

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

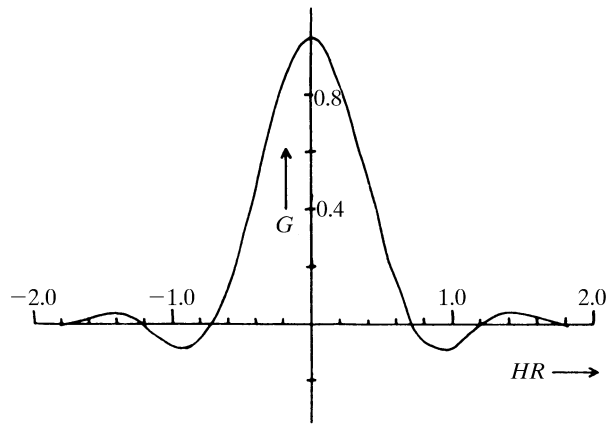


Fig. 2.3.6.1. Shape of the interference function G for a spherical envelope of radius R at a distance H from the reciprocal-space origin. [Reprinted from Rossmann & Blow (1962).]

quite small. Indeed, all terms with $HR > 1$ might well be neglected. Thus, in general, the only terms that need be considered are those where $-\mathbf{h}'$ is within one lattice point of \mathbf{h} . However, in dealing with a small molecular fragment for which R is small compared to the unit-cell dimensions, more reciprocal-lattice points must be included for the summation over \mathbf{p} in the rotation-function expression (2.3.6.3).

In practice, the equation

$$\mathbf{h} + \mathbf{h}' = 0,$$

that is

$$[\mathbf{C}^T]\mathbf{p} = -\mathbf{h}$$

or

$$\mathbf{p} = [\mathbf{C}^T]^{-1}(-\mathbf{h}), \quad (2.3.6.5)$$

determines \mathbf{p} , given a set of Miller indices \mathbf{h} . This will give a non-integral set of Miller indices. The terms included in the inner summation of (2.3.6.3) will be integral values of \mathbf{p} around the non-integral lattice point found by solving (2.3.6.5).

Details of the conventional program were given by Tollin & Rossmann (1966) and follow the principles outlined above. They discussed various strategies as to which crystal should be used to calculate the first (\mathbf{h}) and second (\mathbf{p}) Patterson. Rossmann & Blow (1962) noted that the factor $\sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 G_{\mathbf{h}\mathbf{p}}$ in expression (2.3.6.3) represents an interpolation of the squared transform of the self-Patterson of the second (\mathbf{p}) crystal. Thus, the rotation function is a sum of the products of the two molecular transforms taken over all the \mathbf{h} reciprocal-lattice points. Lattman & Love (1970) therefore computed the molecular transform explicitly and stored it in the computer, sampling it as required by the rotation operation. A discussion on the suitable choice of variables in the computation of rotation functions has been given by Lifchitz (1983).

2.3.6.2. Matrix algebra

The initial step in the rotation-function procedure involves the orthogonalization of both crystal systems. Thus, if fractional coordinates in the first crystal system are represented by \mathbf{x} , these can be orthogonalized by a matrix $[\beta]$ to give the coordinates \mathbf{X} in units of length (Fig. 2.3.6.2); that is,

$$\mathbf{X} = [\beta]\mathbf{x}.$$

If the point \mathbf{X} is rotated to the point \mathbf{X}' , then

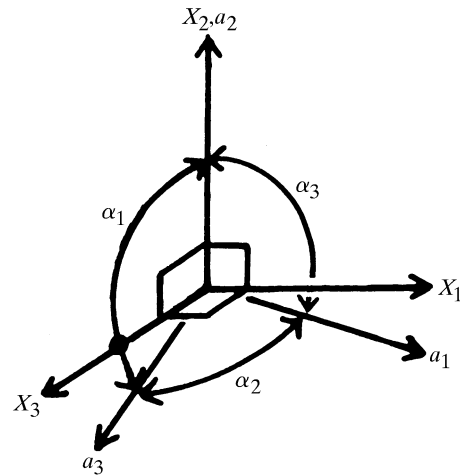


Fig. 2.3.6.2. Relationships of the orthogonal axes X_1, X_2, X_3 to the crystallographic axes a_1, a_2, a_3 . [Reprinted from Rossmann & Blow (1962).]

