chapter 1.1 and Sands (1982*a*)]

$$g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j. \tag{3.1.2.5}$$

Subscripts are used for quantities that transform the same way as the basis vectors $\mathbf{a}_i$; such quantities are said to transform covariantly. Superscripts denote quantities that transform the same way as coordinates x^i; these quantities are said to transform contravariantly (Sands, 1982*a*).

Equation (3.1.2.4) is in a form convenient for computer evaluation, with indices i and j taking successively all values from 1 to 3. The matrix form of (3.1.2.4) is useful both for symbolic manipulation and for computation,

$$\mathbf{u} \cdot \mathbf{v} = \boldsymbol{u}^T \boldsymbol{g} \boldsymbol{v}, \tag{3.1.2.6}$$

where the superscript italic T following a matrix symbol indicates a transpose. Written out in full, (3.1.2.6) is

$$\mathbf{u} \cdot \mathbf{v} = (u^1 u^2 u^3) \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} \begin{pmatrix} v^1 \\ v^2 \\ v^3 \end{pmatrix}. \tag{3.1.2.7}$$

If $\boldsymbol{u}$ is the column vector with components u^1, u^2, u^3, $\boldsymbol{u}^T$ is the corresponding row vector shown in (3.1.2.7).

3.1.3. Length of a vector

By (3.1.2.1), the scalar product of a vector with itself is

$$\mathbf{v} \cdot \mathbf{v} = (v)^2. \tag{3.1.3.1}$$

The length of **v** is, therefore, given by

$$v = (v^i v^j g_{ij})^{1/2}. \tag{3.1.3.2}$$

Computation of lengths in a generalized rectilinear coordinate system is thus simply a matter of evaluating the double summation $v^i v^j g_{ij}$ and taking the square root.

3.1.4. Angle between two vectors

By (3.1.2.1) and (3.1.2.4), the angle φ between vectors **u** and **v** is given by

$$\varphi = \cos^{-1}[u^i v^j g_{ij}/(uv)]. \tag{3.1.4.1}$$

An even more concise expression of equations such as (3.1.4.1) is possible by making use of the ability of the metric tensor $\boldsymbol{g}$ to convert components from contravariant to covariant (Sands, 1982*a*). Thus,

$$v_i = g_{ij} v^j, \quad u_j = g_{ij} u^i, \tag{3.1.4.2}$$

and (3.1.2.4) may be written succinctly as

$$\mathbf{u} \cdot \mathbf{v} = u^i v_i \tag{3.1.4.3}$$

or

$$\mathbf{u} \cdot \mathbf{v} = u_i v^i. \tag{3.1.4.4}$$

With this notation, the angle calculation of (3.1.4.1) becomes

$$\varphi = \cos^{-1}[u^i v_i/(uv)] = \cos^{-1}[u_i v^i/(uv)]. \tag{3.1.4.5}$$

The summations in (3.1.4.3), (3.1.4.4) and (3.1.4.5) include only three terms, and are thus equivalent in numerical effort to the computation in a Cartesian system, in which the metric tensor is represented by the unit matrix and there is no numerical distinction between covariant components and contravariant components.

Appreciation of the elegance of tensor formulations may be enhanced by noting that corresponding to the metric tensor $\boldsymbol{g}$ with components g_{ij} there is a contravariant metric tensor $\boldsymbol{g}^*$ with components

$$g^{ij} = \mathbf{a}^i \cdot \mathbf{a}^j. \tag{3.1.4.6}$$

The $\mathbf{a}^i$ are contravariant basis vectors, known to crystallographers as reciprocal axes. Expressions parallel to (3.1.4.2) may be written, in which $\boldsymbol{g}^*$ plays the role of converting covariant components to contravariant components. These tensors thus express mathematically the crystallographic notions of crystal space and reciprocal space [see Chapter 1.1 and Sands (1982*a*)].

