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).]

![Diagram](image)

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 $-h'$ is within one lattice point of $h$. 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 $p$ in the rotation-function expression (2.3.6.3).

In practice, the equation

$$h + h' = 0,$$

that is

$$[C^T]p = -h$$

or

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

(2.3.6.5)
determines $p$, given a set of Miller indices $h$. 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 $p$ 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 ($h$) and second ($p$) Patterson. Rossmann & Blow (1962) noted that the factor $\sum_p [F_p]^2 G_{h0}$ in expression (2.3.6.3) represents an interpolation of the squared transform of the self-Patterson of the second ($p$) crystal. Thus, the rotation function is a sum of the products of the two molecular transforms taken over all the $h$ 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 Lifschitz (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 $x$, these can be orthogonalized by a matrix $[\alpha]$ to give the coordinates $X$ in units of length (Fig. 2.3.6.2); that is,

$$X = [\alpha]x.$$  

If the point $X$ is rotated to the point $X'$, then

$$X' = [\rho]X,$$

(2.3.6.6)

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

$$x' = [\alpha]X'.$$

Thus, by substitution,

$$x' = [\alpha][\rho]x = [\alpha][\rho][\beta]x,$$

(2.3.6.7)

and by comparison with (2.3.6.2) it follows that

$$[C] = [\alpha][\rho][\beta].$$

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

$$[\alpha] = \begin{pmatrix} 1/(a_1 \sin \alpha_3 \sin \omega) & 0 & 0 \\ 1/(a_2 \tan \alpha_3 \tan \omega) & 1/a_2 & -1/(a_2 \tan \alpha_1) \\ -1/(a_3 \tan \alpha_2 \sin \omega) & 0 & 1/(a_3 \sin \alpha_1) \end{pmatrix},$$

and

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

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 ($\kappa, \psi, \varphi$) 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 $[\beta]$ in terms of rotation angle $\kappa$ and the spherical polar coordinates $\psi, \varphi$: