

Determination of one-dimensional crystal structures using the double Patterson function

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Abstract. The properties and previous use of the double Patterson function in x-ray crystallography are briefly reviewed followed by an account of a new iterative technique, based on the double Patterson, which is being developed by the author. The technique starts with an approximation to the double Patterson which does not require phases, then improves the approximation by making it conform to the known projections and known magnitudes of the Fourier coefficients. The latter are 3-phase structure invariants and estimating their phases is an important step in the direct determination of structure factor phases. Tests carried out on one-dimensional centro-symmetric structures show that the technique is successful. At best, it determines correct phases for all 3-phase invariants. At worst, it fails to improve on the estimate of all phases being zero. It consistently does very much better than the $B_{3,0}$ formula which is also based on the double Patterson. Further development is necessary to apply the technique to non-centrosymmetric structures and to real structures in three dimensions.

Keywords. X-ray crystallography; double Patterson; crystal structure determination; direct method; image reconstruction.

1. Introduction

A project to investigate the feasibility of using the double Patterson function to solve crystal structures has recently been started by the author. Some of the interesting early results are presented in this paper, but as very little use has been made of the double Patterson, it will be helpful to start with a brief review of the properties and previous use of the function.

The Patterson function itself was introduced by Patterson (1935)

$$\begin{aligned} P(\mathbf{u}) &= \int_V \rho(\mathbf{x})\rho(\mathbf{x} + \mathbf{u})dV, \\ &= \frac{1}{V} \sum_{\mathbf{h}} |F(\mathbf{h})|^2 \exp(-2\pi i\mathbf{h} \cdot \mathbf{u}). \end{aligned} \quad (1)$$

The importance of this function stems from the fact that its Fourier coefficients are the intensities $|F(\mathbf{h})|^2$ and it requires no knowledge of phases for its calculation. It has an appreciable value only when \mathbf{u} is an interatomic vector and so gives information on vector distances between atoms in the structure.

A generalisation of this function was given by Sayre (1953) who pointed out the existence of the double Patterson function, defined as:

$$\begin{aligned} D(\mathbf{u}, \mathbf{v}) &= \int_V \rho(\mathbf{x})\rho(\mathbf{x} + \mathbf{u})\rho(\mathbf{x} + \mathbf{v})dV \\ &= \frac{1}{V^2} \sum_{\mathbf{h}} \sum_{\mathbf{k}} F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h} - \mathbf{k}) \exp[-2\pi i(\mathbf{h} \cdot \mathbf{u} + \mathbf{k} \cdot \mathbf{v})] \end{aligned} \quad (2)$$

This is a six-dimensional function which has an appreciable value only when \mathbf{u} and \mathbf{v} are interatomic vectors referred to the same atom as origin, *i.e.* if there are atoms at vector displacements \mathbf{u} and \mathbf{v} from any other atom in the structure. It is therefore a vector map of the structure, but unlike the Patterson function, requires a knowledge of the phases for its calculation. The Fourier coefficients are the 3-phase structure invariants $F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h}-\mathbf{k})$ which clearly depend upon phases as well as magnitudes. This is precisely the interest in the double Patterson function. Use of the 3-phase structure invariants forms the basis of most direct methods of phase determination which are now widely used in crystal structure analysis. It follows that if an approximation to the double Patterson can somehow be obtained, phases for the 3-phase structure invariants may be estimated, thus making direct phase determination very much easier.

Sayre's generalisation went further than equation (2) indicates. He pointed out the existence of the set of density functions

$$\begin{aligned}
 D_n(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_n) &= \int_V \rho(\mathbf{x})\rho(\mathbf{x} + \mathbf{u}_1)\rho(\mathbf{x} + \mathbf{u}_2) \dots \rho(\mathbf{x} + \mathbf{u}_n) dV \\
 &= \frac{1}{V^n} \sum_{\mathbf{h}_1} \dots \sum_{\mathbf{h}_n} \left(\prod_{j=1}^n F(\mathbf{h}_j) \right) F(-\mathbf{h}_1 - \mathbf{h}_2 \dots - \mathbf{h}_n) \\
 &\quad \exp[-2\pi i(\mathbf{h}_1 \cdot \mathbf{u}_1 + \mathbf{h}_2 \cdot \mathbf{u}_2 \dots + \mathbf{h}_n \cdot \mathbf{u}_n)] \quad (3)
 \end{aligned}$$

which can have appreciable values only when $\mathbf{u}_1, \mathbf{u}_2 \dots \mathbf{u}_n$ are all inter-atomic vectors referred to the same atom as origin. These functions were written down explicitly by Vaughan (1958). Note that $D_0 (\equiv F(\mathbf{O}))$ gives the contents of the unit cell, D_1 corresponds to the Patterson function and D_2 is the double Patterson. The Fourier coefficients of all these functions D_n are structure invariants of order $n+1$. This paper considers only the D_2 function which uses the 3-phase invariants.