3.1.5. Vector product

The scalar product defined in Section 3.1.2 is one multiplicative operation of two vectors that may be defined; another is the vector product, which is denoted as $\mathbf{u} \wedge \mathbf{v}$ (or $\mathbf{u} \times \mathbf{v}$ or $[\mathbf{uv}]$). The vector product of vectors $\mathbf{u}$ and $\mathbf{v}$ is defined as a vector of length $uv \sin\varphi$, where φ is the angle between the vectors, and of direction perpendicular to both $\mathbf{u}$ and $\mathbf{v}$ in the sense that $\mathbf{u}$, $\mathbf{v}$ and $\mathbf{u} \wedge \mathbf{v}$ form a right-handed system; $\mathbf{u} \wedge \mathbf{v}$ is generated by rotating $\mathbf{u}$ into $\mathbf{v}$ and advancing in the direction of a right-handed screw. The magnitude of $\mathbf{u} \wedge \mathbf{v}$, given by

$$|\mathbf{u} \wedge \mathbf{v}| = uv \sin\varphi \tag{3.1.5.1}$$

is equal to the area of the parallelogram defined by $\mathbf{u}$ and $\mathbf{v}$.

It follows from the definition that

$$\mathbf{u} \wedge \mathbf{v} = -\mathbf{v} \wedge \mathbf{u}. \tag{3.1.5.2}$$

3.1.6. Permutation tensors

Many relationships involving vector products may be expressed compactly and conveniently in terms of the permutation tensors, defined as

$$\varepsilon_{ijk} = \mathbf{a}_i \cdot \mathbf{a}_j \wedge \mathbf{a}_k \tag{3.1.6.1}$$

$$\varepsilon^{ijk} = \mathbf{a}^i \cdot \mathbf{a}^j \wedge \mathbf{a}^k. \tag{3.1.6.2}$$

Since $\mathbf{a}_i \cdot \mathbf{a}_j \wedge \mathbf{a}_k$ represents the volume of the parallelepiped defined by vectors $\mathbf{a}_i$, $\mathbf{a}_j$, $\mathbf{a}_k$, it follows that ε_{ijk} vanishes if any two indices are equal to each other. The same argument applies, of course, to ε^{ijk}. That is,

$$\varepsilon_{ijk} = 0, \quad \varepsilon^{ijk} = 0, \quad \text{if } j = i \text{ or } k = i \text{ or } k = j. \tag{3.1.6.3}$$

If the indices are all different,

$$\varepsilon_{ijk} = PV, \quad \varepsilon^{ijk} = PV^* \tag{3.1.6.4}$$

for even permutations of *ijk* (123, 231, or 312), and

$$\varepsilon_{ijk} = -PV, \quad \varepsilon^{ijk} = -PV^* \tag{3.1.6.5}$$

for odd permutations (132, 213, or 321). Here, $P = +1$ for right-handed axes, $P = -1$ for left-handed axes, V is the unit-cell volume, and $V^* = 1/V$ is the volume of the reciprocal cell defined by the reciprocal basis vectors $\mathbf{a}^i$, $\mathbf{a}^j$, $\mathbf{a}^k$.

A discussion of the properties of the permutation tensors may be found in Sands (1982*a*). In right-handed Cartesian systems, where $P = 1$, and $V = V^* = 1$, the permutation tensors are equivalent to the permutation symbols denoted by e_{ijk}.

3.1.7. Components of vector product

As is shown in Sands (1982*a*), the components of the vector product $\mathbf{u} \wedge \mathbf{v}$ are given by

$$\mathbf{u} \wedge \mathbf{v} = \varepsilon_{ijk} u^i v^j \mathbf{a}^k, \tag{3.1.7.1}$$

where again $\mathbf{a}^k$ is a reciprocal basis vector (some writers use $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ to represent the reciprocal axes). A special case of (3.1.7.1) is

$$\mathbf{a}_i \wedge \mathbf{a}_j = \varepsilon_{ijk} \mathbf{a}^k, \tag{3.1.7.2}$$

which may be taken as a defining equation for the reciprocal basis vectors. Similarly,

$$\mathbf{a}^i \wedge \mathbf{a}^j = \varepsilon^{ijk} \mathbf{a}_k, \tag{3.1.7.3}$$

which completes the characterization of the dual vector system with basis vectors $\mathbf{a}_i$ and $\mathbf{a}^j$ obeying

$$\mathbf{a}_i \cdot \mathbf{a}^j = \delta_i^j. \tag{3.1.7.4}$$

In (3.1.7.4), δ_i^j is the Kronecker delta, which equals 1 if $i = j$, 0 if $i \neq j$. The relationships between these quantities are explored at some length in Sands (1982*a*).

