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A Relation Between Structure Factor, Triple Products and a Single Patterson Vector, and its Application to Sign Determination

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The Fourier coefficients $D_{\mathbf{h}}$ of a hypersection of the double Patterson function at a fixed value of $\mathbf{U}$ can be written as

$$D_{\mathbf{h}}=(1/V)\ \textstyle\sum_{\mathbf{h}'}F_{\mathbf{h}}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}\ \cos 2\pi\mathbf{h}'\,.\,\mathbf{U}/\cos 2\pi\mathbf{h}\,.\,(\mathbf{U}/2)\,.$$

It is shown that also $D_{\mathbf{h}}=F_{\mathbf{h}}G_{\mathbf{h}}$, where $G_{\mathbf{h}}$ is the Fourier coefficient of a reduced structure derived from the original structure by positioning an atom with form factor $\sum_{\mathbf{h}'}f_i(\mathbf{h}')f_j(\overline{\mathbf{h}+\mathbf{h}'})$ halfway in between those atoms i and j, which are a vector $\mathbf{U}$ apart. If $\mathbf{U}$ is a single vector between two atoms with form factor $f(\mathbf{h})$, then the reduced structure contains only one atom, at the origin, and $G_{\mathbf{h}}=(1/V)\ \sum_{\mathbf{h}'}f(\mathbf{h}')f(\overline{\mathbf{h}+\mathbf{h}'})$. We obtain the relation $\sum_{\mathbf{h}'}F_{\mathbf{h}}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}/[\cos 2\pi\mathbf{h}\,.\,(\mathbf{U}/2)\sum_{\mathbf{h}'}f(\mathbf{h}')f(\overline{\mathbf{h}+\mathbf{h}'})]=F_{\mathbf{h}}$. Using this formula with probabilities for the signs of the triple products, the single vectors $\mathbf{U}$ are found by a scanning process, as we demonstrate on a heavy atom structure. The signs of the structure factors have thus been calculated directly from the triple products.

Introduction

The double Patterson function (Sayre, 1953) is defined as $T(\mathbf{U},\mathbf{V})\equiv\int\varrho(\mathbf{r})\varrho(\mathbf{r}+\mathbf{U})\varrho(\mathbf{r}+\mathbf{V})d\mathbf{r}$. Its Fourier coefficients are the triple products $F_{\mathbf{h}}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}$, divided by V^2. Hypersections* of this six-dimensional function can be synthesized because the phases of triple products show a tendency towards zero. A hypersection at a fixed value of $\mathbf{U}$ contains the structure once if $\mathbf{U}$ corresponds to a single Patterson vector (Hoppe, 1957) and twice if $\mathbf{U}$ is a double Patterson vector, *etc.*

In this paper we relate the Fourier coefficient $F_{\mathbf{h}}$ of a centrosymmetric structure to the Fourier coefficients of a Hoppe section. This leads to a relation between $F_{\mathbf{h}}$, triple products and a single Patterson vector $\mathbf{U}$. By scanning $\mathbf{U}$ through the asymmetric unit of the Patterson space† we expect to find the positions of the single peaks, and the signs of $F_{\mathbf{h}}$, at values of $\mathbf{U}$ where

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* In this paper a coset of the subspace $\mathbf{U}=\mathbf{0}$ (or $\mathbf{V}=\mathbf{0}$) is called a hypersection.

† Each peak in the linear subspace $\mathbf{U}=\mathbf{0}$ or $\mathbf{V}=\mathbf{0}$ of the double Patterson function corresponds to a peak with the same position but not the same height in the Patterson function. For this reason we will refer to such a linear subspace as a Patterson space.

the disagreement factor, between left- and right-hand sides of the equations, attains a minimum value.*

Fourier coefficients of a hypersection of the double Patterson

The double Patterson function

$$T(\mathbf{U},\mathbf{V})\equiv\int\varrho(\mathbf{r})\varrho(\mathbf{r}+\mathbf{U})\varrho(\mathbf{r}+\mathbf{V})d\mathbf{r}$$

can be written as

$$T(\mathbf{U},\mathbf{V})=\frac{2}{V^2}\sum_{\mathbf{h}=0}^{\infty}\sum_{\mathbf{h}'=-\infty}^{+\infty}\tau_{\mathbf{hh}'}\cos 2\pi(\mathbf{h}'\,.\,\mathbf{U}+\mathbf{h}\,.\,\mathbf{V})\quad(1)$$

for a centrosymmetrical structure, where $\tau_{\mathbf{hh}'}\equiv F_{\mathbf{h}}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}$ and $\mathbf{h}(h,k,l)$ and $\mathbf{h}'(h',k',l')$ are reciprocal lattice vectors.