2. Elementary properties

Since there is no single source giving properties of the double Patterson, some of the more important and useful of them are collected together here.

2.1 Number and content of peaks

From the definition of the double Patterson function in (2), it is possible to deduce that the total number of peaks in the function is N^3 , where N is the number of atoms in the unit cell. These peaks are distributed as follows:

- (i) N peaks superimposed at the origin.
- (ii) $N(N-1)$ peaks in each of the principal sections $D(\mathbf{u}, \mathbf{O})$, $D(\mathbf{O}, \mathbf{v})$ and $D(\mathbf{u}, \mathbf{u})$, excluding the origin.
- (iii) $N(N-1)(N-2)$ peaks elsewhere in the function.

The definition also shows that the content of each peak is proportional to the product of atomic numbers of the three atoms giving rise to the peak.

From (iii) above, it is clear that if $N \leq 2$ there will be no peaks in general positions in the double Patterson. For the set of density functions given in (3), this may be stated more generally as

$$D_n(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_n) = 0, \mathbf{u}_1 \dots \mathbf{u}_n \neq 0, \text{ when } n \geq N. \quad (4)$$

It is interesting to compare this condition with that for Karle-Hauptman determinants (Karle and Hauptman 1950) whereby a determinant of order m is identically zero if $m > N$, i.e.

$$\Delta_m = 0, \text{ when } m > N. \quad (5)$$

The lowest order determinant which fulfils this criterion is $N + 1$. Such a determinant contains structure invariants up to order $N + 1$ in its expansion. This is the same as the order of structure invariants in the lowest order D_n function which fulfils the criterion (4).

2.2 Symmetry

The complete symmetry of the double Patterson function has been described by Vaisberg (1974), so only the symmetry used later in this paper will be given here. The double Patterson has the same lattice, in the appropriate three-dimensional subspaces, as that of the crystal. It also possesses a particular minimum symmetry which is easily worked out. If there are two atoms at vector displacements \mathbf{u} and \mathbf{v} from a third, the two atoms are related by a vector displacement of $\mathbf{u} - \mathbf{v}$. Taking each atom in turn as origin gives rise to three related peaks in the double Patterson. The resulting symmetry can be represented by

$$D(\mathbf{u}, \mathbf{v}) = D(-\mathbf{v}, \mathbf{u} - \mathbf{v}) = D(\mathbf{v} - \mathbf{u}, -\mathbf{u}), \quad (6)$$

which is a 3-fold axis. In addition, the identities of \mathbf{u} and \mathbf{v} are arbitrary and can therefore be interchanged. This gives

$$D(\mathbf{u}, \mathbf{v}) = D(\mathbf{v}, \mathbf{u}), \quad (7)$$

which is a mirror plane. This means $D(\mathbf{u}, \mathbf{v})$ has a 3-fold axis and a mirror plane as minimum symmetry.

The equivalent symmetry can also be demonstrated in reciprocal space. The \mathbf{h} , \mathbf{k} Fourier coefficient of $D(\mathbf{u}, \mathbf{v})$ is given by (2) as $F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h} - \mathbf{k})$. Clearly we have

$$F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h} - \mathbf{k}) = F(\mathbf{k})F(-\mathbf{h} - \mathbf{k})F(\mathbf{h}) = F(-\mathbf{h} - \mathbf{k})F(\mathbf{h})F(\mathbf{k}),$$

and

$$F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h} - \mathbf{k}) = F(\mathbf{k})F(\mathbf{h})F(-\mathbf{k} - \mathbf{h}). \quad (8)$$

For a one-dimensional noncentrosymmetric crystal, these results show that the two-dimensional space group of the double Patterson must be $p3m1$. Similarly, for a centrosymmetric crystal, the symmetry of the double Patterson will be $p6mm$.

