2.3. Patterson and molecular replacement techniques, and the use of noncrystallographic symmetry in phasing

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2.3.1. Introduction

2.3.1.1. Background

Historically, the Patterson has been used in a variety of ways to effect the solutions of crystal structures. While some simple structures (Ketelaar & de Vries, 1939; Hughes, 1940; Speakman, 1949; Shoemaker *et al.*, 1950) were solved by direct analysis of Patterson syntheses, alternative methods have largely superseded this procedure. An early innovation was the heavy-atom method which depends on the location of a small number of relatively strong scatterers (Harker, 1936). Image-seeking methods and Patterson superposition techniques were first contemplated in the late 1930s (Wrinch, 1939) and applied sometime later (Beevers & Robertson, 1950; Clastre & Gay, 1950; Garrido, 1950a; Buerger, 1959). This experience provided the encouragement for computerized vector-search methods to locate individual atoms automatically (Mighell & Jacobson, 1963; Kraut, 1961; Hamilton, 1965; Simpson *et al.*, 1965) or to position known molecular fragments in unknown crystal structures (Nordman & Nakatsu, 1963; Huber, 1965). The Patterson function has been used extensively in conjunction with the isomorphous replacement method (Rossmann, 1960; Blow, 1958) or anomalous dispersion (Rossmann, 1961a) to determine the position of heavy-atom substitution. Pattersons have been used to detect the presence and relative orientation of multiple copies of a given chemical motif in the crystallographic asymmetric unit in the same or different crystals (Rossmann & Blow, 1962). Finally, the orientation and placement of known molecular structures ('molecular replacement') into unknown crystal structures can be accomplished *via* Patterson techniques.

The function, introduced by Patterson in 1934 (Patterson, 1934a,b), is a convolution of electron density with itself and may be defined as

$$P(\mathbf{u}) = \int_V \rho(\mathbf{x}) \cdot \rho(\mathbf{u} + \mathbf{x}) \, d\mathbf{x}, \qquad (2.3.1.1)$$

where $P(\mathbf{u})$ is the 'Patterson' function at $\mathbf{u}$, $\rho(\mathbf{x})$ is the crystal's periodic electron density and V is the volume of the unit cell. The Patterson function, or F^2 series, can be calculated directly from the experimentally derived X-ray intensities as

$$P(\mathbf{u}) = \frac{2}{V^2} \sum_{\mathbf{h}}^{\text{hemisphere}} |\mathbf{F_h}|^2 \cos 2\pi \mathbf{h} \cdot \mathbf{u}. \qquad (2.3.1.2)$$

The derivation of (2.3.1.2) from (2.3.1.1) can be found in this volume (see Section 1.3.4.2.1.6) along with a discussion of the physical significance and symmetry of the Patterson function, although the principal properties will be restated here.

The Patterson can be considered to be a vector map of all the pairwise interactions between the atoms in a unit cell. The vectors in a Patterson correspond to vectors in the real (direct) crystal cell but translated to the Patterson origin. Their weights are proportional to the product of densities at the tips of the vectors in the real cell. The Patterson unit cell has the same size as the real crystal cell. The symmetry of the Patterson comprises the Laue point group of the crystal cell plus any additional lattice symmetry due to Bravais centring. The reduction of the real

space group to the Laue symmetry is produced by the translation of all vectors to the Patterson origin and the introduction of a centre of symmetry. The latter is a consequence of the relationship between the vectors **AB** and **BA**. The Patterson symmetries for all 230 space groups are tabulated in *IT* A (2005).