In equation (1) the summation $\sum\limits_{\mathbf{h}=0}$ means that the summation is to be taken over one half of the reciprocal net (*e.g.* $h=0(1)\infty$, $k=-\infty(1)+\infty$, $l=-\infty(1)+\infty$), while the borderline terms are assumed to be properly weighted.

Since $\tau_{\mathbf{hh}'}=\tau_{\mathbf{h},\,\overline{\mathbf{h}+\mathbf{h}'}}$, we have

$$\begin{aligned}T(\mathbf{U},\mathbf{V})&=\frac{2}{V^2}\sum_{\mathbf{h}=0}^{\infty}\sum_{\mathbf{h}'=-\infty}^{+\infty}{}'\,\tau_{\mathbf{hh}'}\,\{\cos 2\pi(\mathbf{h}'\,.\,\mathbf{U}+\mathbf{h}\,.\,\mathbf{V})\\&\quad+\cos 2\pi[(-\mathbf{h}-\mathbf{h}')\,.\,\mathbf{U}+\mathbf{h}\,.\,\mathbf{V})]\}\\&=\frac{4}{V^2}\sum_{\mathbf{h}=0}^{\infty}\sum_{\mathbf{h}'=-\infty}^{+\infty}{}'\,\tau_{\mathbf{hh}'}\cos 2\pi[\mathbf{h}\,.\,\mathbf{V}-\mathbf{h}\,.\,(\mathbf{U}/2)\\&\quad\times\cos 2\pi[\mathbf{h}'\,.\,\mathbf{U}+\mathbf{h}\,.\,(\mathbf{U}/2)]\end{aligned}\qquad(2)$$

where the summation $\sum'$ is restricted over terms containing independent coefficients $\tau_{\mathbf{hh}'}$. Now

$$2\cos 2\pi[\mathbf{h}'\,.\,\mathbf{U}+\mathbf{h}\,.\,(\mathbf{U}/2)]=\frac{\cos 2\pi(\mathbf{h}+\mathbf{h}')\,.\,\mathbf{U}+\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}}{\cos 2\pi[\mathbf{h}\,.\,(\mathbf{U}/2)]\,.}\,.$$

Changing the summation from $\sum'_{\mathbf{h}'}$ to $\sum_{\mathbf{h}'}$ so that $\tau_{\mathbf{hh}'}$ and $\tau_{\mathbf{h},\overline{\mathbf{h}+\mathbf{h}'}}$ appear separately again, (2) gives

$$\begin{aligned}T(\mathbf{U},\mathbf{V})&=\frac{2}{V^2}\sum_{\mathbf{h}=0}^{\infty}\cos 2\pi\mathbf{h}\,.\left(\mathbf{V}-\frac{\mathbf{U}}{2}\right)\\&\quad\times\sum_{\mathbf{h}'=-\infty}^{+\infty}\frac{\tau_{\mathbf{hh}'}\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}}{\cos 2\pi[\mathbf{h}\,.\,(\mathbf{U}/2)]}\,.\end{aligned}\qquad(3)$$

If we define

$$D_{\mathbf{h}}(\mathbf{U})\equiv\frac{1}{V}\sum_{\mathbf{h}'=-\infty}^{+\infty}\frac{\tau_{\mathbf{hh}'}\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}}{\cos 2\pi[\mathbf{h}\,.\,(\mathbf{U}/2)]}\qquad(4)$$

then $D_{\mathbf{h}}(\mathbf{U})$ is the Fourier coefficient of a hypersection of the double Patterson at any value of **U**. The double Patterson can thus be written as

$$T(\mathbf{U},\mathbf{V})=\frac{2}{V}\sum_{\mathbf{h}=0}^{\infty}D_{\mathbf{h}}(\mathbf{U})\cos 2\pi\mathbf{h}\,.\left(\mathbf{V}-\frac{\mathbf{U}}{2}\right)\qquad(5)$$

which means that for a centrosymmetric structure any hypersection at a fixed value of **U** has a centre of symmetry at $\mathbf{V}=\mathbf{U}/2$, and also, that a hypersection at a fixed value of **V** has a centre of symmetry at $\mathbf{U}=\mathbf{V}/2$.