3.1.8. Some vector relationships

The results developed above lead to several useful relationships between vectors; for derivations, see Sands (1982*a*).

3.1.8.1. Triple vector product

$$\mathbf{u} \wedge (\mathbf{v} \wedge \mathbf{w}) = (\mathbf{u} \cdot \mathbf{w})\mathbf{v} - (\mathbf{u} \cdot \mathbf{v})\mathbf{w} \tag{3.1.8.1}$$

$$(\mathbf{u} \wedge \mathbf{v}) \wedge \mathbf{w} = -(\mathbf{v} \cdot \mathbf{w})\mathbf{u} + (\mathbf{u} \cdot \mathbf{w})\mathbf{v}. \tag{3.1.8.2}$$

3.1.8.2. Scalar product of vector products

$$(\mathbf{u} \wedge \mathbf{v}) \cdot (\mathbf{w} \wedge \mathbf{z}) = (\mathbf{u} \cdot \mathbf{w})(\mathbf{v} \cdot \mathbf{z}) - (\mathbf{u} \cdot \mathbf{z})(\mathbf{v} \cdot \mathbf{w}). \quad (3.1.8.3)$$

A derivation of this result may be found also in Shmueli (1974).

3.1.8.3. Vector product of vector products

$$(\mathbf{u} \wedge \mathbf{v}) \wedge (\mathbf{w} \wedge \mathbf{z}) = (\mathbf{u} \cdot \mathbf{w} \wedge \mathbf{z})\mathbf{v} - (\mathbf{v} \cdot \mathbf{w} \wedge \mathbf{z})\mathbf{u} \quad (3.1.8.4)$$

$$(\mathbf{u} \wedge \mathbf{v}) \wedge (\mathbf{w} \wedge \mathbf{z}) = (\mathbf{u} \cdot \mathbf{v} \wedge \mathbf{z})\mathbf{w} - (\mathbf{u} \cdot \mathbf{v} \wedge \mathbf{w})\mathbf{z}. \quad (3.1.8.5)$$

3.1.9. Planes

Among several ways of characterizing a plane in a general rectilinear coordinate system is a description in terms of the coordinates of three non-collinear points that lie in the plane. If the points are U, V and W, lying at the ends of vectors **u**, **v** and **w**, the vectors $\mathbf{u} - \mathbf{v}$, $\mathbf{v} - \mathbf{w}$ and $\mathbf{w} - \mathbf{u}$ are in the plane. The vector

$$\mathbf{z} = (\mathbf{u} - \mathbf{v}) \wedge (\mathbf{v} - \mathbf{w}) \quad (3.1.9.1)$$

is normal to the plane. Expansion of (3.1.9.1) yields

$$\mathbf{z} = (\mathbf{u} \wedge \mathbf{v}) + (\mathbf{v} \wedge \mathbf{w}) + (\mathbf{w} \wedge \mathbf{u}). \quad (3.1.9.2)$$

Making use of (3.1.7.1),

$$\mathbf{z} = \varepsilon_{ijk}(u^j v^k + v^j w^k + w^j u^k)\mathbf{a}^i. \quad (3.1.9.3)$$

If now **x** is any vector from the origin to the plane, $\mathbf{x} - \mathbf{u}$ is in the plane, and

$$(\mathbf{x} - \mathbf{u}) \cdot \mathbf{z} = 0. \quad (3.1.9.4)$$

From (3.1.9.2),

$$\mathbf{u} \cdot \mathbf{z} = \mathbf{u} \cdot \mathbf{v} \wedge \mathbf{w}. \quad (3.1.9.5)$$

Rearrangement of (3.1.9.4) with $\mathbf{x} \cdot \mathbf{z}$ on the left and $\mathbf{u} \cdot \mathbf{z}$ on the right, and using (3.1.9.3) for **z** on the left leads to

$$\varepsilon_{ijk}x^i(u^j v^k + v^j w^k + w^j u^k) = \varepsilon_{ijk}u^i v^j w^k. \quad (3.1.9.6)$$