An analysis of Patterson peaks can be obtained by considering N atoms with form factors f_i in the unit cell. Then

$$\mathbf{F_h} = \sum_{i=1}^{N} f_i \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_i).$$

Using Friedel's law,

$$|\mathbf{F_h}|^2 = \mathbf{F_h} \cdot \mathbf{F_h^*}$$
$$= \left[\sum_{i=1}^{N} f_i \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_i)\right] \left[\sum_{j=1}^{N} f_j \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}_j)\right],$$

which can be decomposed to

$$|\mathbf{F_h}|^2 = \sum_{i=1}^{N} f_i^2 + \sum_{i \neq j}^{N} \sum^{N} f_i f_j \exp[2\pi i \mathbf{h} \cdot (\mathbf{x}_i - \mathbf{x}_j)]. \qquad (2.3.1.3)$$

On substituting (2.3.1.3) in (2.3.1.2), we see that the Patterson consists of the sum of N^2 total interactions of which N are of weight f_i^2 at the origin and $N(N-1)$ are of weight $f_i f_j$ at $\mathbf{x}_i - \mathbf{x}_j$.

The weight of a peak in a real cell is given by

$$w_i = \int_U \rho_i(\mathbf{x}) \, d\mathbf{x} = Z_i \text{ (the atomic number)},$$

where U is the volume of the atom i. By analogy, the weight of a peak in a Patterson (form factor $f_i f_j$) will be given by

$$w_{ij} = \int_U P_{ij}(\mathbf{u}) \, d\mathbf{u} = Z_i Z_j.$$

Although the maximum height of a peak will depend on the spread of the peak, it is reasonable to assume that heights of peaks in a Patterson are proportional to the products of the atomic numbers of the interacting atoms.

There are a total of N^2 interactions in a Patterson due to N atoms in the crystal cell. These can be represented as an $N \times N$ square matrix whose elements $\mathbf{u}_{ij}$, w_{ij} indicate the position and weight of the peak produced between atoms i and j (Table 2.3.1.1). The N vectors corresponding to the diagonal of this matrix are located at the Patterson origin and arise from the convolution of each atom with itself. This leaves $N(N-1)$ vectors whose locations depend on the relative positions of all of the atoms in the crystal cell and whose weights depend on the atom types related by the vector. Complete specification of the unique non-origin Patterson vectors requires description of only the $N(N-1)/2$ elements in either the upper or the lower triangle of this matrix, since the two sets of vectors represented by the two triangles are related by a centre of symmetry

Table 2.3.1.1. *Matrix representation of Patterson peaks*

The $N \times N$ matrix represents the position $\mathbf{u}_{ij}$ and weights w_{ij} of atomic interactions in a Patterson arising from N atoms at $\mathbf{x}_i$ and weight w_i in the real cell.

	$\mathbf{x}_1, w_1$	$\mathbf{x}_2, w_2$	$\ldots$	$\mathbf{x}_N, w_N$
$\mathbf{x}_1, w_1$	$\mathbf{u}_{11} = \mathbf{x}_1 - \mathbf{x}_1,$ $w_{11} = w_1^2$	$\mathbf{u}_{12} = \mathbf{x}_1 - \mathbf{x}_2,$ $w_{12} = w_1 w_2$	$\ldots$	$\mathbf{u}_{1N} = \mathbf{x}_1 - \mathbf{x}_N,$ $w_{1N} = w_1 w_N$
$\mathbf{x}_2, w_2$	$\mathbf{x}_2 - \mathbf{x}_1, w_2 w_1$	$0, w_2^2$	$\ldots$	$\mathbf{x}_2 - \mathbf{x}_N, w_2 w_N$
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
$\mathbf{x}_N, w_N$	$\mathbf{x}_N - \mathbf{x}_1, w_N w_1$	$\mathbf{x}_N - \mathbf{x}_2, w_N w_2$	$\ldots$	$0, w_N^2$

$[\mathbf{u}_{ij} \equiv \mathbf{x}_i - \mathbf{x}_j = -\mathbf{u}_{ij} \equiv -(\mathbf{x}_j - \mathbf{x}_i)]$. Patterson vector positions are usually represented as $\langle uvw \rangle$, where u, v and w are expressed as fractions of the Patterson cell axes.

