Use of the Anti-Symmetric Component of the Patterson and Fourier Functions for the Solution of Problems Involving Small Atomic Shifts from Positions of Super-Symmetry

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For small departures from super-symmetry, commonly encountered among the structures of inorganic compounds, it is shown that a solution may be obtained from the anti-symmetrical component of the Patterson synthesis. This ΔP function is evaluated with only those reflections which are forbidden by the super-group. An outline is given of the properties of the ΔP function and the corresponding anti-symmetric Fourier synthesis. An illustrative example is taken from the structure determination of conichalcite.

1. Introduction

The problem of pseudo-symmetry often occurs in the course of structure determinations where the structure approximates to a higher symmetry than that envisaged by the proper space group. It can be of two main types, (a) where the extra pseudo-symmetry places the atoms in a higher space group that produces (or simulates) additional absences *e.g.* the positions on one of the screw axes or with one coordinate halfway between a pair of parallel screw axes in $P2_12_12_1$, and (b) where the higher space group is not distinguished by any additional absences. Examples of the latter are (i) the apparent centre of symmetry contributed by a nearly centro-symmetric molecular arrangement, and (ii) the ambiguity arising from small possible displacements of light atoms resulting in a lowering of the crystallographic symmetry from a centro-symmetrical space group to a non-centro-symmetrical one with the same diffraction symmetry, and presumably undetected by physical methods such as a positive piezo- or pyro-electric effect.

Pseudo-symmetry of type (a) is frequently shown by inorganic structures, where the metal atoms may be in (or near) the higher-symmetry positions, with the oxygen and other light atoms displaced towards the lower-symmetry positions, and it is often extremely difficult to determine the precise extent and directions of these displacements, because mathematically they occur in a region of zero gradient in a least-squares or equivalent Fourier treatment. For the complete solution of such structures, it seems logical to utilize a Patterson component based on those weak low-symmetry reflections that would disappear in the super-symmetrical arrangement, and which will form an anti-symmetric component of the normal Patterson function. If we consider an orthogonal $0kl$ Patterson

projection in $P2_12_12_1$, for example, it is readily seen that whereas the reflections with $k+l=$even give a Patterson map symmetrical about a 2-fold axis ($\|a$) through $(-, \frac{1}{4}, \frac{1}{4})$, the map for the reflections with $k+l=$odd is anti-symmetric about this axis. The actual total Patterson map will consist of the sum of the two, so that we may think of any particular Patterson interaction peak, P_{total}, as composed of a symmetric interaction, $P_{\text{sym.}}$, and an anti-symmetric component, (ΔP), this latter being very much smaller in the type of case being considered here. Thus, in general,

$$P_{\text{total}} = P_{\text{sym.}} + (\Delta P) \qquad (1)$$

and $P_{\text{sym.}}$ will lead to atomic positions with the super symmetry, while the analysis of the ΔP peaks will yield quantitative estimates of the actual departures from these positions of higher symmetry. This analysis being in some respects similar to that for a $(\varrho_o - \varrho_c)$ difference Fourier, it may conceivably be advantageous in other cases also to separate the two Patterson components of equation (1).

2. Illustrative example

For developing the theory, we take as an illustrative example the space group *Pnma* as a super-symmetrical group of the common $P2_12_12_1$, as occurs in the structures of the descloizite and adelite series of minerals (Qurashi & Barnes, 1954; Donaldson & Barnes, 1955). Conichalcite, $CuCa(AsO_4)OH$, a typical arsenate of this series, would be placed in the group *Pnma*, except for the presence of 8 weak $0kl$ reflections with $k+l=$ odd and 9 very weak $hk0$ reflections with $h=$odd, and the metal atoms in the approximate structure in *Pnma* symmetry proposed earlier (Qurashi & Barnes, 1954) are shown schematically in the (100) projection of Fig. 1(*a*). Consider only the calcium atoms, indicated by the large solid circles; their x and z-coordinates are not restricted by the higher symmetry (*Pnma*),

