

3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

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

That is, the covariant components of \mathbf{h} are given by the reciprocals of the intercepts of the plane on the axes. The vector \mathbf{h} is normal to the plane it describes (Sands, 1982a) and the length of \mathbf{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 \mathbf{h} is introduced. Thus, the distance l from a point P with coordinates p^i to a plane characterized by \mathbf{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 \mathbf{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 \mathbf{u} in the first plane, vector \mathbf{w} in the second plane, and vector \mathbf{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 \mathbf{t} and \mathbf{u} onto the plane with normal \mathbf{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 \mathbf{h} (Sands, 1982b). 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 \mathbf{X} given by

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

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

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

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

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

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

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

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

[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 \mathbf{C} of k functions of m parameters is given in terms of the $m \times m$ variance–covariance matrix of the parameters by

$$\mathbf{C} = \mathbf{D} \mathbf{M} \mathbf{D}^T, \quad (3.1.10.5)$$

in which the ij th element of the $k \times m$ matrix \mathbf{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 \mathbf{C} must, of course, include the contributions of all sources of error, so \mathbf{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 non-vanishing 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^j the positional parameters i of atoms A and B , respectively, we define \mathbf{M}_{AA} , \mathbf{M}_{AB} , \mathbf{M}_{BA} and \mathbf{M}_{BB} as 3×3 matrices with ij th elements $\text{cov}(x_A^i, x_A^j)$, $\text{cov}(x_A^i, x_B^j)$, $\text{cov}(x_B^i, x_A^j)$ and $\text{cov}(x_B^i, x_B^j)$, respectively. If atom B' is generated from atom B by symmetry operator \mathbf{S} , such that

$$\mathbf{x}_{B'} = \mathbf{S} \mathbf{x}_B \quad (3.1.10.6)$$

$$x_{B'}^i = S_j^i x_B^j, \quad (3.1.10.7)$$

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

$$\mathbf{M}_{AB'} = \mathbf{M}_{AB} \mathbf{S}^T \quad (3.1.10.8)$$

$$\mathbf{M}_{B'A} = \mathbf{S} \mathbf{M}_{BA} \quad (3.1.10.9)$$

$$\mathbf{M}_{B'B'} = \mathbf{S} \mathbf{M}_{BB} \mathbf{S}^T. \quad (3.1.10.10)$$

If symmetry operator \mathbf{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

$$\begin{pmatrix} \mathbf{M}_{A'A'} & \mathbf{M}_{A'B'} \\ \mathbf{M}_{B'A'} & \mathbf{M}_{B'B'} \end{pmatrix} = \begin{pmatrix} \mathbf{S} \mathbf{M}_{AA} \mathbf{S}^T & \mathbf{S} \mathbf{M}_{AB} \mathbf{S}^T \\ \mathbf{S} \mathbf{M}_{BA} \mathbf{S}^T & \mathbf{S} \mathbf{M}_{BB} \mathbf{S}^T \end{pmatrix}. \quad (3.1.10.11)$$

3.1. DISTANCES, ANGLES, AND THEIR STANDARD UNCERTAINTIES

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

$$\mathbf{a}' = \mathbf{G}\mathbf{a}, \quad (3.1.10.12)$$

the transformed variance–covariance matrix of the atomic parameters is

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

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,

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

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

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

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

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

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

$$\begin{aligned} \text{cov}(l_1, l_2) &= \mathbf{l}_1^T \mathbf{g}(\mathbf{M}_{AA}\mathbf{S}^T - \mathbf{S}\mathbf{M}_{AA}\mathbf{S}^T \\ &\quad - \mathbf{M}_{AC} + \mathbf{S}\mathbf{M}_{AC}) \mathbf{g} \mathbf{l}_2 / l_1 l_2 \end{aligned} \quad (3.1.10.19)$$

$$\begin{aligned} \text{cov}(l_1, l_3) &= \mathbf{l}_1^T \mathbf{g}(-\mathbf{M}_{AA} + \mathbf{S}\mathbf{M}_{AA} \\ &\quad + \mathbf{M}_{AC} - \mathbf{S}\mathbf{M}_{AC}) \mathbf{g} \mathbf{l}_3 / l_1 l_3 \end{aligned} \quad (3.1.10.20)$$

$$\begin{aligned} \text{cov}(l_2, l_3) &= \mathbf{l}_2^T \mathbf{g}(-\mathbf{S}\mathbf{M}_{AA} + \mathbf{M}_{CA} \\ &\quad + \mathbf{S}\mathbf{M}_{AC} - \mathbf{M}_{CC}) \mathbf{g} \mathbf{l}_3 / l_2 l_3. \end{aligned} \quad (3.1.10.21)$$

In equations (3.1.10.14)–(3.1.10.21), \mathbf{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 $\alpha_1, \alpha_2, \alpha_3$ are

$$\begin{aligned} \sigma^2(\alpha_1) &= [\cos^2 \alpha_2 \sigma^2(l_1) - 2 \cos \alpha_2 \text{cov}(l_1, l_2) \\ &\quad + 2 \cos \alpha_2 \cos \alpha_3 \text{cov}(l_1, l_3) + \sigma^2(l_2) \\ &\quad - 2 \cos \alpha_3 \text{cov}(l_2, l_3) \\ &\quad + \cos^2 \alpha_3 \sigma^2(l_3)] (l_2 / l_1 l_3 \sin \alpha_1)^2 \end{aligned} \quad (3.1.10.22)$$

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

$$\begin{aligned} \text{cov}(\alpha_1, l_1) &= [-\cos \alpha_2 \sigma^2(l_1) + \text{cov}(l_1, l_2) \\ &\quad - \cos \alpha_3 \text{cov}(l_1, l_3)] (l_2 / l_1 l_3 \sin \alpha_1) \end{aligned} \quad (3.1.10.24)$$

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

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)

$$\sigma^2(\tau) = \sum_k \sum_n \frac{\partial \tau}{\partial x_{(k)}^i} \frac{\partial \tau}{\partial x_{(n)}^j} \text{cov}[x_{(k)}^i, x_{(n)}^j], \quad (3.1.10.26)$$

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

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

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

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

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

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

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,

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

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

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).