Relation between hypersection and structure

Rearranging (4) we get

$$D_{\mathbf{h}}(\mathbf{U})=\frac{F_{\mathbf{h}}}{V\cos 2\pi\mathbf{h}\,.\,(\mathbf{U}/2)}\sum_{\mathbf{h}'=-\infty}^{+\infty}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}\,.\qquad(6)$$

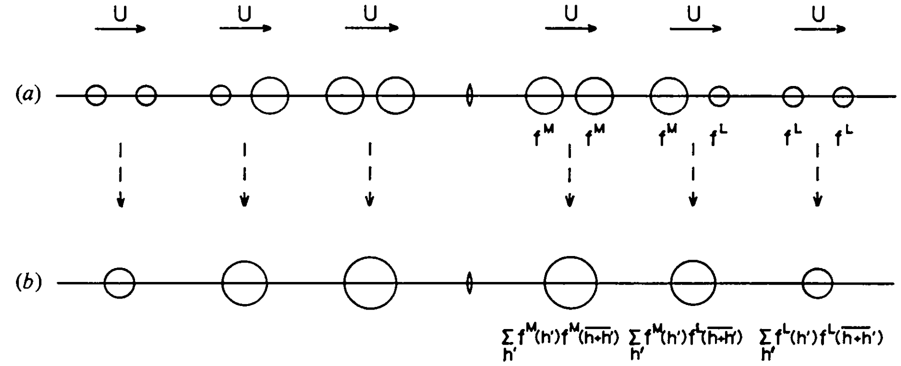

Fig. 1. (*a*) A centrosymmetrical structure, with two kinds of atoms, with form factors f^M and f^L respectively. (*b*) The reduced structure, based on the sixfold vector **U**, with atoms halfway in between atoms of the original structure.

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* We thank the referee for sending us a copy of a recent article by Simonov & Weissberg (1970). These authors have calculated the signs of the Fourier coefficients of a Hoppe section and they have used those signs to synthesize an F_{obs} map. We ourselves derived a quantitative relation between triple products, single Patterson vector and structure factor, which enabled us to locate a Hoppe section.

Now

$$F_{\mathbf{h}'} \cos 2\pi\mathbf{h}' . \mathbf{U} = \sum_{j=1}^{N} \tfrac{1}{2} f_j(\mathbf{h}') \left[\cos 2\pi\mathbf{h}' . (\mathbf{r}_j + \mathbf{U}) + \cos 2\pi\mathbf{h}' . (\mathbf{r}_j - \mathbf{U})\right] = X_{\mathbf{h}'}, \text{ say.}$$

$X_{\mathbf{h}'}$ is the Fourier coefficient of a structure with half-weight atoms at $\mathbf{r}_j - \mathbf{U}$ and $\mathbf{r}_j + \mathbf{U}$. According to the convolution theorem $\frac{1}{V} \sum_{\mathbf{h}'=-\infty}^{+\infty} X_{\mathbf{h}'} F_{\overline{\mathbf{h}+\mathbf{h}'}}$ is the Fourier coefficient of index $-\mathbf{h}$ of the product of the electron density with the 'density' of which the Fourier coefficients are $X_{\mathbf{h}}$. Consequently this product has peaks at $\mathbf{r}_j$ if $\mathbf{r}_j - \mathbf{r}_i = \mathbf{U}$ or $\mathbf{r}_j - \mathbf{r}_i = -\mathbf{U}$. As the product density at $\mathbf{r}_j$ equals $\frac{1}{2}\varrho(\mathbf{r}_i)\varrho(\mathbf{r}_j)$ the form factors of the pseudo atoms in this product function are

$$\frac{1}{2V} \sum_{\mathbf{h}'=-\infty}^{+\infty} f_i(\mathbf{h}') f_j(\overline{\mathbf{h}+\mathbf{h}'}) \equiv \tfrac{1}{2} g_{ij}(\mathbf{h}) \ . \tag{7}$$