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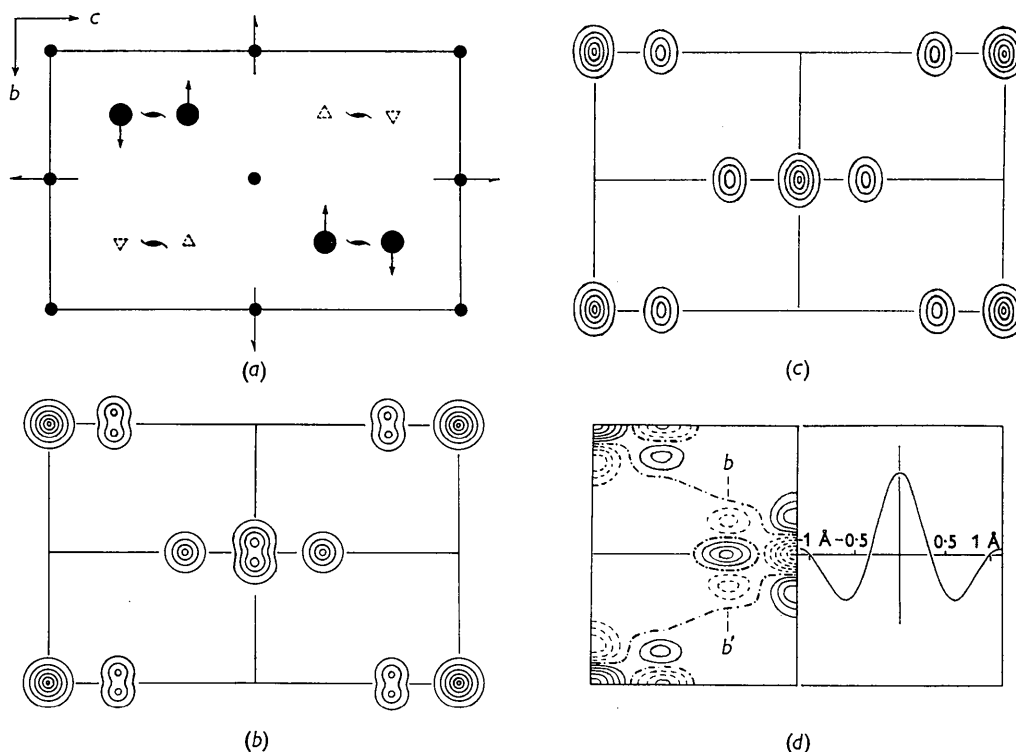
Fig. 1. Schematic representation of the relationship between the actual $P2_12_12_1$, and the super-symmetric $Pnma$, Patterson $0kl$ maps for the calcium atoms in conichalcite, $CaCu(AsO_4)(OH)$; (a) $Pnma$ structure projection of calcium (large circles), copper (small circles), arsenic (triangles), the arrows indicating small anti-symmetric displacements of calcium atoms only; (b) actual $P2_12_12_1$ Patterson map for calcium only; (c) corresponding super-symmetric $Pnma$ map; (d) left, corresponding anti-symmetric component (zero contour, chain line) and, right, cross-section along the line $b–b'$ or along the b-axis through the origin.

but y is limited to $\pm \frac{1}{4}$, whereas in the actual $P2_12_12_1$ symmetry, y is also free to take any value. The permissible small displacements of the calcium atom are shown by the arrows in Fig. 1(a), and the idealized Patterson maps for the actual calcium positions only and for the averaged positions in $Pnma$ symmetry are indicated schematically in Fig. 1(b) and 1(c), respectively. The left-hand half of Fig. 1(d) shows schematically the difference between the two maps, which corresponds to the anti-symmetric part of the Patterson synthesis referred to above, and it is at once seen that the contiguous +positive and −negative peaks in such a difference Patterson are somewhat similar to the corresponding peaks obtained in a $(\rho_0 - \rho_c)$ difference Fourier map. We can see that in Fig. 1(d) the line (e.g. bb') joining the corresponding maxima and minima is parallel to the displacements, the magnitude of which for the simple case of the calcium displacements is approximately proportional to the square root of the peak heights. This is generally true, and the detailed theory follows.