Since the double Patterson is a vector map of the structure, the (three-dimensional) crystal space group translations do not affect its symmetry. Vaisberg has shown that the number of possible symmetry groups of the double Patterson is 73, corresponding to the 73 symmorphic three-dimensional space groups.

2.3 Principal projections

The projection of the double Patterson function on to a three-dimensional crystal subspace is given by

$$D(\mathbf{u}) = \int_{\mathbf{v}} D(\mathbf{u}, \mathbf{v}) d\mathbf{v}$$

$$\begin{aligned}
&= \int_V \frac{1}{V^2} \sum_{\mathbf{h}} \sum_{\mathbf{k}} F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h}-\mathbf{k}) \exp[-2\pi i(\mathbf{h} \cdot \mathbf{u} + \mathbf{k} \cdot \mathbf{v})] d\mathbf{v} \\
&= \frac{F(\mathbf{O})}{V} \sum_{\mathbf{h}} |F(\mathbf{h})|^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{u})
\end{aligned} \tag{9}$$

which is the Patterson function multiplied by $F(\mathbf{O})$ and therefore known. Because of the symmetry of the double Patterson, there will be three such identical projections.

2.4 Principal sections

Consider now the three identical principal sections $D(\mathbf{u}, \mathbf{O})$, $D(\mathbf{O}, \mathbf{v})$, $D(\mathbf{u}, \mathbf{u})$. An expression for $D(\mathbf{u}, \mathbf{O})$ can be obtained directly from (2) as

$$\begin{aligned}
D(\mathbf{u}, \mathbf{O}) &= \int_V \rho^2(\mathbf{x})\rho(\mathbf{x} + \mathbf{u}) dV, \\
&= \frac{1}{V^2} \sum_{\mathbf{h}} \sum_{\mathbf{k}} F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h}-\mathbf{k}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{u}),
\end{aligned} \tag{10}$$

where the section is seen to be the convolution of the electron density inverted in the origin with the squared structure.

An interesting result is obtained if we assume the structure factors obey Sayre's equation (1952) so that

$$F(-\mathbf{h}) = \frac{1}{V} \frac{f}{g} \sum_{\mathbf{k}} F(\mathbf{k})F(-\mathbf{h}-\mathbf{k}), \tag{11}$$

where f and g are the scattering factors of the real and squared atoms respectively. From (10) and (11) we obtain

$$D(\mathbf{u}, \mathbf{O}) = \frac{1}{V} \sum_{\mathbf{h}} \frac{g}{f} |F(\mathbf{h})|^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{u}), \tag{12}$$

which is a sharpened Patterson function. The three principal sections mentioned above can therefore be calculated if the structure factors obey Sayre's equation, *i.e.* if the atoms are equal and resolved.

3. Vector space methods

A small number of people have used the double Patterson in different ways for crystal structure analysis. The methods used can be classed as either vector space or reciprocal space methods and a representative selection of both types are presented in this and the next section.

As the double Patterson is a six-dimensional function, it is impractical to use it as a common means of structure determination. It is only recently that computers have become sufficiently powerful to contemplate calculating it at all. However, certain three-dimensional sections have interesting properties which have proved to be useful.

3.1 Hoppe section

Hoppe (1957) considered the three-dimensional section

$$D(\mathbf{u}, \mathbf{r}) = \int_V \rho(\mathbf{x} + \mathbf{u}) [\rho(\mathbf{x}) \rho(\mathbf{x} + \mathbf{r})] dV \quad (13)$$

where \mathbf{r} is a fixed vector. If \mathbf{r} is a unique interatomic vector, the function $\rho(\mathbf{x}) \rho(\mathbf{x} + \mathbf{r})$ will contain a single peak. The convolution of this with the electron density, as in (13), will therefore give a single image of the structure. If such a section can be calculated, even approximately, the structure will be solved. On the other hand, if \mathbf{r} is an n -fold interatomic vector $D(\mathbf{u}, \mathbf{r})$ will contain n translated and superimposed images of the structure and will not be easy to interpret. The situation becomes much simpler if \mathbf{r} is a vector between two heavy atoms. In this case, the peak in $\rho(\mathbf{x}) \rho(\mathbf{x} + \mathbf{r})$ corresponding to the superposition of the heavy atoms will be much greater than all other peaks. This results in the corresponding image of the structure in $D(\mathbf{u}, \mathbf{r})$ being stronger than the rest, allowing it to be recognised.