Formula (6) can then be written as

$$D_{\mathbf{h}}(\mathbf{U}) = \frac{F_{\mathbf{h}}}{2V} \sum_{j=1}^{N} g_{ij}(\mathbf{h}) \frac{\exp 2\pi i\mathbf{h} . (\mathbf{r}_j + \mathbf{U}) + \exp 2\pi i\mathbf{h} . \mathbf{r}_j}{\cos 2\pi\mathbf{h} . (\mathbf{U}/2)} \tag{8}$$

provided that we restrict the summation over the atoms j so that $\mathbf{r}_j + \mathbf{U} = \mathbf{r}_i$. This becomes

$$D_{\mathbf{h}}(\mathbf{U}) = F_{\mathbf{h}} G_{\mathbf{h}} \tag{9a}$$

with

$$G_{\mathbf{h}} = \sum_{\substack{j=1 \\ \mathbf{r}_j + \mathbf{U} = \mathbf{r}_i}}^{N} g_{ij}(\mathbf{h}) \exp 2\pi i\mathbf{h} . \left((\mathbf{r}_j + \frac{\mathbf{U}}{2}\right) \tag{9b}$$

According to (9*a*) a hypersection of the double Patterson can be regarded as a convolution of the structure itself (Fourier coefficients $F_{\mathbf{h}}$) and a *reduced structure* (Fourier coefficients $G_{\mathbf{h}}$). As follows from (9*b*), this reduced structure has atoms halfway between those atoms, that are a vector **U** apart in the original structure. An atom in this reduced structure, in between the original atoms i and j, has a form factor $g_{ij}(\mathbf{h})$ as is given by (7).

As an example Fig. 1(*a*) shows a one-dimensional structure consisting of two kinds of atoms M and L with form factors f^M and f^L respectively. The corresponding reduced structure, for a sixfold vector **U**, contains atoms with form factors

$$(1/V)\textstyle\sum_{\mathbf{h}'} f^M(\mathbf{h}') f^M(\overline{\mathbf{h}+\mathbf{h}'}),\ (1/V)\sum_{\mathbf{h}'} f^M(\mathbf{h}') f^L(\overline{\mathbf{h}+\mathbf{h}'})$$

$$\text{and } (1/V)\textstyle\sum_{\mathbf{h}'} f^L(\mathbf{h}') f^L(\overline{\mathbf{h}+\mathbf{h}'})$$

respectively [Fig. 1(*b*)].

It should be remarked that our reduced structure (based on a vector **U**) is closely related to the set of all centres of symmetry at position vectors $\mathbf{R}_m$, each provided with a weight W_m, as they occur in a minimum function over a multiple Patterson vector **U**, expressed by Germain & Woolfson (1966) in their formula (3)

$$\psi_{\mathbf{h}} = 2K_s F_{\mathbf{h}} \sum_{m=1}^{N/2} W_m \cos 2\pi\mathbf{h} . \mathbf{R}_m$$

which resembles our formula (9*a*) which, taking into account the fact that the reduced structure is centrosymmetric, can be written as:

$$D_{\mathbf{h}}(\mathbf{U}) = 2F_{\mathbf{h}} \sum_{\substack{j=1 \\ \mathbf{r}_j + \mathbf{U} = \mathbf{r}_i}}^{N/2} g_{ij}(\mathbf{h}) \cos 2\pi\mathbf{h} . \left(\mathbf{r}_j + \frac{\mathbf{U}}{2}\right) . \tag{9c}$$

If **U** is a single vector between atoms M, $G_{\mathbf{h}}$ reduces to $G_{\mathbf{h}} = g_{ij}(\mathbf{h})$ because the corresponding reduced structure has only one peak, *viz*. at the origin [Fig. 2(*b*)]. Equations (6), (7) and (9*a*) then finally give the relation we are aiming at

$$F_{\mathbf{h}} = \left[1/\textstyle\sum_{\mathbf{h}'} f_i^M(\mathbf{h}') f_j^M(\overline{\mathbf{h}+\mathbf{h}'})\right] \times \sum_{\mathbf{h}'=-\infty}^{+\infty} \frac{F_{\mathbf{h}} F_{\mathbf{h}'} F_{\overline{\mathbf{h}+\mathbf{h}'}} \cos 2\pi\mathbf{h}' . \mathbf{U}}{\cos 2\pi[\mathbf{h} . (\mathbf{U}/2)]} , \tag{10}$$