3. Basic mathematical analysis

In this example, the calcium atom introduces a special value for only one coordinate, and is thus very suitable

for discussion. Let the coordinates of the calcium atoms in $Pnma$ symmetry be $(-, \frac{1}{4}, z')$ and let the displacements from this position be Δ, parallel to the y-axis, cf. Fig. 1(a). Then the actual coordinates in $P2_12_12_1$ symmetry (plane group pgg) are $(-, \frac{1}{4} - \Delta/b, z')$, etc., so that (*International Tables for X-ray Crystallography*, 1952)

$$|F_{total}|^2 = [4f \cos 2\pi\{(k+l)/4 + l(\tfrac{1}{4} - z'/c)\}$$
$$\times \cos 2\pi\{(k+l)/4 - k(\Delta/b)\}]^2 \quad (2)$$

$$= [4f \cos 2\pi l(\tfrac{1}{4} - z'/c) \cos 2\pi k(\Delta/b)]^2$$
$$\text{for } k+l = \text{even}$$
and
$$= [4f \sin 2\pi l(\tfrac{1}{4} - z'/c) \sin 2\pi k(\Delta/b)]^2$$
whence
$$\text{for } k+l = \text{odd}$$

$$|F_{sym.}|^2 = 16f^2 \cos^2 2\pi l(\tfrac{1}{4} - z'/c) \cos^2 2\pi k(\Delta/b), \quad (3a)$$
and
$$|F_{antisym.}|^2 = 16f^2 \sin^2 2\pi l(\tfrac{1}{4} - z'/c) \sin^2 2\pi k(\Delta/b), \quad (3b)$$

with corresponding expressions for the symmetrical and anti-symmetrical components of the Patterson synthesis. Equation 3(a) shows that the symmetric Patterson map will correspond to the mean of two atoms, one displaced $+\Delta$ parallel to the y-axis and

the other displaced through $-\Delta$. (When $\Delta = 0$, equations (3) clearly correspond to a stationary value for $F_{sym.}$ and zero value for $F_{antisym.}$.) From equation (3(b)), the expression for the anti-symmetric Patterson is

$$\Delta P(-, y, z) = \sum_k \sum_l 16f^2 \sin^2 2\pi l(\tfrac{1}{4} - z'/c) \sin^2 2\pi k(\Delta/b)$$
$$\times \cos 2\pi(k.y/b + l.z/c)$$

$$= \sum_k \{\sin (2\pi k.\Delta/b)/2\pi k(\Delta/b)\}^2 (2\pi k.\Delta/b)^2 \sum_l 8f^2$$
$$\times [1 - \cos 2\pi l(\tfrac{1}{2} - 2.z'/c)] \cos 2\pi(k.y/b + l.z/c) \quad (4)$$

which will give maxima and minima at $(-, 0, 0)$ and $(-, 0, \tfrac{1}{2} - 2z'/c)$, together with other symmetrically located points by applying the usual mathematical analysis for the Patterson function (James, 1948). Along the line $z = 0$, we get

$$\Delta P(-, y, 0) = \sum_k \{\sin (2\pi k.\Delta/b)/2\pi k(\Delta/b)\}^2 (2\pi k.\Delta/b)^2$$
$$\times \cos 2\pi k(y/b) \sum_l 8f^2$$
$$[1 - \cos 2\pi l(\tfrac{1}{2} - 2.z'/c)]$$

$$= \sum_k 8 (\sum_l f^2) \{\sin (2\pi k.\Delta/b)/2\pi k(\Delta/b)\}^2$$
$$\times (2\pi k.\Delta/b)^2 \cos 2\pi k(y/b) \quad (5)$$

because the quantity in the square brackets in the last factor will average out to unity.

A graph of the function represented by equation (5) for small Δ is drawn against y (in Å), in the right-hand half of Fig. 1(d), and is seen to be a maximum at $y = 0$, becoming zero at $y \approx 0.4$ Å and attaining a negative minimum at $y \approx 0.6$ Å. The ratio of the depth of the trough to the height of the maximum is nearly 0.55. In contrast, it can be shown that $\Delta P(-, 0, z)$ falls uniformly to zero as z increases, so that the contours near the origin resemble the $(\varrho_o - \varrho_c)$ map for a pair of atoms with a thermal anisotropy (or else only a slight separation) parallel to y. Using equation (4), it can further be shown that the contours in the neighbourhood of the point $(-, 0, \tfrac{1}{2} - 2z'/c)$ have a similar distribution (Fig. 1(d) left), but with a negative minimum at this particular point; this negative 'peak' corresponds to the interaction between the opposite displacements, $+\Delta$ and $-\Delta$, of the two atoms with $y = \tfrac{1}{4}$ in Fig. 1(a). In three dimensions, it can readily be seen that the contours of the ΔP peaks will show cylindrical symmetry about the direction $(bb'$ in Fig. 1(d)) of the anti-symmetrical displacements of the set of atoms being considered.