Simonov and Vaisberg (1970) made use of the Hoppe section in the solution of the synthetic silicate $\text{Na}_2\text{Mn}_2\text{Si}_2\text{O}_7$ in the space group $P2_1/n$. Since phases are not known, they used the approximation that the phase of $F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h}-\mathbf{k})$ is zero for all \mathbf{h} and \mathbf{k} . It is well-known that this is the most likely phase if only the unit cell contents are known (Cochran 1955). If the magnitudes of the corresponding normalized structure factors are large, the approximation is good for structures of this size. The Mn-Mn vector was easily identified in an ordinary Patterson function, then the appropriate Hoppe section based on this vector was calculated using the approximate formula

$$D(\mathbf{u}, \mathbf{r}) = \frac{1}{V^2} \sum_{\mathbf{h}} |F(\mathbf{h})| \left\{ \sum_{\mathbf{k}} |F(\mathbf{k})F(-\mathbf{h}-\mathbf{k})| \exp(-2\pi i \mathbf{k} \cdot \mathbf{r}) \right\} \exp(-2\pi i \mathbf{h} \cdot \mathbf{u}), \quad (14)$$

where \mathbf{r} is the known Mn-Mn vector. Most of the structure was recognised in the resulting map.

A more usual method of solving this structure would be to use the minimum function (Buerger 1953) since a unique heavy atom vector is available. Simonov and Vaisberg did, in fact, calculate the minimum function based on the Mn-Mn vector and obtained very similar results to the Hoppe section. Since the Hoppe section requires a lot more computing, it would appear to offer no advantage over the minimum function under these circumstances.

3.2 Symmetry section

Let us assume the crystal space group contains a pair of symmetry elements such that an atom at \mathbf{r} is reproduced at $\mathbf{C}_1\mathbf{r} + \mathbf{d}_1$ and $\mathbf{C}_2\mathbf{r} + \mathbf{d}_2$, where \mathbf{C}_1 and \mathbf{C}_2 are point group operators and \mathbf{d}_1 and \mathbf{d}_2 are translation vectors. Taking the point \mathbf{r} as origin, the vector distances to the other two atoms are

$$\mathbf{u} = \mathbf{C}_1\mathbf{r} + \mathbf{d}_1 - \mathbf{r}, \quad (15)$$

and

$$\mathbf{v} = \mathbf{C}_2\mathbf{r} + \mathbf{d}_2 - \mathbf{r}.$$

That is, a single atom at \mathbf{r} gives rise to a peak at (\mathbf{u}, \mathbf{v}) given by (15) in the double Patterson due to this pair of symmetry elements. The double Patterson can therefore be expressed in terms of \mathbf{r} only as

$$D(\mathbf{r}) = \frac{1}{V^2} \sum_{\mathbf{h}} \sum_{\mathbf{k}} F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h}-\mathbf{k}) \exp\{-2\pi i[\mathbf{h}^T(\mathbf{C}_1 - \mathbf{I}) + \mathbf{k}^T(\mathbf{C}_2 - \mathbf{I})] \cdot \mathbf{r} + \mathbf{h} \cdot \mathbf{d}_1 + \mathbf{k} \cdot \mathbf{d}_2\}. \quad (16)$$

Such a three-dimensional section of the double Patterson is called a symmetry section and it contains peaks at atomic sites. Symmetry sections are the equivalent of Harker sections in ordinary Patterson functions and have been studied by Biyushkin (1973).

As with the calculation of the Hoppe section, phases will not be known but the approximation that all phases are zero may be made. Since the peak heights are proportional to Z^3 , heavy atoms should be identified easily even with this approximation to the phases. Biyushkin and Belov (1965) calculated such approximations to symmetry sections in order to solve $\text{CoCl}(\text{NO}_2)_2 \cdot (\text{NH}_3) \cdot \text{CH}_2\text{C}(\text{NH}_2)_2$ in the space group $P2_1/c$. They calculated two different two-dimensional sections through the four-dimensional double Patterson of a projection of the structure. The symmetry sections gave the coordinates of the Co and Cl atoms and one light atom, from which the complete structure was obtained using weighted Fourier syntheses.