2.3.1.2. Limits to the number of resolved vectors

If we assume a constant number of atoms per unit volume, the number of atoms N in a unit cell increases in direct proportion with the volume of the unit cell. Since the number of non-origin peaks in the Patterson function is $N(N-1)$ and the Patterson cell is the same size as the real cell, the problem of overlapping peaks in the Patterson function becomes severe as N increases. To make matters worse, the breadth of a Patterson peak is roughly equal to the sum of the breadth of the original atoms. The effective width of a Patterson peak will also increase with increasing thermal motion, although this effect can be artificially reduced by sharpening techniques. Naturally, a loss of attainable resolution at high scattering angles will affect the resolution of atomic peaks in the real cell as well as peaks in the Patterson cell. If U is the van der Waals volume per average atom, then the fraction of the cell occupied by atoms will be $f = NU/V$. Similarly, the fraction of the cell occupied by Patterson peaks will be $2UN(N-1)/V$ or $2f(N-1)$. With the reasonable assumption that $f \simeq 0.1$ for a typical organic crystal, then the cell can contain at most five atoms ($N \leq 5$) for there to be no overlap, other than by coincidence, of the peaks in the Patterson. As N increases there will occur a background of peaks on which are superimposed features related to systematic properties of the structure.

The contrast of selected Patterson peaks relative to the general background level can be enhanced by a variety of techniques. For instance, the presence of heavy atoms not only enhances the size of a relatively small number of peaks but ordinarily ensures a larger separation of the peaks due to the light-atom skeleton on which the heavy atoms are hung. That is, the factor f (above) is substantially reduced. Another example is the effect of systematic atomic arrangements (*e.g.* α-helices or aromatic rings) resulting in multiple peaks which stand out above the background. In the isomorphous replacement method, isomorphous difference Pattersons are utilized in which the contrast of the Patterson interactions between the heavy atoms is enhanced by removal of the predominant interactions which involve the rest of the structure.

2.3.1.3. Modifications: origin removal, sharpening etc.

A. L. Patterson, in his first in-depth exposition of his newly discovered F^2 series (Patterson, 1935), introduced the major modifications to the Patterson which are still in use today. He illustrated, with one-dimensional Fourier series, the techniques of removing the Patterson origin peak, sharpening the overall function and also removing peaks due to atoms in special positions. Each one of these modifications can improve the interpretability of Pattersons, especially those of simple structures. Whereas the recommended extent of such modifications is controversial (Buerger, 1966), most studies which utilize Patterson functions do incorporate some of these techniques [see,

for example, Jacobson *et al.* (1961), Braun *et al.* (1969) and Nordman (1980*a*)]. Since Patterson's original work, other workers have suggested that the Patterson function itself might be modified; Fourier inversion of the modified Patterson then provides a new and perhaps more tractable set of structure factors (McLachlan & Harker, 1951; Simonov, 1965; Raman, 1966; Corfield & Rosenstein, 1966). Karle & Hauptman (1964) suggested that an improved set of structure factors could be obtained from an origin-removed Patterson modified such that it was everywhere non-negative and that Patterson density values less than a bonding distance from the origin were set to zero. Nixon (1978) was successful in solving a structure which had previously resisted solution by using a set of structure factors which had been obtained from a Patterson in which the largest peaks had been attenuated.

The N origin peaks [see expression (2.3.1.3)] may be removed from the Patterson by using coefficients

$$|\mathbf{F}_{\mathbf{h}, \text{mod}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2 - \sum_{i=1}^{N} f_i^2.$$

A Patterson function using these modified coefficients will retain all interatomic vectors. However, the observed structure factors $\mathbf{F}_{\mathbf{h}}$ must first be placed on an absolute scale (Wilson, 1942) in order to match the scattering-factor term. In practice, Patterson origins can also be removed by using coefficients

$$\left|\mathbf{F}_{\mathbf{h},\text{mod}}\right|^2 = \left|\mathbf{F}_{\mathbf{h}}\right|^2 - \langle |\mathbf{F}_{\mathbf{h}}|^2 \rangle,$$

where $\langle |\mathbf{F}_{\mathbf{h}}|^2 \rangle$ is the average reflection intensity, usually calculated in several resolution shells. This formula has the advantage that the observed structure factors do not need to be on absolute scale.