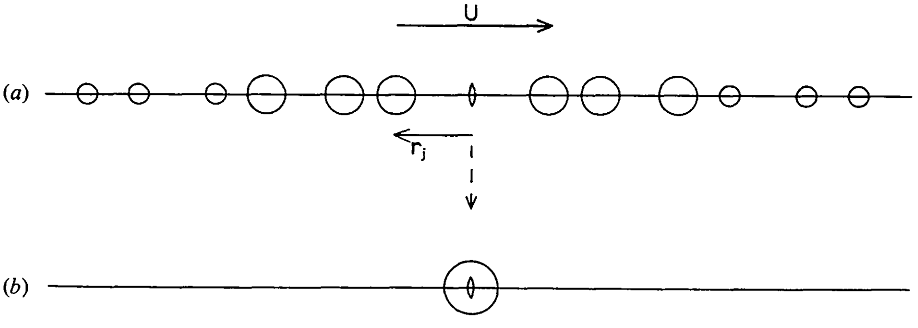


Fig. 2. (*a*) A centrosymmetrical structure, as in Fig. (1*a*), with a single vector drawn. (*b*) The reduced structure, based on the single vector **U**, containing only one atom, with form factor $\sum_{\mathbf{h}'} f^M(\mathbf{h}') f^M(\mathbf{h}+\mathbf{h}')$, at the centre of symmetry.

or statistically,

$$F_{\mathbf{h}} = \frac{\sum_{\mathbf{h}'=-\infty}^{+\infty} |F_{\mathbf{h}}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}|\,(P_+ - P_-)\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}}{\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^M(\overline{\mathbf{h}+\mathbf{h}'})\cos 2\pi[\mathbf{h}\,.\,(\mathbf{U}/2)]} \quad (11)$$

where $P_+ - P_- = \tanh \varepsilon_3/\varepsilon^3 |U_{\mathbf{h}}U_{\mathbf{h}'}U_{\overline{\mathbf{h}+\mathbf{h}'}}|$ according to Cochran & Woolfson (1955).*

Equations (10) and (11) express a relation between triple products, a single Patterson vector **U** and a structure factor. With the aid of (11) the sign of a structure factor can be estimated directly from the triple products if a single vector is known. We will show how this formula can be used both to find the position of a single vector and to calculate the signs of the structure factors.

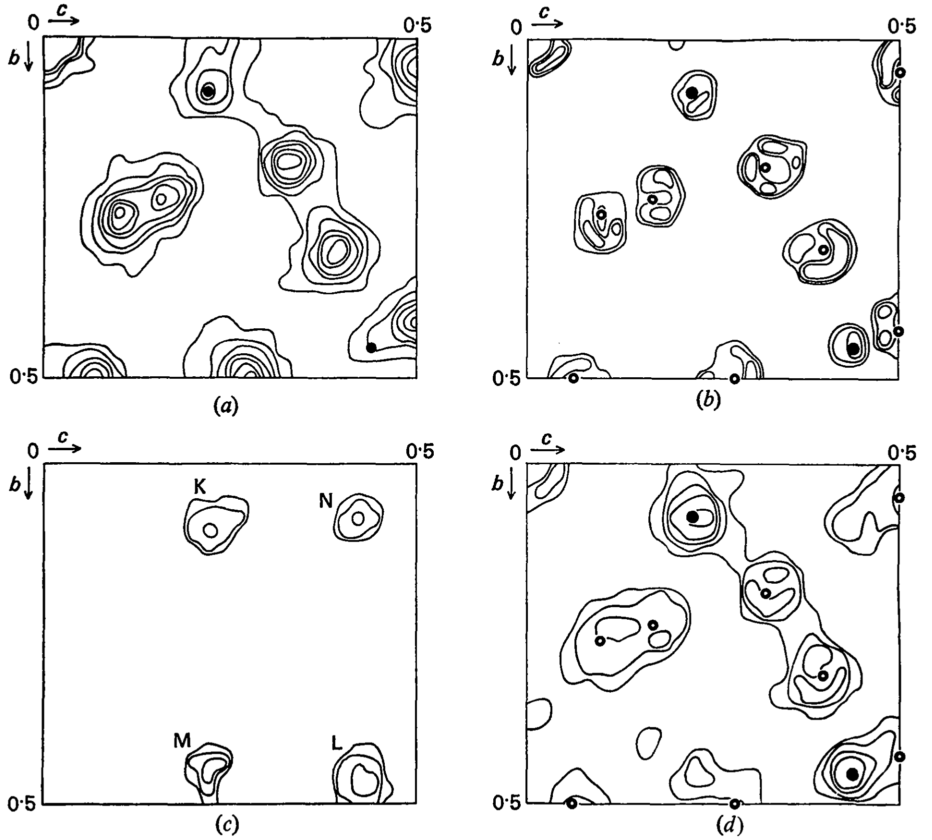
It should be remarked that if **U** is a single vector, the hypersection of the double Patterson at this value of **U** will contain the structure only once, which corresponds to the fact that the reduced structure contains only one atom at the centre of symmetry. This hypersection is known as the Hoppe section (Hoppe, 1957).