4. Reciprocal space methods

In both examples of vector space methods, the double Patterson function or its sections were calculated under the assumption that the phase of $F(\mathbf{h})F(\mathbf{k})F(-\mathbf{h}-\mathbf{k})$ is zero for all \mathbf{h} and \mathbf{k} . This is precisely the assumption made in direct methods of phase determination which are now widely used in crystal structure analysis. It would seem therefore that double Patterson methods as described in the previous section add no new information to the analysis and so cannot be made more powerful than direct methods. In order to make progress, better estimates for the phases of the double Patterson coefficients must be obtained. This is the purpose of the $B_{3,0}$ formula of Karle and Hauptman (1958) which is based on an approximation to the double Patterson function as shown by Vaughan (1958) and will be derived here.

Consider the product of three Patterson functions defined by

$$Q(\mathbf{u}, \mathbf{v}) = P(\mathbf{u})P(\mathbf{v})P(\mathbf{u} - \mathbf{v}). \quad (17)$$

If \mathbf{u} , \mathbf{v} and $\mathbf{u} - \mathbf{v}$ are all interatomic vectors, $Q(\mathbf{u}, \mathbf{v})$ will have a large value. This should be compared with the double Patterson function $D(\mathbf{u}, \mathbf{v})$, which has a large value when \mathbf{u} and \mathbf{v} are interatomic vectors referred to the same atom as origin. Thus $Q(\mathbf{u}, \mathbf{v})$, which can be calculated without knowledge of phases, contains all the peaks present in $D(\mathbf{u}, \mathbf{v})$. Unfortunately, it also contains many more peaks not present in the double Patterson and it will always be centrosymmetric. However, using $Q(\mathbf{u}, \mathbf{v})$ as an approximation to $D(\mathbf{u}, \mathbf{v})$ gives an estimate of the Fourier coefficients of the double Patterson.

The Fourier transform of the product of Pattersons involves the convolution of their Fourier coefficients. Leaving out the origin peak and the principal sections of $Q(\mathbf{u}, \mathbf{v})$, the \mathbf{h} , \mathbf{k} Fourier coefficient is proportional to

$$\langle (|E(\mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{k} + \mathbf{l})|^2 - 1) \rangle_{\mathbf{l}}. \quad (18)$$

To put this on the correct scale, we divide by the average value of $(|E(\mathbf{l})|^2 - 1)^3$ and multiply by the total double Patterson density represented by (18). The latter is given by the total density less that contained in the three missing sections, giving

$$(\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3) \frac{\langle (|E(\mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{k} + \mathbf{l})|^2 - 1) \rangle_1}{\langle (|E(\mathbf{l})|^2 - 1)^3 \rangle_1}, \quad (19)$$

where $\sigma_n = \sum_{j=1}^N Z_j^n$.

The three principal sections are restored by assuming they are Patterson functions as in (12), giving the quantity

$$(\sigma_1\sigma_2 - \sigma_3) \frac{(|E(\mathbf{h})|^2 - 1) + (|E(\mathbf{k})|^2 - 1) + (|E(-\mathbf{h} - \mathbf{k})|^2 - 1)}{\langle |E(\mathbf{l})|^2 - 1 \rangle_1} + \sigma_3, \quad (20)$$

where the origin peak has also been added. Since the function $Q(\mathbf{u}, \mathbf{v})$ is centrosymmetric, the Fourier coefficient represented by (19) and (20) is always real and is given by

$$\sigma_2^{3/2} |E(\mathbf{h})E(\mathbf{k})E(-\mathbf{h} - \mathbf{k})| \cos(\phi(\mathbf{h}) + \phi(\mathbf{k}) + \phi(-\mathbf{h} - \mathbf{k})). \quad (21)$$

Remembering that $\langle |E(\mathbf{l})|^2 - 1 \rangle_1 = 1$, a combination of (19), (20) and (21) yields the formula

$$\begin{aligned} |E(\mathbf{h})E(\mathbf{k})E(-\mathbf{h} - \mathbf{k})| \cos(\phi(\mathbf{h}) + \phi(\mathbf{k}) + \phi(-\mathbf{h} - \mathbf{k})) &= \frac{(\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3)}{\sigma_2^{3/2}} \\ &\frac{\langle (|E(\mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{k} + \mathbf{l})|^2 - 1) \rangle_1}{\langle (|E(\mathbf{l})|^2 - 1)^3 \rangle_1} \\ &+ \frac{\sigma_1\sigma_2 - \sigma_3}{\sigma_2^{3/2}} (|E(\mathbf{h})|^2 + |E(\mathbf{k})|^2 + |E(-\mathbf{h} - \mathbf{k})|^2 - 3) + \frac{\sigma_3}{\sigma_2^{3/2}}. \end{aligned} \quad (22)$$