$$\mathbf{X}' = [\rho]\mathbf{X}, \quad (2.3.6.6)$$

where ρ represents the rotation matrix relating the two vectors in the orthogonal system. Finally, \mathbf{X}' is converted back to fractional coordinates measured along the oblique cell dimension in the second crystal by

$$\mathbf{x}' = [\alpha]\mathbf{X}'.$$

Thus, by substitution,

$$\mathbf{x}' = [\alpha][\rho]\mathbf{X} = [\alpha][\rho][\beta]\mathbf{x}, \quad (2.3.6.7)$$

and by comparison with (2.3.6.2) it follows that

$$[\mathbf{C}] = [\alpha][\rho][\beta].$$

Fig. 2.3.6.2 shows the mode of orthogonalization used by Rossmann & Blow (1962). With their definition it can be shown that

$$[\alpha] = \begin{pmatrix} 1/(a_1 \sin \alpha_3 \sin \omega) & 0 & 0 \\ 1/(a_2 \tan \alpha_1 \tan \omega) & 1/a_2 & -1/(a_2 \tan \alpha_1) \\ -1/(a_2 \tan \alpha_3 \sin \omega) & 0 & 1/(a_3 \sin \alpha_1) \\ -1/(a_3 \sin \alpha_1 \tan \omega) & 0 & 1/(a_3 \sin \alpha_1) \end{pmatrix}$$

and

$$[\beta] = \begin{pmatrix} a_1 \sin \alpha_3 \sin \omega & 0 & 0 \\ a_1 \cos \alpha_3 & a_2 & a_3 \cos \alpha_1 \\ a_1 \sin \alpha_3 \cos \omega & 0 & a_3 \sin \alpha_1 \end{pmatrix},$$

where $\cos \omega = (\cos \alpha_2 - \cos \alpha_1 \cos \alpha_3)/(\sin \alpha_1 \sin \alpha_3)$ with $0 \leq \omega < \pi$. For a Patterson compared with itself, $[\alpha] = [\beta]^{-1}$.

Both spherical (κ, ψ, φ) and Eulerian ($\theta_1, \theta_2, \theta_3$) angles are used in evaluating the rotation function. The usual definitions employed are given diagrammatically in Figs. 2.3.6.3 and 2.3.6.4. They give rise to the following rotation matrices.

(a) Matrix $[\rho]$ in terms of Eulerian angles $\theta_1, \theta_2, \theta_3$:

$$\begin{pmatrix} -\sin \theta_1 \cos \theta_2 \sin \theta_3 & \cos \theta_1 \cos \theta_2 \sin \theta_3 & \sin \theta_2 \sin \theta_3 \\ +\cos \theta_1 \cos \theta_3 & +\sin \theta_1 \cos \theta_3 & \\ -\sin \theta_1 \cos \theta_2 \cos \theta_3 & \cos \theta_1 \cos \theta_2 \cos \theta_3 & \sin \theta_2 \cos \theta_3 \\ -\cos \theta_1 \sin \theta_3 & -\sin \theta_1 \sin \theta_3 & \\ \sin \theta_1 \sin \theta_2 & -\cos \theta_1 \sin \theta_2 & \cos \theta_2 \end{pmatrix}$$

and (b) matrix $[\rho]$ in terms of rotation angle κ and the spherical polar coordinates ψ, φ :

2.3. PATTERSON AND MOLECULAR-REPLACEMENT TECHNIQUES

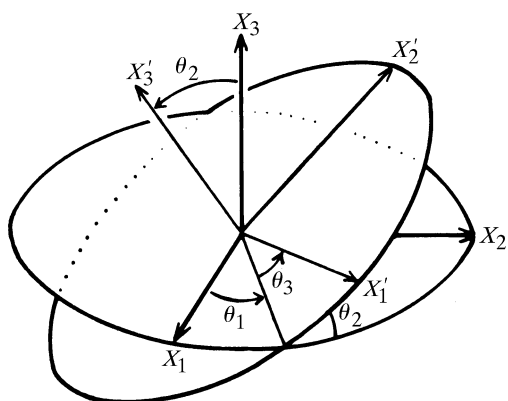


Fig. 2.3.6.3. Eulerian angles $\theta_1, \theta_2, \theta_3$ relating the rotated axes X'_1, X'_2, X'_3 to the original unrotated orthogonal axes X_1, X_2, X_3 . [Reprinted from Rossmann & Blow (1962).]

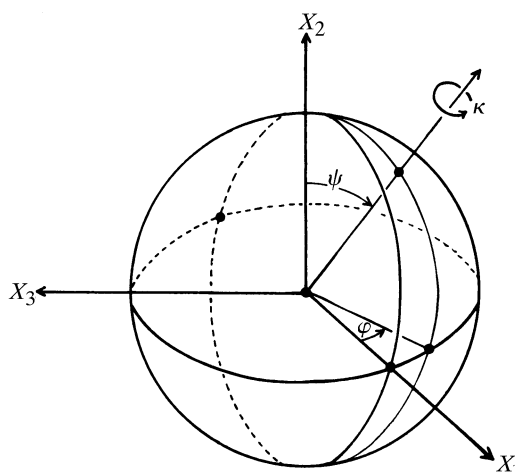


Fig. 2.3.6.4. Variables ψ and φ are polar coordinates which specify a direction about which the axes may be rotated through an angle κ . [Reprinted from Rossmann & Blow (1962).]