It is useful to know what happens to the left-hand side of equation (10) if **U** is not a single vector, but a multiple vector. In that case we obtain directly from (6), (7) and (9*a*):

$$F_{\mathbf{h}}G'_{\mathbf{h}} = \frac{\sum_{\mathbf{h}'=-\infty}^{+\infty} F_{\mathbf{h}}F_{\mathbf{h}'}F_{\overline{\mathbf{h}+\mathbf{h}'}}\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}}{\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^M(\overline{\mathbf{h}+\mathbf{h}'})\cos 2\pi\mathbf{h}\,.\,(\mathbf{U}/2)} \quad (12)$$

where $G'_{\mathbf{h}}$ is the structure factor of the reduced structure, now with atoms with possible form factors

$$\textstyle\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^M(\overline{\mathbf{h}+\mathbf{h}'})/\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^M(\overline{\mathbf{h}+\mathbf{h}'})\,,$$
$$\textstyle\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^L(\overline{\mathbf{h}+\mathbf{h}'})/\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^M(\overline{\mathbf{h}+\mathbf{h}'})\,,$$
$$\textstyle\sum_{\mathbf{h}'} f^L(\mathbf{h}')f^L(\overline{\mathbf{h}+\mathbf{h}'})/\sum_{\mathbf{h}'} f^M(\mathbf{h}')f^M(\overline{\mathbf{h}+\mathbf{h}'})\,.$$



(*a*) (*b*) (*c*) (*d*)

Fig. 3. (100) Projection of hexamethylenediamine dihydrobromide. (*a*) The Patterson function. (*b*) $R_A(\mathrm{U})$, showing minima at the positions of the single bromine vectors and minima in circles round the double bromine vectors. The single and double bromine vectors are indicated with closed and open circles respectively. Contour lines at 0·50, 0·45 and 0·40. (*c*) $R_B(\mathrm{U})$; the minima corresponding to single bromine vectors indicated with *K* and *L*, the additional minima with *M* and *N*. (*d*) $R_C(\mathrm{U})$; the minima at the positions of the single bromine vectors are now definitely lower than the other minima. Contour lines at 0·80, 0·70, 0·60, 0·50 and 0·40.

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* Scanning through the unit cell the position of a heavy atom *M* (at U/2) might be used as structural information to increase the reliability of the triple product sign probability P_+ (Kroon & Krabbendam, 1970). Then P_+ is a function of U.

Space groups of hypersections

According to (9*a*) the Fourier coefficients $D_{\mathbf{h}}$ of a hypersection of the double Patterson at a fixed value of **U** can be written as $D_{\mathbf{h}}=F_{\mathbf{h}}G_{\mathbf{h}}$. If $\mathbf{h}_1, \mathbf{h}_2, \ldots$ *etc.* are reciprocal vectors related by symmetry, then there are relations between $F_{\mathbf{h}_1}, F_{\mathbf{h}_2}, \ldots$ *etc.* However, as $G_{\mathbf{h}}$ is the Fourier coefficient of the reduced structure, of which the space group is in general $P\bar{1}$, the same relations will not exist for $G_{\mathbf{h}_1}, G_{\mathbf{h}_2} \ldots$ *etc.*, not even for $|G_{\mathbf{h}_1}|, |G_{\mathbf{h}_2}|, \ldots$ *etc.* Consequently there are no relations between $D_{\mathbf{h}_1}, D_{\mathbf{h}_2}, \ldots$ *etc.*; the space group of the corresponding hypersection is therefore $P\bar{1}$.

However, if **U** is a single vector then the corresponding hypersection (Hoppe section), being a convolution of the structure and the reduced structure with only one peak at the origin, has the same space group as the original structure.

Occasionally it may happen that for some **U** a reduced structure belongs to a space group for which the symmetry relations in reciprocal space are $G_{\mathbf{h}_1}=G_{\mathbf{h}_2}= \ldots$ *etc.* In that case the symmetry relations between the $D_{\mathbf{h}}$'s are the same as those between the $F_{\mathbf{h}}$'s; this special hypersection then belongs to the same space group as the original structure.

