

## 2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

## 2.3.1.5. The Patterson synthesis of the second kind

Patterson also defined a second, less well known, function (Patterson, 1949) as

$$P_{\pm}(\mathbf{u}) = \int \rho(\mathbf{u} + \mathbf{x}) \cdot \rho(\mathbf{u} - \mathbf{x}) \, d\mathbf{x}$$

$$= \frac{2}{V^2} \sum_{\mathbf{h}}^{\text{hemisphere}} F_{\mathbf{h}}^2 \cos(2\pi 2\mathbf{h} \cdot \mathbf{u} - 2\alpha_{\mathbf{h}}).$$

This function can be computed directly only for centrosymmetric structures. It can be calculated for noncentrosymmetric structures when the phase angles are known or assumed. It will represent the degree to which the known or assumed structure has a centre of symmetry at  $\mathbf{u}$ . That is, the product of the density at  $\mathbf{u} + \mathbf{x}$  and  $\mathbf{u} - \mathbf{x}$  is large when integrated over all values  $\mathbf{x}$  within the unit cell. Since atoms themselves have a centre of symmetry, the function will contain peaks at each atomic site roughly proportional in height to the square of the number of electrons in each atom plus peaks at the midpoint between atoms proportional in height to the product of the electrons in each atom. Although this function has not been found very useful in practice, it is useful for demonstrating the presence of weak enantiomorphic images in a given tentative structure determination.

## 2.3.2. Interpretation of Patterson maps

## 2.3.2.1. Simple solutions in the triclinic cell. Selection of the origin

A hypothetical one-dimensional centrosymmetric crystal structure containing an atom at  $x$  and at  $-x$  and the corresponding Patterson is illustrated in Fig. 2.3.2.1. There are two different centres of symmetry which may be chosen as convenient origins. If the atoms are of equal weight, we expect Patterson vectors at positions  $u = \pm 2x$  with weights equal to half the origin peak. There are two symmetry-related peaks,  $u_1$  and  $u_2$  (Fig. 2.3.2.1) in the Patterson. It is an arbitrary choice whether  $u_1 = 2x$  or  $u_2 = 2x$ . This choice is equivalent to selecting the origin at the centre of symmetry I or II in the real structure (Fig. 2.3.2.1). Similarly in a three-dimensional  $P\bar{1}$  cell, the Patterson will contain peaks at  $\langle uvw \rangle$  which can be used to solve for the atom coordinates  $\pm \langle 2x, 2y, 2z \rangle$ . Solving for the same coordinates by starting from symmetric representations of the same vector will lead to alternate origin choices. For example, use of  $\langle 1+u, 1+v, w \rangle$  will lead to translating the origin by  $\langle +\frac{1}{2}, +\frac{1}{2}, 0 \rangle$  relative to the solution based on  $\langle uvw \rangle$ . There are eight distinct inversion centres in  $P\bar{1}$ , each one of which represents a valid origin choice. Although any choice of origin would be allowable, an inversion centre is

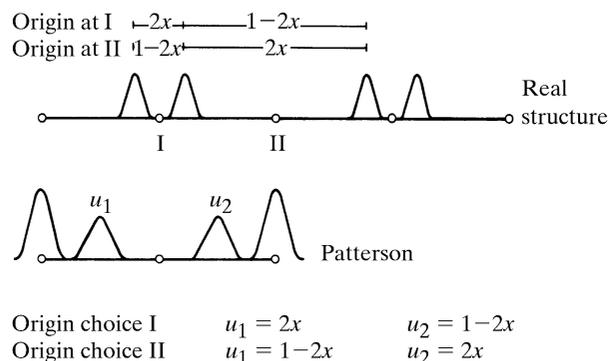


Fig. 2.3.2.1. Origin selection in the interpretation of a Patterson of a one-dimensional centrosymmetric structure.

convenient because then the structure factors are all real. Typically, one of the vector peaks closest to the Patterson origin is selected to start the solution, usually in the calculated asymmetric unit of the Patterson. Care must be exercised in selecting the same origin for all atomic positions by considering cross-vectors between atoms.