Analogous to origin removal, the vector interactions due to atoms in known positions can also be removed from the Patterson function. Patterson showed that non-origin Patterson peaks arising from known atoms 1 and 2 may be removed by using the expression

$$|\mathbf{F}_{\mathbf{h}, \text{mod}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2 - \sum_{i=1}^{N} f_i^2 t_i^2 - 2f_1 f_2 t_1 t_2 \cos 2\pi \mathbf{h} \cdot (\mathbf{x}_1 - \mathbf{x}_2),$$

where $\mathbf{x}_1$ and $\mathbf{x}_2$ are the positions of atoms 1 and 2 and t_1 and t_2 are their respective thermal correction factors. Using one-dimensional Fourier series, Patterson illustrated how interactions due to known atoms can obscure other information.

Patterson also introduced a means by which the peaks in a Patterson function may be artificially sharpened. He considered the effect of thermal motion on the broadening of electron-density peaks and consequently their Patterson peaks. He suggested that the F^2 coefficients could be corrected for thermal effects by simulating the atoms as point scatterers and proposed using a modified set of coefficients

$$|\mathbf{F}_{\mathbf{h}, \text{sharp}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2 / \bar{f}^2,$$

where $\bar{f}$, the average scattering factor per electron, is given by

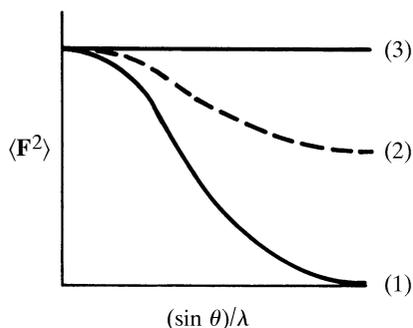$$\bar{f} = \sum_{i=1}^{N} f_i \Bigg/ \sum_{i=1}^{N} Z_i.$$

Fig. 2.3.1.1. Effect of 'sharpening' Patterson coefficients. (1) shows a mean distribution of $|\mathbf{F}|^2$ values with resolution, $(\sin \theta)/\lambda$. The normal decline of this curve is due to increasing destructive interference between different portions within diffuse atoms at larger Bragg angles. (2) shows the distribution of 'sharpened' coefficients. (3) shows the theoretical distribution of $|\mathbf{F}|^2$ produced by a point-atom structure. To represent such a structure with a Fourier series would require an infinite series in order to avoid large errors caused by truncation.

A common formulation for this type of sharpening expresses the atomic scattering factors at a given angle in terms of an overall isotropic thermal parameter B as

$$ f(s) = f_0 \exp(-Bs^2). $$

The Patterson coefficients then become

$$ \mathbf{F}_{\mathbf{h}, \text{sharp}} = \frac{Z_{\text{total}}}{\sum_{i=l}^{N} f(s)} \mathbf{F}_{\mathbf{h}}. $$

The normalized structure factors, E (see Chapter 2.2), which are used in crystallographic direct methods, are also a common source of sharpened Patterson coefficients ($E^2 - 1$). Although the centre positions and total contents of Patterson peaks are unaltered by sharpening, the resolution of individual peaks may be enhanced. The degree of sharpening can be controlled by adjusting the size of the assumed B factor; Lipson & Cochran (1966, pp. 165–170) analysed the effect of such a choice on Patterson peak shape.

All methods of sharpening Patterson coefficients aim at producing a point atomic representation of the unit cell. In this quest, the high-resolution terms are enhanced (Fig. 2.3.1.1). Unfortunately, this procedure must also produce a serious Fourier truncation error which will be seen as large ripples about each Patterson peak (Gibbs, 1898). Consequently, various techniques have been used (mostly unsuccessfully) in an attempt to balance the advantages of sharpening with the disadvantages of truncation errors.