If, in particular, the points are on the coordinate axes, their designations are $[u^1, 0, 0]$, $[0, v^2, 0]$ and $[0, 0, w^3]$, and (3.1.9.6) becomes

$$x^1/u^1 + x^2/v^2 + x^3/w^3 = 1, \quad (3.1.9.7)$$

which may be written

$$x^i h_i = 1 \quad (3.1.9.8)$$

or

$$\mathbf{x} \cdot \mathbf{h} = 1 \quad (3.1.9.9)$$

in which the vector **h** has coordinates

$$\mathbf{h} = (1/u^1, 1/v^2, 1/w^3). \quad (3.1.9.10)$$

That is, the covariant components of **h** are given by the reciprocals of the intercepts of the plane on the axes. The vector **h** is normal to the plane it describes (Sands, 1982*a*) and the length of **h** is the reciprocal of the distance d of the plane from the origin; *i.e.*,

$$h = 1/d. \quad (3.1.9.11)$$

If the indices h_i are relatively prime integers, the theory of numbers tells us that the Diophantine equation (3.1.9.8) has solutions x^i that are integers. Points whose contravariant components are integers are lattice points, and such a plane passes through an infinite number of lattice points and is called a *lattice plane*. Thus, the h_i for lattice planes are the familiar Miller indices of crystallography.

Calculations involving planes become quite manageable when the normal vector **h** is introduced. Thus, the distance l from a point P with coordinates p^i to a plane characterized by **h** is

$$l = (1 - \mathbf{p} \cdot \mathbf{h})/h, \quad (3.1.9.12)$$

where a negative sign indicates that the point is on the opposite side of the plane from the origin.

The dihedral angle τ between planes with normals **h** and $\mathbf{h}'$ is

$$\tau = \cos^{-1}[-\mathbf{h} \cdot \mathbf{h}'/(hh')]. \quad (3.1.9.13)$$

A variation of (3.1.9.13) expresses τ in terms of vector **u** in the first plane, vector **w** in the second plane, and vector **v**, the intersection of the planes, as (Shmueli, 1974)

$$\tau = \cos^{-1}[(\mathbf{u} \wedge \mathbf{v}) \cdot (\mathbf{v} \wedge \mathbf{w})/|\mathbf{u} \wedge \mathbf{v}||\mathbf{v} \wedge \mathbf{w}|]. \quad (3.1.9.14)$$

A similar calculation gives angles of torsion. Let $\mathbf{t}_h$ and $\mathbf{u}_h$ be, respectively, the projections of vectors **t** and **u** onto the plane with normal **h**.

$$\mathbf{t}_h = \mathbf{t} - (\mathbf{t} \cdot \mathbf{h})\mathbf{h}/h^2 \quad (3.1.9.15)$$

$$\mathbf{u}_h = \mathbf{u} - (\mathbf{u} \cdot \mathbf{h})\mathbf{h}/h^2. \quad (3.1.9.16)$$

The angle between $\mathbf{t}_h$ and $\mathbf{u}_h$ represents a torsion about **h** (Sands, 1982*b*). Another approach to the torsion angle, which gives equivalent results (Shmueli, 1974), is to compute the angle between $\mathbf{t} \wedge \mathbf{h}$ and $\mathbf{u} \wedge \mathbf{h}$ using (3.1.8.3).

3.1.10. Variance–covariance matrices

Refinement of a crystal structure yields both the parameters that describe the structure and estimates of the uncertainties of those parameters. Refinement by the method of least squares minimizes a weighted sum of squares of residuals. In the matrix notation of Hamilton's classic book (Hamilton, 1964), values of

the m parameters to be determined are expressed by the $m \times 1$ column vector $\boldsymbol{X}$ given by

$$\boldsymbol{X} = (\boldsymbol{A}^T\boldsymbol{P}\boldsymbol{A})^{-1}\boldsymbol{A}^T\boldsymbol{P}\boldsymbol{F}, \tag{3.1.10.1}$$

where $\boldsymbol{F}$ is an $n \times 1$ matrix representing the observations (structure factors or squares of structure factors), $\boldsymbol{P}$ is an $n \times n$ weight matrix that is proportional to the variance–covariance matrix of the observed $\boldsymbol{F}$, $\boldsymbol{A}$ is an $n \times m$ design matrix consisting of the derivatives of each element of $\boldsymbol{F}$ with respect to each of the parameters and $\boldsymbol{A}^T$ is the transpose of $\boldsymbol{A}$. The variance–covariance matrix of the parameters is then given by

$$\boldsymbol{M} = \boldsymbol{V}^T\boldsymbol{P}\boldsymbol{V}(\boldsymbol{A}^T\boldsymbol{P}\boldsymbol{A})^{-1}/(n-m). \tag{3.1.10.2}$$

