

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

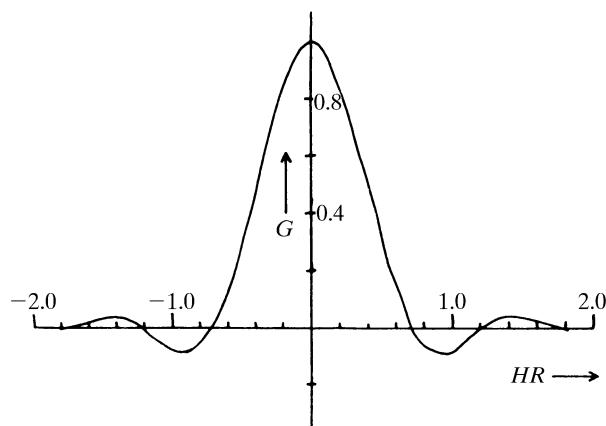


Fig. 2.3.6.1. Shape of the interference function G for a spherical envelope of radius R at a distance HR from the reciprocal-space origin. [Reprinted from Rossmann & Blow (1962).]

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 $\sum_{\mathbf{p}} |\mathbf{F}_{\mathbf{p}}|^2 G_{\mathbf{hp}}$ 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

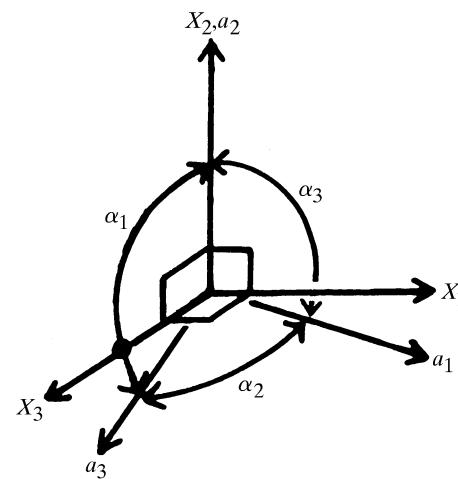


Fig. 2.3.6.2. Relationships of the orthogonal axes X_1, X_2, X_3 to the crystallographic axes a_1, a_2, a_3 . [Reprinted from Rossmann & Blow (1962).]

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

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

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

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 :