

2.3. PATTERSON AND MOLECULAR-REPLACEMENT TECHNIQUES

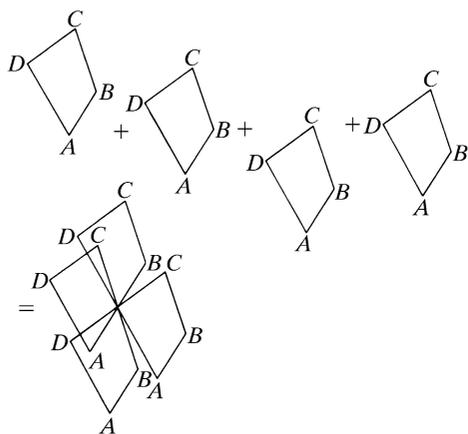


Fig. 2.3.2.3. Atoms $ABCD$, arranged as a quadrilateral, generate a Patterson which is the sum of the images of the quadrilateral when each atom is placed on the origin in turn.

deconvoluted by superimposing two of these Pattersons after translating these (without rotation) by, for instance, the vector \mathbf{AB} . A further improvement could be obtained by superimposing a third Patterson translated by \mathbf{AC} . This would have the additional advantage in that ABC is a noncentrosymmetric arrangement and, therefore, selects the enantiomorph corresponding to the hand of the atomic arrangement ABC [cf. Buerger (1951, 1959)].

A basic problem is that knowledge of the vectors \mathbf{AB} and \mathbf{AC} also implies some knowledge of the structure at a time when the structure is not yet known. In practice 'good-looking' peaks, estimated to be single peaks by assessing the absolute scale of the structure amplitudes with Wilson statistics, can be assumed to be the result of single interatomic vectors within a molecule. Superposition can then proceed and the result can be inspected for reasonable chemical sense. As many apparently single peaks can be tried systematically using a computer, this technique is useful for selecting and testing a series of reasonable Patterson interpretations (Jacobson *et al.*, 1961).

Three major methods have been used for the detection of molecular images of superimposed Pattersons. These are the sum, product and minimum 'image seeking' functions (Raman & Lipscomb, 1961). The concept of the sum function is to add the images where they superimpose, whereas elsewhere the summed Pattersons will have a lower value owing to lack of image superposition. Therefore, the sum function determines the average Patterson density for superimposed images, and is represented analytically as

$$S(\mathbf{x}) = \sum_{i=1}^N P(\mathbf{x} + \mathbf{u}_i),$$

where $S(\mathbf{x})$ is the sum function at \mathbf{x} given by the superposition of the i th Patterson translated by \mathbf{u}_i , or

$$S(\mathbf{x}) = \sum_{\mathbf{h}} \left\{ F_{\mathbf{h}}^2 \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) \left[\sum_{i=1}^N \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_i) \right] \right\}.$$

Setting

$$m \exp(i\varphi_{\mathbf{h}}) = \sum_{i=1}^N \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_i)$$

(m and $\varphi_{\mathbf{h}}$ can be calculated from the translational vectors used for the superposition),

$$S(\mathbf{x}) = \sum_{\mathbf{h}} F_{\mathbf{h}}^2 m \exp(2\pi i \mathbf{h} \cdot \mathbf{x} + \varphi_{\mathbf{h}}).$$

Thus, the sum function is equivalent to a weighted 'heavy atom' method based on the known atoms assumed by the superposition translation vectors.

The product function is somewhat more vigorous in that the images are enhanced by the product. If an image is superimposed on no image, then the product should be zero.

The product function can be expressed as

$$Pr(\mathbf{x}) = \prod_{i=1}^N P(\mathbf{x} + \mathbf{u}_i).$$

When $N = 2$ (\mathbf{h} and \mathbf{p} are sets of Miller indices),

$$Pr(\mathbf{x}) = \sum_{\mathbf{h}} \sum_{\mathbf{p}} F_{\mathbf{h}}^2 F_{\mathbf{p}}^2 \exp[2\pi i (\mathbf{h} + \mathbf{p}) \cdot \mathbf{x}] \\ \times \exp[2\pi i (\mathbf{h} \cdot \mathbf{u}_1 + \mathbf{p} \cdot \mathbf{u}_2)].$$

Successive superpositions using the product functions will quickly be dominated by a few terms with very large coefficients.

Finally, the minimum function is a clever invention of Buerger (Buerger, 1950b, 1951, 1953a,b,c; Taylor, 1953; Rogers, 1951). If a superposition is correct then each Patterson must represent an image of the structure. Whenever there are two or more images that intersect in the Patterson, the Patterson density will be greater than a single image. When two different images are superimposed, it is a reasonable hope that at least one of these is a single image. Thus by taking the value of that Patterson which is the minimum, it should be possible to select a single image and eliminate noise from interfering images as far as possible. Although the minimum function is perhaps the most powerful algorithm for image selection of well sharpened Pattersons, it is not readily amenable to Fourier representation.

The minimum function was conceived on the basis of selecting positive images on a near-zero background. If it were desired to select negative images [e.g. the $(\mathbf{F}_1 - \mathbf{F}_2)^2$ correlation function discussed in Section 2.3.3.4], then it would be necessary to use a maximum function. In fact, normally, an image has finite volume with varying density. Thus, some modification of the minimum function is necessary in those cases where the image is large compared to the volume of the unit cell, as in low-resolution protein structures (Rossmann, 1961b). Nordman (1966) used the average of the Patterson values of the lowest 10 to 20 per cent of the vectors in comparing Pattersons with hypothetical point Pattersons. A similar criterion was used by High & Kraut (1966).

Image-seeking methods using Patterson superposition have been used extensively (Beevers & Robertson, 1950; Garrido, 1950b; Robertson, 1951). For a review the reader is referred to *Vector Space* (Buerger, 1959) and a paper by Fridrichsons & Mathieson (1962). However, with the advent of computerized direct methods (see Chapter 2.2), such techniques are no longer popular. Nevertheless, they provide the conceptual framework for the rotation and translation functions (see Sections 2.3.6 and 2.3.7).

2.3.2.5. Systematic computerized Patterson vector-search procedures. Looking for rigid bodies

The power of the modern digital computer has enabled rapid access to the large number of Patterson density values which can serve as a lookup table for systematic vector-search procedures. In the late 1950s, investigators began to use systematic searches for the placement of single atoms, of known chemical groups or fragments and of entire known structures. Methods for locating single atoms were developed and called variously: vector verification (Mighell & Jacobson, 1963), symmetry minimum function (Kraut, 1961; Simpson *et al.*, 1965; Corfield & Rosenstein, 1966) and consistency functions (Hamilton, 1965). Patterson superposition techniques using stored function values were often used to image the structure