Here, $\boldsymbol{V}$ is the $n \times 1$ matrix of residuals, consisting of the differences between the observed and calculated values of the elements of $\boldsymbol{F}$. Since $\boldsymbol{V}^T\boldsymbol{P}\boldsymbol{V}/(n-m)$ is just a single number, $\boldsymbol{M}$ is proportional to the inverse least-squares matrix $(\boldsymbol{A}^T\boldsymbol{P}\boldsymbol{A})^{-1}$.

Once the variance–covariance matrix of the parameters is known, the variances and covariances of any quantities derived from these parameters can be computed. The variance of a single function f is given by

$$\sigma^2(f) = \frac{\partial f}{\partial x^i}\frac{\partial f}{\partial x^j}\mathrm{cov}(x^i, x^j), \tag{3.1.10.3}$$

where, as usual, we are using the summation convention and summing over all parameters included in f. A generalization of (3.1.10.3) for two functions is

$$\mathrm{cov}(f_1, f_2) = \frac{\partial f_1}{\partial x^i}\frac{\partial f_2}{\partial x^j}\mathrm{cov}(x^i, x^j). \tag{3.1.10.4}$$

[The covariance of two quantities is, of course, just the variance if the two quantities are the same. For an elementary discussion of statistical covariance and correlation, see Sands (1977).] Equation (3.1.10.4) may now be extended to any number of functions (Sands, 1966); the $k \times k$ variance–covariance matrix $\boldsymbol{C}$ of k functions of m parameters is given in terms of the $m \times m$ variance–covariance matrix of the parameters by

$$\boldsymbol{C} = \boldsymbol{D}\boldsymbol{M}\boldsymbol{D}^T, \tag{3.1.10.5}$$

in which the ijth element of the $k \times m$ matrix $\boldsymbol{D}$ is the derivative of function f_i with respect to parameter j. Element C_{II} (no summation implied over I) is the variance of function f_I, and C_{IJ} is the covariance of functions f_I and f_J.

The calculation of $\boldsymbol{C}$ must, of course, include the contributions of all sources of error, so $\boldsymbol{M}$ in (3.1.10.5) should include the variances and covariances of the unit-cell dimensions and of any other relevant parameters with non-negligible uncertainties.

It may be easier, in some cases, to carry out calculations of variances and covariances in steps. For example, the variance–covariance matrix of a set of distances may be computed and then other quantities may be determined as functions of the distances. It is imperative that all nonvanishing covariances be included in every stage of the calculation; only in special cases are the covariances negligible, and often they are large enough to affect the results seriously (Sands, 1977).

These principles may be used to explore the effects of symmetry or of transformations on the variance–covariance matrices of atomic parameters and derived quantities. Using the notation of Sands (1966), with x_A^i and x_B^i the positional parameters i of atoms A and B, respectively, we define $\boldsymbol{M}_{AA}$, $\boldsymbol{M}_{AB}$, $\boldsymbol{M}_{BA}$ and $\boldsymbol{M}_{BB}$ as 3×3 matrices with ijth elements $\mathrm{cov}(x_A^i, x_A^j)$, $\mathrm{cov}(x_A^i, x_B^j)$, $\mathrm{cov}(x_B^i, x_A^j)$ and $\mathrm{cov}(x_B^i, x_B^j)$, respectively. If atom B' is generated from atom B by symmetry operator $\boldsymbol{S}$, such that

$$\mathbf{x}_{B'} = \boldsymbol{S}\mathbf{x}_B \tag{3.1.10.6}$$

$$x_{B'}^i = S_j^i x_B^j, \tag{3.1.10.7}$$

it is shown in Sands (1966) that the variance–covariance matrices involving atom B' are

$$\boldsymbol{M}_{AB'} = \boldsymbol{M}_{AB}\boldsymbol{S}^T \tag{3.1.10.8}$$

$$\boldsymbol{M}_{B'A} = \boldsymbol{S}\boldsymbol{M}_{BA} \tag{3.1.10.9}$$

$$\boldsymbol{M}_{B'B'} = \boldsymbol{S}\boldsymbol{M}_{BB}\boldsymbol{S}^T. \tag{3.1.10.10}$$