Examine, for example, the  $c$ -axis Patterson projection of a cuprous chloride azomethane complex ( $C_2H_6Cl_2Cu_2N_2$ ) in  $P\bar{1}$  as shown in Fig. 2.3.2.2. The largest Patterson peaks should correspond to vectors arising from Cu ( $Z = 29$ ) and Cl ( $Z = 17$ ) atoms. There will be copper atoms at  $\mathbf{x}_{Cu}(x_{Cu}, y_{Cu})$  and  $-\mathbf{x}_{Cu}(-x_{Cu}, -y_{Cu})$  as well as chlorine atoms at analogous positions. The interaction matrix is

	$\mathbf{x}_{Cu}, 29$	$\mathbf{x}_{Cl}, 17$	$-\mathbf{x}_{Cu}, 29$	$-\mathbf{x}_{Cl}, 17$
$\mathbf{x}_{Cu}, 29$	0, 841	$\mathbf{x}_{Cu} - \mathbf{x}_{Cl}, 493$	$2\mathbf{x}_{Cu}, 841$	$\mathbf{x}_{Cu} + \mathbf{x}_{Cl}, 493$
$\mathbf{x}_{Cl}, 17$		0, 289	$\mathbf{x}_{Cl} + \mathbf{x}_{Cu}, 493$	$2\mathbf{x}_{Cl}, 289$
$-\mathbf{x}_{Cu}, 29$			0, 841	$\mathbf{x}_{Cu} - \mathbf{x}_{Cl}, 493$
$-\mathbf{x}_{Cl}, 17$				0, 289

which shows that the Patterson should contain the following types of vectors:

Position	Weight	Multiplicity	Total weight
$2\mathbf{x}_{Cu}$	841	1	841
$2\mathbf{x}_{Cl}$	289	1	289
$\mathbf{x}_{Cu} - \mathbf{x}_{Cl}$	493	2	986
$\mathbf{x}_{Cu} + \mathbf{x}_{Cl}$	493	2	986

The coordinates of the largest Patterson peaks are given in Table 2.3.2.1 for an asymmetric half of the cell chosen to span  $0 \rightarrow \frac{1}{2}$  in  $u$  and  $0 \rightarrow 1$  in  $v$ . Since the three largest peaks are in the same ratio (7:7:6) as the three largest expected vector types (986:986:841), it is reasonable to assume that peak III corresponds to the copper-copper interaction at  $2\mathbf{x}_{Cu}$ . Hence,  $x_{Cu} = 0.08$  and  $y_{Cu} = 0.20$ . Peaks I and II should be due to the double-weight Cu-Cl vectors at  $\mathbf{x}_{Cu} - \mathbf{x}_{Cl}$  and  $\mathbf{x}_{Cu} + \mathbf{x}_{Cl}$ . Now suppose that peak I is at position  $\mathbf{x}_{Cu} + \mathbf{x}_{Cl}$ , then  $x_{Cl} = 0.25$  and  $y_{Cl} = 0.14$ . Peak II should now check out as the remaining double-weight Cu-Cl interaction at  $\mathbf{x}_{Cu} - \mathbf{x}_{Cl}$ . Indeed,  $\mathbf{x}_{Cu} - \mathbf{x}_{Cl} = \langle -0.17, 0.06 \rangle = -\langle 0.17, -0.06 \rangle$  which agrees tolerably well with the position of peak II. The chlorine position also predicts the position of a peak at  $2\mathbf{x}_{Cl}$  with

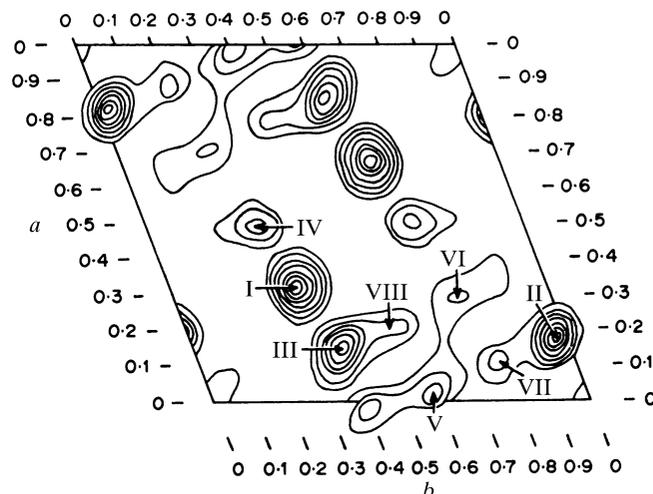


Fig. 2.3.2.2. The  $c$ -axis projection of cuprous chloride azomethane complex ( $C_2H_6Cl_2Cu_2N_2$ ). The space group is  $P\bar{1}$  with one molecule per unit cell. [Adapted from and reprinted with permission from Woolfson (1970, p. 321).]