Schomaker and Shoemaker [unpublished; see Lipson & Cochran (1966, p. 168)] used a function

$$ |\mathbf{F}_{\mathbf{h}, \text{sharp}}|^2 = \frac{|\mathbf{F}_{\mathbf{h}}|^2}{\bar{f}^2} s^2 \exp\left[-\frac{\pi^2}{p} s^2\right], $$

in which s is the length of the scattering vector, to produce a Patterson synthesis which is less sensitive to errors in the low-order terms. Jacobson *et al.* (1961) used a similar function,

$$ |\mathbf{F}_{\mathbf{h}, \text{sharp}}|^2 = \frac{|\mathbf{F}_{\mathbf{h}}|^2}{\bar{f}^2} (k + s^2) \exp\left[-\frac{\pi}{p} s^2\right], $$

which they rationalize as the sum of a scaled exponentially sharpened Patterson and a gradient Patterson function (the value
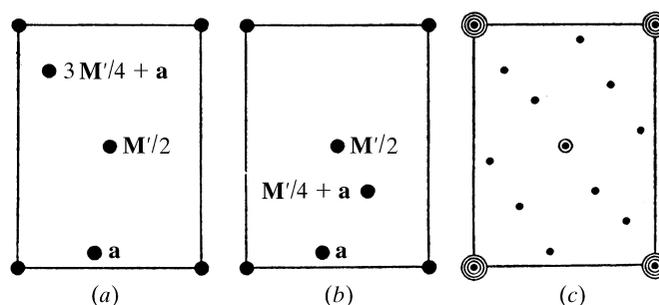

Fig. 2.3.1.2. (c) The point Patterson of the two homometric structures in (a) and (b). The latter are constructed by taking points at $\mathbf{a}$ and $\frac{1}{2}\mathbf{M}'$, where $\mathbf{M}'$ is a cell diagonal, and adding a third point which is (a) at $\frac{3}{4}\mathbf{M}' + \mathbf{a}$ or (b) at $\frac{1}{4}\mathbf{M}' + \mathbf{a}$. [Reprinted with permission from Patterson (1944).]

of k was empirically chosen as $\frac{2}{3}$). This approach was subsequently further developed and generalized by Wunderlich (1965).

2.3.1.4. Homometric structures and the uniqueness of structure solutions; enantiomorphic solutions

Interpretation of any Patterson requires some assumption, such as the existence of discrete atoms. A complete interpretation might also require an assumption of the number of atoms and may require other external information (*e.g.* bond lengths, bond angles, van der Waals separations, hydrogen bonding, positive density *etc.*). To what extent is the solution of a Patterson function unique? Clearly the greater is the supply of external information, the fewer will be the number of possible solutions. Other constraints on the significance of a Patterson include the error involved in measuring the observed coefficients and the resolution limit to which they have been observed. The larger the error, the larger the number of solutions. When the error on the amplitudes is infinite, it is only the other physical constraints, such as packing, which limit the structural solutions. Alternative solutions of the same Patterson are known as homometric structures.

During their investigation of the mineral bixbyite, Pauling & Shappell (1930) made the disturbing observation that there were two solutions to the structure, with different arrangements of atoms, which yielded the same set of calculated intensities. Specifically, atoms occupying equipoint set $24d$ in space group $I(2_1/a)\bar{3}$ can be placed at either $x, 0, \frac{1}{4}$ or $-x, 0, \frac{1}{4}$ without changing the calculated intensities. Yet the two structures were not chemically equivalent. These authors resolved the ambiguity by placing the oxygen atoms in question at positions which gave the most acceptable bonding distances with the rest of the structure.

Patterson interpreted the above ambiguity in terms of the F^2 series: the distance vector sets or Patterson functions of the two structures were the same since each yielded the same calculated intensities (Patterson, 1939). He defined such a pair of structures a homometric pair and called the degenerate vector set which they produced a homometric set. Patterson went on to investigate the likelihood of occurrence of homometric structures and, indeed, devoted a great deal of his time to this matter. He also developed algebraic formalisms for examining the occurrence of homometric pairs and multiplets in selected one-dimensional sets of points, such as cyclotomic sets, and also sets of points along a line (Patterson, 1944). Some simple homometric pairs are illustrated in Fig. 2.3.1.2.