If symmetry operator $\boldsymbol{S}$ is applied to both atoms A and B to generate atoms A' and B', the corresponding matrices may be expressed by the matrix equation

$$\begin{pmatrix} \boldsymbol{M}_{A'A'} & \boldsymbol{M}_{A'B'} \\ \boldsymbol{M}_{B'A'} & \boldsymbol{M}_{B'B'} \end{pmatrix} = \begin{pmatrix} \boldsymbol{S}\boldsymbol{M}_{AA}\boldsymbol{S}^T & \boldsymbol{S}\boldsymbol{M}_{AB}\boldsymbol{S}^T \\ \boldsymbol{S}\boldsymbol{M}_{BA}\boldsymbol{S}^T & \boldsymbol{S}\boldsymbol{M}_{BB}\boldsymbol{S}^T \end{pmatrix}. \tag{3.1.10.11}$$

If $\boldsymbol{G}$ is a matrix that transforms to a new set of axes,

$$\mathbf{a}' = \boldsymbol{G}\mathbf{a}, \tag{3.1.10.12}$$

the transformed variance–covariance matrix of the atomic parameters is

$$\boldsymbol{M}' = (\boldsymbol{G}^{\boldsymbol{T}})^{-1}\boldsymbol{M}\boldsymbol{G}^{-1}. \tag{3.1.10.13}$$

To apply these formulae to calculations of the errors and covariances of interatomic distances and angles, consider the triangle of atoms A, B, C with edges $l_1 = AB$, $l_2 = BC$, $l_3 = CA$, and angles $\alpha_1, \alpha_2, \alpha_3$ at A, B, C, respectively. If the atoms are not related by symmetry,

$$\sigma^2(l_1) = \boldsymbol{l}_1^T\mathbf{g}(\boldsymbol{M}_{AA} - \boldsymbol{M}_{AB} - \boldsymbol{M}_{BA} + \boldsymbol{M}_{BB})\mathbf{g}\boldsymbol{l}_1/l_1^2 \tag{3.1.10.14}$$

$$\mathrm{cov}(l_1, l_2) = \boldsymbol{l}_1^T\mathbf{g}(\boldsymbol{M}_{AB} - \boldsymbol{M}_{AC} - \boldsymbol{M}_{BB} + \boldsymbol{M}_{BC})\mathbf{g}\boldsymbol{l}_2/l_1 l_2. \tag{3.1.10.15}$$

If atom B is generated from atom A by symmetry matrix $\boldsymbol{S}$, the results, as derived in Sands (1966), are

$$\sigma^2(l_1) = \boldsymbol{l}_1^T\mathbf{g}(\boldsymbol{M}_{AA} - \boldsymbol{S}\boldsymbol{M}_{AA} - \boldsymbol{M}_{AA}\boldsymbol{S}^T + \boldsymbol{S}\boldsymbol{M}_{AA}\boldsymbol{S}^T)\mathbf{g}\boldsymbol{l}_1/l_1^2 \quad (3.1.10.16)$$

$$\sigma^2(l_2) = \boldsymbol{l}_2^T\mathbf{g}(\boldsymbol{S}\boldsymbol{M}_{AA}\boldsymbol{S}^T - \boldsymbol{M}_{AC}\boldsymbol{S}^T - \boldsymbol{S}\boldsymbol{M}_{AC} + \boldsymbol{M}_{CC})\mathbf{g}\boldsymbol{l}_2/l_2^2 \quad (3.1.10.17)$$

$$\sigma^2(l_3) = \boldsymbol{l}_3^T\mathbf{g}(\boldsymbol{M}_{AA} - \boldsymbol{M}_{AC} - \boldsymbol{M}_{CA} + \boldsymbol{M}_{CC})\mathbf{g}\boldsymbol{l}_3/l_3^2 \quad (3.1.10.18)$$

