

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

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

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 (1980a)]. 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.

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

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

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

$$\mathbf{F}_{\mathbf{h}, \text{sharp}} = \frac{Z_{\text{total}}}{\sum_{i=1}^N f(s)} \mathbf{F}_{\mathbf{h}}.$$

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