$$\begin{pmatrix} \cos \kappa + \sin^2 \psi \cos^2 \varphi (1 - \cos \kappa) & \sin \psi \cos \psi \cos \varphi (1 - \cos \kappa) \\ & + \sin \psi \sin \varphi \sin \kappa \\ \sin \psi \cos \psi \cos \varphi (1 - \cos \kappa) & \cos \kappa + \cos^2 \psi (1 - \cos \kappa) \\ & - \sin \psi \sin \varphi \sin \kappa \\ - \sin^2 \psi \sin \varphi \cos \varphi (1 - \cos \kappa) & - \sin \psi \cos \psi \sin \varphi (1 - \cos \kappa) \\ & + \sin \psi \cos \varphi \sin \kappa \\ & - \sin^2 \psi \cos \varphi \sin \varphi (1 - \cos \kappa) \\ & + \cos \psi \sin \kappa \\ & - \sin \psi \cos \psi \sin \varphi (1 - \cos \kappa) \\ & - \sin \psi \cos \varphi \sin \kappa \\ \cos \kappa + \sin^2 \psi \sin^2 \varphi (1 - \cos \kappa) & \end{pmatrix}$$

$$\begin{aligned} \cos(\kappa/2) &= \cos(\theta_2/2) \cos\left(\frac{\theta_1 + \theta_3}{2}\right), \\ \tan \varphi &= -\cot(\theta_2/2) \sin\left(\frac{\theta_1 + \theta_3}{2}\right) \sec\left(\frac{\theta_1 - \theta_3}{2}\right), \\ \cos \varphi \tan \psi &= \cot\left(\frac{\theta_1 - \theta_3}{2}\right). \end{aligned}$$

Since φ and ψ can always be chosen in the range 0 to π , these equations suffice to find (κ, ψ, φ) from any set $(\theta_1, \theta_2, \theta_3)$.

Alternatively, (b) can be expressed as

$$\begin{pmatrix} \cos \kappa + u^2(1 - \cos \kappa) & uv(1 - \cos \kappa) - w \sin \kappa \\ vu(1 - \cos \kappa) + w \sin \kappa & \cos \kappa + v^2(1 - \cos \kappa) \\ wu(1 - \cos \kappa) - v \sin \kappa & wv(1 - \cos \kappa) + u \sin \kappa \\ & uw(1 - \cos \kappa) + v \sin \kappa \\ & uw(1 - \cos \kappa) - u \sin \kappa \\ & \cos \kappa + w^2(1 - \cos \kappa) \end{pmatrix},$$

where u, v and w are the direction cosines of the rotation axis given by

$$\begin{aligned} u &= \sin \psi \cos \varphi, \\ v &= \cos \psi, \\ w &= -\sin \psi \sin \varphi. \end{aligned}$$

This latter form also demonstrates that the trace of a rotation matrix is $2 \cos \kappa + 1$.

The relationship between the two sets of variables established by comparison of the elements of the two matrices yields

2.3.6.3. Symmetry

In analogy with crystal lattices, the rotation function is periodic and contains symmetry. The rotation function has a cell whose periodicity is 2π in each of its three angles. This may be written as

$$R(\theta_1, \theta_2, \theta_3) \equiv R(\theta_1 + 2\pi n_1, \theta_2 + 2\pi n_2, \theta_3 + 2\pi n_3)$$

or

$$R(\kappa, \psi, \varphi) \equiv R(\kappa + 2\pi n_1, \psi + 2\pi n_2, \varphi + 2\pi n_3),$$

where n_1, n_2 and n_3 are integers. A redundancy in the definition of either set of angles leads to the equivalence of the following points:

$$R(\theta_1, \theta_2, \theta_3) \equiv R(\theta_1 + \pi, -\theta_2, \theta_3 + \pi) \quad \text{in Eulerian space}$$

or

$$R(\kappa, \psi, \varphi) \equiv R(\kappa, 2\pi - \psi, \varphi + \pi) \quad \text{in polar space.}$$

These relationships imply an n glide plane perpendicular to θ_2 for Eulerian space or a φ glide plane perpendicular to ψ in polar space.

In addition, the Laue symmetry of the two Pattersons themselves must be considered. This problem was first discussed by Rossmann & Blow (1962) and later systematized by Tollin *et al.* (1966), Burdina (1970, 1971, 1973) and Rao *et al.* (1980). A closely related problem was considered by Hirshfeld (1968). The rotation function will have the same value whether the Patterson density at \mathbf{X} or $[\mathbf{T}_i]\mathbf{X}$ in the first crystal is multiplied by the Patterson density at \mathbf{X}' or $[\mathbf{T}_j]\mathbf{X}'$ in the second crystal. $[\mathbf{T}_i]$ and $[\mathbf{T}_j]$ refer to the i th and j th crystallographic rotations in the orthogonalized coordinate systems of the first and second crystal, respectively. Hence, from (2.3.6.6)

$$([\mathbf{T}_j]\mathbf{X}') = [\rho]([\mathbf{T}_i]\mathbf{X})$$

or