$$\mathrm{cov}(l_1, l_2) = \boldsymbol{l}_1^T\mathbf{g}(\boldsymbol{M}_{AA}\boldsymbol{S}^T - \boldsymbol{S}\boldsymbol{M}_{AA}\boldsymbol{S}^T - \boldsymbol{M}_{AC} + \boldsymbol{S}\boldsymbol{M}_{AC})\mathbf{g}\boldsymbol{l}_2/l_1l_2 \quad (3.1.10.19)$$

$$\mathrm{cov}(l_1, l_3) = \boldsymbol{l}_1^T\mathbf{g}(-\boldsymbol{M}_{AA} + \boldsymbol{S}\boldsymbol{M}_{AA} + \boldsymbol{M}_{AC} - \boldsymbol{S}\boldsymbol{M}_{AC})\mathbf{g}\boldsymbol{l}_3/l_1l_3 \quad (3.1.10.20)$$

$$\mathrm{cov}(l_2, l_3) = \boldsymbol{l}_2^T\mathbf{g}(-\boldsymbol{S}\boldsymbol{M}_{AA} + \boldsymbol{M}_{CA} + \boldsymbol{S}\boldsymbol{M}_{AC} - \boldsymbol{M}_{CC})\mathbf{g}\boldsymbol{l}_3/l_2l_3. \quad (3.1.10.21)$$

In equations (3.1.10.14)–(3.1.10.21), $\boldsymbol{l}_i$ is a column vector with components the differences of the coordinates of the atoms connected by the vector. Representative formulae involving the angles α_1, α_2, α_3 are

$$\sigma^2(\alpha_1) = [\cos^2\alpha_2\sigma^2(l_1) - 2\cos\alpha_2\ \mathrm{cov}(l_1, l_2) + 2\cos\alpha_2\cos\alpha_3\ \mathrm{cov}(l_1, l_3) + \sigma^2(l_2) - 2\cos\alpha_3\ \mathrm{cov}(l_2, l_3) + \cos^2\alpha_3\sigma^2(l_3)](l_2/l_1l_3\sin\alpha_1)^2 \quad (3.1.10.22)$$

$$\mathrm{cov}(\alpha_1, \alpha_2) = [\cos\alpha_1\cos\alpha_2\sigma^2(l_1) + (\cos\alpha_2\cos\alpha_3 - \cos\alpha_1)\ \mathrm{cov}(l_1, l_2) + (\cos\alpha_1\cos\alpha_3 - \cos\alpha_2)\ \mathrm{cov}(l_1, l_3) - \cos\alpha_3\sigma^2(l_2) + (1 + \cos^2\alpha_3)\ \mathrm{cov}(l_2, l_3) - \cos\alpha_3\sigma^2(l_3)]/(l_1^2\sin\alpha_1\sin\alpha_2) \quad (3.1.10.23)$$

$$\mathrm{cov}(\alpha_1, l_1) = [-\cos\alpha_2\sigma^2(l_1) + \mathrm{cov}(l_1, l_2) - \cos\alpha_3\ \mathrm{cov}(l_1, l_3)](l_2/l_1l_3\sin\alpha_1) \quad (3.1.10.24)$$

$$\mathrm{cov}(\alpha_1, l_2) = [-\cos\alpha_2\ \mathrm{cov}(l_1, l_2) + \sigma^2(l_2) - \cos\alpha_3\ \mathrm{cov}(l_2, l_3)](l_2/l_1l_3\sin\alpha_1). \quad (3.1.10.25)$$

If any of the angles approach 0 or 180°, the denominators in (3.1.10.22)–(3.1.10.25) will become very small, necessitating high-precision arithmetic. Indeterminacies resulting from special relationships between atomic positions may require rederivation of the equations for variances and covariances, to take the relationships into account explicitly and avoid the indeterminacies. A true symmetry condition requiring, for example, a linear bond should cause little problem, and the corresponding variance will be zero. It is the indeterminacies not originating from crystal symmetry that demand caution, in recognizing them and in coping with them correctly.