Drawing heavily from Patterson's inquiries into the structural uniqueness allowed by the diffraction data, Hosemann, Bagchi and others have given formal definitions of the different types of homometric structures (Hosemann & Bagchi, 1954). They suggested a classification divided into pseudohomometric structures and homomorphs, and used an integral equation representing a convolution operation to express their examples of finite homometric structures. Other workers have chosen various
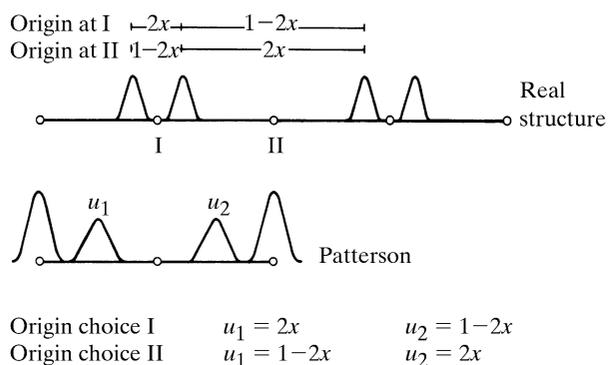
Fig. 2.3.2.1. Origin selection in the interpretation of a Patterson of a one-dimensional centrosymmetric structure.

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).]

means for describing homometric structures [Buerger (1959, pp. 41–50), Menzer (1949), Bullough (1961, 1964), Hoppe (1962)].

Since a Patterson function is centrosymmetric, the Pattersons of a crystal structure and of its mirror image are identical. Thus the enantiomeric ambiguity present in noncentrosymmetric crystal structures cannot be overcome by using the Patterson alone and represents a special case of homometric structures. Assignment of the correct enantiomorph in a crystal structure analysis is generally not possible unless a recognizable fragment of known chirality emerges (*e.g.* L-amino acids in proteins, D-riboses in nucleic acids, the known framework of steroids and other natural products, the right-handed twist of α-helices, the left-handed twist of successive strands in a β-sheet, the fold of a known protein subunit *etc.*) or anomalous-scattering information is available and can be used to resolve the ambiguity (Bijvoet *et al.*, 1951).

It is frequently necessary to select arbitrarily one enantiomorph over another in the early stages of a structure solution. Structure-factor phases calculated from a single heavy atom in space group $P1$, $P2$ or $P2_1$ (for instance) will be centrosymmetric and both enantiomorphs will be present in Fourier calculations based on these phases. In other space groups (*e.g.* $P2_12_12_1$), the selected heavy atom is likely to be near one of the planes containing the 2_1 axes and thus produce a weaker 'ghost' image of the opposite enantiomorph. The mixture of the two overlapped enantiomorphic solutions can cause interpretive difficulties. As the structure solution progresses, the 'ghosts' are exorcized owing to the dominance of the chosen enantiomorph in the phases.

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
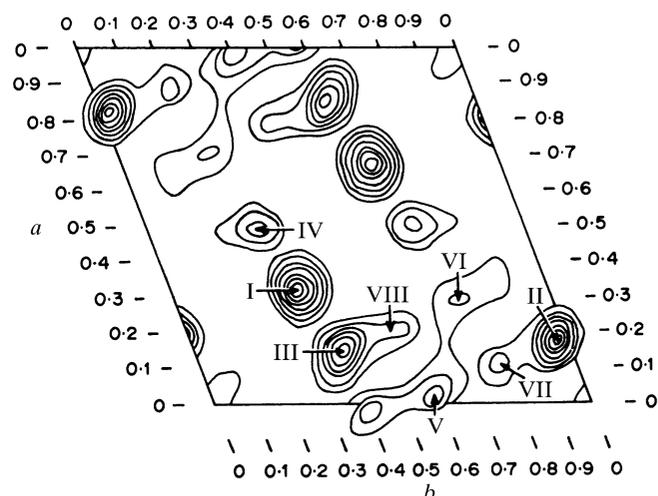
height to the product of the electrons in each atom. Although this function has not been found very useful in practice, it is useful for demonstrating the presence of weak enantiomorphic images in a given tentative structure determination.

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 $(+\frac{1}{2}, +\frac{1}{2}, 0)$ 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 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

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

references