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*

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

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

3.1.8.3. *Vector product of vector products*

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

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

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 $\mathbf{u}$, $\mathbf{v}$ and $\mathbf{w}$, the vectors $\mathbf{u} - \mathbf{v}$, $\mathbf{v} - \mathbf{w}$ and $\mathbf{w} - \mathbf{u}$ are in the plane. The vector

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

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

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

Making use of (3.1.7.1),

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

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

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

From (3.1.9.2),

$$\mathbf{u} \cdot \mathbf{z} = \mathbf{u} \cdot \mathbf{v} \wedge \mathbf{w}. \tag{3.1.9.5}$$

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 $\mathbf{z}$ on the left leads to

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

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

$$x^1/u^1 + x^2/v^2 + x^3/w^3 = 1, \tag{3.1.9.7}$$

which may be written

$$x^i h_i = 1 \tag{3.1.9.8}$$

or

$$\mathbf{x} \cdot \mathbf{h} = 1 \tag{3.1.9.9}$$

in which the vector $\mathbf{h}$ 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 **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

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

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

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

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

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

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

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

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

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

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 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^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

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

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

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

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

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

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

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

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

references