A general expression for the variance of a dihedral angle, in terms of the variances and covariances of the coordinates of the four atoms, is (Shmueli, 1974)

$$\sigma^2(\tau) = \sum_k\sum_n \frac{\partial\tau}{\partial x^i_{(k)}}\frac{\partial\tau}{\partial x^j_{(n)}}\mathrm{cov}[x^i_{(k)}, x^j_{(n)}], \quad (3.1.10.26)$$

where, in addition to the usual tensor summation over i and j from 1 to 3, summation must be carried out over the four atoms (*i.e.*, k and n vary from 1 to 4). Special cases of (3.1.10.26), corresponding to various levels of approximation of diagonal matrices and isotropic errors, are given in Shmueli (1974). Formulae in dyadic notation are given in Waser (1973) for the variances and covariances of dihedral angles, of best planes, of torsion angles, and of other molecular parameters.

3.1.11. Mean values

The weighted mean of a set of quantities X_i is

$$\langle X\rangle = \sum w_iX_i/\sum w_i, \quad (3.1.11.1)$$

where the weights are typically chosen to minimize the variance of $\langle X\rangle$. The variance may be computed from the variance–covariance matrix $\boldsymbol{M}$ of the X_i by

$$\sigma^2(\langle X\rangle) = \mathbf{w}^T\boldsymbol{M}\mathbf{w}/(\sum w_i)^2. \quad (3.1.11.2)$$

Minimization of $\sigma^2(\langle X\rangle)$ leads to weights given by

$$\mathbf{w} = \boldsymbol{M}^{-1}\mathbf{v}, \quad (3.1.11.3)$$

where the components of vector $\mathbf{v}$ are all equal ($v_i = v_j$ for all i and j); since (3.1.11.1) and (3.1.11.2) require only relative weights, we can assign $v_i = 1$ for all i. Placing these weights in (3.1.11.2) yields

$$\sigma^2(\langle X\rangle) = 1/\sum w_i. \quad (3.1.11.4)$$

For the case of uncorrelated X_i, the weights are inversely proportional to the corresponding variances

$$w_i = 1/\sigma^2(X_i). \quad (3.1.11.5)$$

For the case of two correlated variables,

$$w_i = 1/[\sigma^2(X_i) - \mathrm{cov}(X_1, X_2)]. \quad (3.1.11.6)$$

Derivation and discussion of these equations may be found in Sands (1966, 1982*b*).

The presence of systematic errors in the experimental data often results in these formulae producing estimates of the standard uncertainties of molecular dimensions that are too small; it has been suggested that such error estimates should be multiplied by 1.5 to make them more realistic (Taylor & Kennard, 1983). It is essential also that averages be computed only of similar quantities, and interatomic distances corresponding to different bond orders or different environments may not represent the same physical quantities; that is, there are reasons for the discrepancies, and averaging may obscure important information. Another source of error in molecular geometry parameters determined from crystallographic measurements is thermal motion, and distances should be corrected for such effects before making comparisons (Busing & Levy, 1964; Johnson, 1970, 1980).

A discussion of the appropriateness of weighted and unweighted means may be found in Taylor & Kennard (1985), which suggests that the unweighted mean might even be preferable if environmental effects are large.

3.1.12. Computation

It has been mentioned that the tensor formulation used in this chapter is particularly amenable to machine computation. As a simple illustration of this point, the following Fortran program will compute the lengths of vectors **X** and **Y** and the angle between them.

```
      DIMENSION X(3),Y(3),G(3,3),SUM(3)
      READ (5,10)(X(I),I = 1,3)
      READ (5,10)(Y(I),I = 1,3)
      READ (5,10)((G(I,J),J = 1,3),I = 1,3)
10    FORMAT (3F10.5)
      DO 20 I = 1,3
20    SUM(I) = 0
      DO 30 I = 1,3
      DO 30 J = 1,3
      SUM(1) = SUM(1) + X(I) * X(J) * G(I,J)
      SUM(2) = SUM(2) + Y(I) * Y(J) * G(I,J)
      SUM(3) = SUM(3) + X(I) * Y(J) * G(I,J)
30    CONTINUE
      DIST1 = SQRT(SUM(1))
      DIST2 = SQRT(SUM(2))
      ANGLE = 57.296 * ACOS(SUM(3)/(DIST1 * DIST2))
      WRITE (6,10) DIST1,DIST2,ANGLE
      END
```

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