The $B_{3,0}$ formula for unequal atoms is given by Hauptman (1964) as

$$\begin{aligned} |E(\mathbf{h})E(\mathbf{k})E(-\mathbf{h} - \mathbf{k})| \cos(\phi(\mathbf{h}) + \phi(\mathbf{k}) + \phi(-\mathbf{h} - \mathbf{k})) &= \frac{(\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3)}{\sigma_2^{3/2}} \\ &\frac{\langle (|E(\mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{l})|^2 - 1)(|E(\mathbf{h} + \mathbf{k} + \mathbf{l})|^2 - 1) \rangle_1}{\langle (|E(\mathbf{l})|^2 - 1)^3 \rangle_1} \\ &+ \frac{\sigma_3}{\sigma_2^{3/2}} (|E(\mathbf{h})|^2 + |E(\mathbf{k})|^2 + |E(-\mathbf{h} - \mathbf{k})|^2 - 2), \end{aligned} \quad (23)$$

which differs from (22) in the magnitude of the second term. Since this is of the order of $1/N$ of the first term, there is little practical difference between the two formulae.

The reason why this formula does not reliably indicate the value of $\cos(\phi(\mathbf{h}) + \phi(\mathbf{k}) + \phi(-\mathbf{h} - \mathbf{k}))$ is that $Q(\mathbf{u}, \mathbf{v})$ is too poor an approximation to $D(\mathbf{u}, \mathbf{v})$. For all but the most trivial structures, most of the peaks in $Q(\mathbf{u}, \mathbf{v})$ do not belong to $D(\mathbf{u}, \mathbf{v})$ at all and the proportion of wrong peaks increases with the size of the structure. This is seen in figure 1 which shows the double Patterson of a four-atom one-dimensional centrosymmetric structure compared with the corresponding $Q(\mathbf{u}, \mathbf{v})$ function. Even for this simple structure, a large proportion of the peaks off the principal sections are spurious.

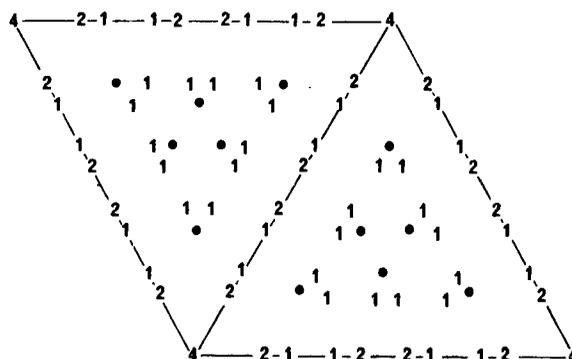


Figure 1. The double Patterson function for a one-dimensional centrosymmetric structure with two atoms in the asymmetric unit. The numbers give the peak heights and positions. The dots indicate the positions of additional (spurious) peaks which will also appear in the $Q(\mathbf{u}, \mathbf{v})$ function.

The successful applications of $B_{3,0}$ have mainly been with fairly small structures and almost never in a situation where the structure could not be solved by other means.

5. A new iterative technique

In the previous section it was shown that the $B_{3,0}$ formula was based on a very poor approximation to the double Patterson function. One way of improving the performance of $B_{3,0}$ will be to obtain a better approximation than the $Q(\mathbf{u}, \mathbf{v})$ function. Fortunately this should be possible, since not all the available information on the double Patterson has been used to set up $Q(\mathbf{u}, \mathbf{v})$. An obvious omission is that the known projections of the double Patterson have not been used and, indeed, $Q(\mathbf{u}, \mathbf{v})$ will not give the correct projections at all. It is proposed, therefore, to use $Q(\mathbf{u}, \mathbf{v})$ as a first approximation to $D(\mathbf{u}, \mathbf{v})$ and then to modify it by making it compatible with the three known principal projections described in § 2.3.