Application to sign determination

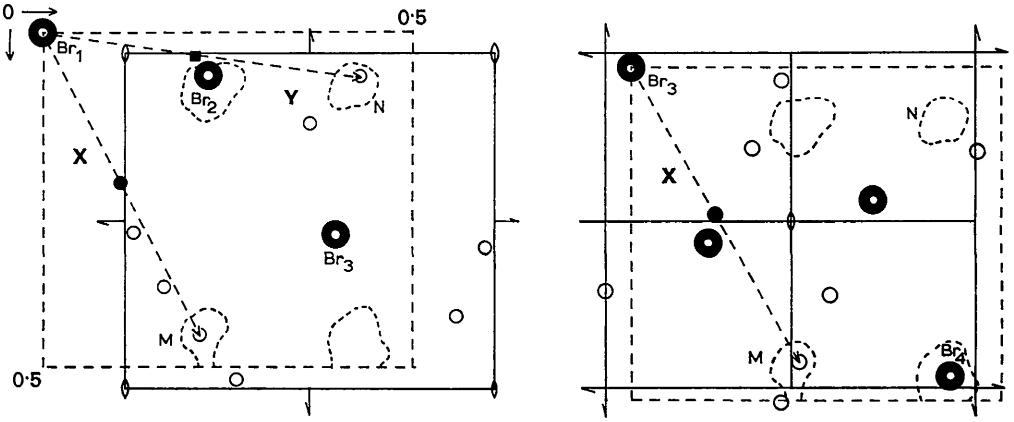
We take as an example the (100) projection of hexamethylenediamine dihydrobromide (Binnie & Robertson, 1949), with plane group *pgg*. Our purpose is to find a bromine–bromine single vector and calculate the structure factors by means of equation (11). In order to find a single vector, the vector **U** in (11) is scanned over discrete points through the asymmetric unit of the Patterson space. The vector **U**, which gives the best agreement between structure factors F^c_{0kl}, as calculated by (11) and the observed structure factor F_0^{okl}, is apt to be a single vector. For this purpose we define:

$$R_A=\frac{\sum_k\sum_l\left||F^o_{0kl}|-|F^c_{0kl}|\right|}{\sum_k\sum_l|F^o_{0kl}|} \qquad (13)$$

in which $k=0(1)k_{\max}$, $l=l_{\min}(1)l_{\max}$. We admit in (13) only those F_{0kl}'s for which in (11) $\cos 2\pi\mathbf{h}.(\mathbf{U}/2)$ exceeds a certain small value, so as to avoid extremely large values of F^c_{0kl}.

R_A as a function of **U** [Fig. 3(*b*)] shows minima at the positions of the two bromine single peaks but, unfortunately, also comparable minima in circles round the double bromine peaks [note the similarity with the Patterson function in Fig. 3(*a*)]. This is explained by the fact that in (13) we compare absolute values of F^o_{0kl} and F^c_{0kl}, so that we are really comparing a Patterson of the structure with a Patterson of the hypersection at **U**. If **U** is a double bromine–bromine vector then the corresponding hypersection contains the structure twice, that is, the original structure superimposed on its image, originated by inversion of the original structure through some pseudo centre. Consequently the Patterson of this hypersection will resemble the Patterson of the original structure (Krabbendam & Kroon, 1971), and F^c_{0kl} will resemble F^o_{0kl}, except for a scaling factor. As the hypersection contains the structure twice, F^c_{0kl} is, on the average, larger than F^o_{0kl}, so that an improvement in the scaling factor can be expected in the direction of the edge of the double bromine–bromine peak. This explains the additional minima round the double peaks in Fig. 3(*b*).

In order to get round this difficulty we devise for plane group *pgg* a function R_B, defined as



(*a*) (*b*)

Fig. 4. Explanation of the additional minima *M* and *N* from Fig. 3(*c*). (*a*) R_B(U) (dotted lines) superimposed on the structure, with its origin at the bromine atom Br$_1$. Bromine atoms: large bold circles, light atoms: small circles. The additional minima *M* and *N* correspond to the Br$_1$–C vectors **X** and **Y**, of which the midpoints (black dot and black square, respectively) are close to the cell edges of the structure. (*b*) R_B(U) superimposed on the structure, with its origin at the bromine atom Br$_3$. The minimum *M* also corresponds to the Br$_3$–C vector **X**, the midpoint of which is again approximately on the cell edge (black dot).