Reconstructing images from projections is now a well-established process and many different techniques for doing it have been developed. The ones worth considering for the present application are the algebraic reconstruction technique (ART) (Gordon *et al* 1970) and the simultaneous iterative reconstruction technique (SIRT) (Gilbert 1972) in either their additive or multiplicative forms. Since the number of known projections of the double Patterson function is very small (only three), the problem of reconstructing the function from them is very underdetermined. However, Minerbo and Sanderson (1977) have investigated the formation of an image from only two or three projections and they report acceptable results for simple images when the multiplicative version of ART is used. They also show this corresponds to the maximum entropy solution in the case of three projections. A multiplicative algorithm was therefore chosen to reconstruct the double Patterson. Since it is easier to maintain the symmetry of the double Patterson using SIRT, the multiplicative version of SIRT (MSIRT) was used.

This is an iterative technique which operates on the double Patterson function evaluated on a grid of points $D(\mathbf{u}_i, \mathbf{v}_j)$. It updates the value of each grid point according to

$$D^{p+1}(\mathbf{u}_i, \mathbf{v}_j) = D^p(\mathbf{u}_i, \mathbf{v}_j) s_i s_j s_{i+j},$$

where

$$s_i = \sigma_1 P(\mathbf{u}_i) / \sum_k D^p(\mathbf{u}_i, \mathbf{v}_k), \quad (24)$$

and p is the number of the iteration. The effect is to modify the double Patterson so its three principal projections match the known projections $\sigma_1 P(\mathbf{u})$.

A small amount of additional information may be used if it is assumed that the principal sections of $D(\mathbf{u}, \mathbf{v})$ are also known as described in § 2.4. In this case the sections are left out of the calculation of scale factors in (24) and they are also left unmodified by the MSIRT algorithm. The scale factors are now calculated as

$$s_i = \left(\frac{\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3}{\sigma_1^2 - \sigma_2} \right) \frac{P(\mathbf{u}_i)}{\sum_k D^p(\mathbf{u}_i, \mathbf{v}_k) - 2D^p(\mathbf{u}_i, \mathbf{O})}. \quad (25)$$

Perfect reconstruction of the double Patterson function will not be possible in a single application of MSIRT since the problem is severely under-determined. At most, only a small improvement over $Q(\mathbf{u}, \mathbf{v})$ can be expected. However, still more information is available since the magnitudes of the Fourier coefficients of $D(\mathbf{u}, \mathbf{v})$ are all known. The simplest way to make use of this is to transform the approximate $D(\mathbf{u}, \mathbf{v})$ into reciprocal space, correct the Fourier coefficients to match the known magnitudes and then to transform them back again. Using the projections in vector space and the magnitudes in reciprocal space should bring a lot more information to bear on the double Patterson than is used in the original $B_{3,0}$ formula.

All of this can be brought together in the following iterative procedure to obtain a good estimate of the double Patterson function:

- (a) use $Q(\mathbf{u}, \mathbf{v})$ defined in (17) as a first approximation to $D(\mathbf{u}, \mathbf{v})$;
- (b) scale the density to match the known total density (total density of principal sections of $D(\mathbf{u}, \mathbf{v})$ is $\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3$) and set all negative regions of $D(\mathbf{u}, \mathbf{v})$ to zero;
- (c) make the approximate $D(\mathbf{u}, \mathbf{v})$ compatible with the known projections by applying MSIRT;
- (d) for equal-atom structures, the principal sections of $D(\mathbf{u}, \mathbf{v})$ can be set equal to their known values;
- (e) transform to reciprocal space;
- (f) alter the calculated magnitudes $|E_{\text{calc}}(\mathbf{h}, \mathbf{k})|$ such that if $|E_{\text{calc}}(\mathbf{h}, \mathbf{k})| > E_{\text{obs}}(\mathbf{h}, \mathbf{k})$ then $|E_{\text{calc}}(\mathbf{h}, \mathbf{k})| = E_{\text{obs}}(\mathbf{h}, \mathbf{k})$. Other magnitudes and all phases are left unchanged.
- (g) other relationships among structure factors may be used here such as Sayre's equation to refine phases—see the next section for a description of this;
- (h) transform back to vector space and repeat from (b) until the double Patterson has converged or until reasonable estimates of the phases of the Fourier coefficients have been obtained.

6. Results

The iterative procedure described in the last section requires a huge amount of computing, even for small structures. However, if it forms the basis of a method of solving structures that could not otherwise be solved, it will be worth developing. To see

in which the right side represents a projection in reciprocal space of the double Patterson coefficients. The left hand side is independent of phase and so is always known. That is, Sayre's equation gives known projections in reciprocal space, corresponding to the known sections in vector space. A simple, though unconventional, way of applying Sayre's equation is to apply SIRT to modify the double Patterson coefficients to give the correct projections and this is what was done.

The second example in table 1 is a more difficult structure than the first. It can be seen that the $B_{3,0}$ results give worse estimates of phases than assuming they are all zero. The double Patterson iteration, on the other hand, rapidly improves the phases and converges to an rms error of about 35° . Even though this is not a complete success, the improvement in phase estimates is significant. As a measure of this improvement, an attempt was made to solve the structure using conventional symbolic addition with estimates of zero for the 3-phase invariants and then with estimates given by the double Patterson iteration technique. In both cases, sixteen plausible sets of signs were obtained for the ten largest E 's and the quantity $\sum_{\mathbf{k}} E(\mathbf{h})E(\mathbf{k})E(-\mathbf{h}-\mathbf{k})$ was calculated for each set as a simple figure of merit. In the conventional calculation, the correct set of signs gave the worst figure of merit. With the double Patterson coefficients as the 3-phase invariants, the correct set of signs gave the best figure of merit. Clearly, the structure is solved much more easily after double Patterson iteration.

The third example is of a more difficult structure still. Here the $B_{3,0}$ formula calculates random phases and the double Patterson iteration cannot improve on the original estimates of all phases equal to zero.

7. Discussion

In all structures tested, the double Patterson iteration technique did significantly better than the $B_{3,0}$ formula in estimating the signs of the 3-phase invariants. At worst, it was as good as assuming all signs were positive as in the example in table 1(c) and at best was capable of estimating all signs correctly, even starting from an rms error of over 100° as in table 1(a).

There are two features of the structures tested which determine their difficulty. One is the number of zeros in the Patterson function. The structure in table 1(a) produces a single zero in the Patterson whereas the example in table 1(b) has no zeros. Since there is a restriction that the double Patterson density cannot be negative, a zero in the Patterson function automatically leads to correct values at all points in the double Patterson contributing to that point in the projection. Therefore, the more zeros there are in the Patterson function, the easier the structure.

The second feature for consideration is how flat the Patterson function is. Structures whose Patterson functions are fairly flat are more difficult to solve than those with prominent peaks or deep troughs. The example in table 1(c) has a much flatter Patterson than that in table 1(b) and it has already been shown to be a more difficult structure. The variances of the Patterson density are 2.7 and 4.3 respectively.

An examination of the structures that failed to solve, or were difficult, revealed another interesting fact. A large proportion of the signs of the Σ_1 -type coefficients, *i.e.* those of the form $E(\mathbf{h})E(\mathbf{h})E(-2\mathbf{h})$, were wrong. The Σ_1 formula can often give wrong results, but it is disturbing that under perfect conditions, without experimental error, the approximation to the double Patterson used here also estimates these signs

wrongly. It ought to be more reliable than the Σ_1 formula itself. This has led the author to abandon the Σ_1 formula as an indicator of phases prior to phase determination by the tangent formula of Karle and Hauptman (1956).

It is clear from these tests that information about 3-phase invariants can be obtained by objective procedures involving the double Patterson function. It is interesting that no use is made of probability relationships as in conventional direct methods; neither is Sayre's equation necessary, although it is useful to accelerate the convergence of the procedure. Unfortunately, it is impossible to predict how the technique will behave with real crystal structures in three dimensions. More elaborate testing will have to be done to determine this.

A problem not yet solved is how to define the enantiomorph for non-centrosymmetric structures. It is possible that the determination of $\cos(\phi(\mathbf{h}) + \phi(\mathbf{k}) + \phi(-\mathbf{h} - \mathbf{k}))$ may be sufficient, but it would be more satisfactory if the actual phases could be obtained.

The larger the structure, the more under-determined is the image reconstruction from projections in vector space. This may well be the limiting factor in the whole procedure, although where the limit lies is completely unknown as yet.

The computing time will be large for real structures, but the fastest computers should now be able to handle a realistic calculation. This will limit the method to those crystal structures that cannot otherwise be solved, or require several man-years work as in macromolecular crystallography. Even if the method proves to be of no practical use, the results presented in this paper are very interesting in themselves.

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