$$R_B=\frac{\sum_k \sum_l |F^c_{0kl}-(-1)^{k+l}F^c_{0k\bar{l}}|}{\frac{1}{2}\sum_k \sum_l (|F^c_{0kl}|+|F^c_{0k\bar{l}}|)}\,. \tag{14}$$

Its definition is based upon the fact that the symmetry relations between F_{0kl} and $F_{0k\bar{l}}$, valid in plane group *pgg*, will show up again in F^c_{0kl} and $F^c_{0k\bar{l}}$, if **U** is a single vector. And indeed, $R_B(\mathbf{U})$ has minima at the positions of the bromine single peaks [K and L in Fig. 3(*c*)] but, remarkably, also at the intersections of lines drawn parallel to the axes through the minima K and L. An explanation is given in Fig. 4. Fig. 4(*a*) shows the function $R_B(\mathbf{U})$ superimposed on the structure, with its origin on a bromine atom Br_1. The function $R_B(\mathbf{U})$ has a minimum at the position of Br_2, a bromine atom which is related to Br_1 by a centre of symmetry. As it happens there is also a light atom at each of the two extra minima (M and N) in R_B. The atoms at M and N are situated such that a vector **X** from Br_1 to M and a vector **Y** from Br_1 to N have their midpoints (black dot and black square, respectively) approximately on one of the cell edges of the structure.

Fig. 4(*b*) shows the function $R_B(\mathbf{U})$ superimposed on the structure, but now with its origin at the bromine atom Br_3. The function $R_B(\mathbf{U})$ has a minimum at the position of Br_4, a bromine atom which is related to Br_3 by a centre of symmetry. There is also a light atom at the minimum in R_B which we have indicated by M. Again the vector **X**, appearing for the second time, has its midpoint (black dot) on one of the cell edges. As the vector **X** fits twice in the assymetric unit, the reduced structure, based on this vector **X**, contains two independent atoms, one indicated with a black dot in Fig. 4(*a*), the other with a black dot in Fig 4(*b*), both situated halfway along the vector **X**. The vector **Y** fits only once in the asymmetric unit, so its reduced structure contains only one independent atom [black square in Fig. 4(*a*)], halfway along the vector **Y**. Both reduced structures belong approximately to plane group *pmm*. The hypersections corresponding to these reduced structures belong (see our remark at the end of the last section) to the original plane group *pgg*, a fact which explains the occurrence of the minima M and N in $R_B(\mathbf{U})$. Indeed, the locus of all points in $R_B(\mathbf{U})$, which can give rise to such a minimum, are lines parallel to the cell edges through K and L.

As the undesirable peaks in $R_A(\mathbf{U})$ have no relations to the undesirable peaks in $R_B(\mathbf{U})$, they might disappear in a function R_C, which is a combination of R_A and R_B.

We define

$$R_C=\frac{\sum_k \sum_l \left||F^o_{0kl}|-\frac{1}{2}\{|F^c_{0kl}+(-1)^{k+l}F^c_{0k\bar{l}}|\}\right|}{\sum_k \sum_l |F^o_{0kl}|} \tag{15}$$

where $k=0(1)k_{\max}$, $l=0(1)l_{\max}$.

R_C as a function of **U** [Fig. 3(*d*)] resembles the function R_A very closely [Fig. 3(*b*)]; only the minima at the positions of the single bromine peaks are now definitely lower than the other minima. Signs of F^c_{0kl}, calculated on the basis of a single vector thus obtained, using formula (11), do not differ from those calculated by an ordinary structure factor calculation from the heavy atom position, but the agreement between F^o_{0kl} and F^c_{0kl} is significantly better if F^c_{0kl} is calculated by (11) ($R_A=0{\cdot}37$ against the conventional $R=0{\cdot}53$).

It should be noted that in practice it is not necessary to calculate the full equation (11) for every value of **U** in the scanning process. According to (11)

$$F^c_{\mathbf{0}}=\frac{F_{\mathbf{0}}}{g(\mathbf{0})}\sum_{\mathbf{h}'} |F_{\mathbf{h}'}|^2\cos 2\pi\mathbf{h}'\,.\,\mathbf{U}\,. \tag{16}$$

Thus $F^c_{\mathbf{0}}$ is proportional to the Patterson function at **U**; values of **U** for which $F^c_{\mathbf{0}}$ is too large or too small concerning the expected height of a single peak, can be disregarded.

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