4. Some properties of the anti-symmetric Patterson function

We can now connect the peak heights (and troughs) in the ΔP map quantitatively with (i) the atomic number Z of the atoms concerned and (ii) their small displacements, Δ. As long as Δ is small enough to keep $2\pi k\Delta/b < 1$, we may replace the factor $\sin (2\pi k\Delta/b)/2\pi k\Delta/b$ by unity with sufficient accuracy, and obtain from equation (5),

$$\Delta P(-, y, 0) = 4\Delta^2 \sum_k 2 (\sum_l f^2) \times 4\pi^2(k^2/b^2) \cos 2\pi ky/b$$
$$= 4\Delta^2 Z^2 \sum_k 2 (\sum_l \hat{f}^2) \times 4\pi^2(k^2/b^2) \cos 2\pi ky/b$$
$$(6)$$

which shows that the contributions to the self-interaction peaks and troughs are proportional to the squares of the corresponding atomic displacements Δ (from the high-symmetry positions) and also approximately proportional to the square of the atomic number Z, since the unitary scattering factor $\hat{f}$ varies in much the same way for all the more common atoms. In particular, the origin peak is proportional to $4\sum(\Delta Z)^2$ summed over all the atoms, and the other self-interaction peaks will have appropriate multiplicity. For a two-dimensional projection, there is the obvious proviso that when two different atoms overlap closely in a projection, the effective ΔZ for the pair is the algebraic sum $(\Delta_1 Z_1 + \Delta_2 Z_2)$ with due regard to the signs of Δ_1, Δ_2.

Similarly, when in equation (3) we consider two different atoms with displacements Δ_1 and Δ_2, it can be shown by the usual type of analysis for the Patterson function (James, 1948) that the peaks corresponding to interatomic vectors will be proportional to the product $\Delta_1 \Delta_2 \times Z_1 Z_2 \times$ multiplicity, which replaces $4\Delta^2 Z^2$ in equation (6), a negative central trough being obtained when $\Delta_1 \Delta_2$ is negative. For a 2- or 3-dimensional anti-symmetric Patterson map, there is then little difficulty in considering problems of overlap, but it is necessary to remember that $\sum \Delta_1 \Delta_2 Z_1 Z_2$ for any particular set of overlapping vectors can add up to zero, in which event the corresponding peaks (and troughs) in the ΔP map will disappear. One consequence of this is that the origin ΔP-peak can differ markedly for projections of the same structure along two different directions.

Of course, when a variety of special positions is possible, some of them can produce components of displacement Δ in two different directions, e.g. the positions on one of the screw axes in $P2_12_12_1$. The corresponding peaks can then be interpreted in terms of these two components quite easily, this concept of component shifts parallel to the axes being quite useful in the actual analysis of a given ΔP map.

The shifts estimated from such an analysis can then be used to carry out an anti-symmetrical Fourier synthesis, using only the limited anti-symmetrical set of reflections, from which additional information can then be gleaned. A portion of an actual anti-symmetrical synthesis corresponding to the calcium displacements shown in the top left quarter of Fig. 1(a) is shown in Fig. 2, and its interpretation follows that of an ordinary difference Fourier map. It is indeed quite possible that such a separation of the anti-
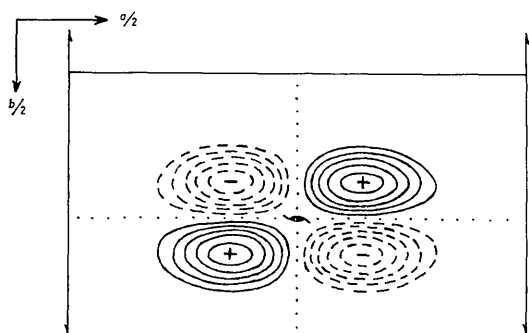
Fig. 2. Part of actual anti-symmetrical Fourier (zero contour, dotted) corresponding to the calcium displacements shown in the top left quarter of Fig. 1(a).

symmetrical component of a Fourier or Patterson map also may be advantageous in cases other than the one envisaged here, e.g. in structures showing pseudosymmetry of type (b) noted in the introduction.

5. Practical application

The use of the anti-symmetrical Patterson and Fourier functions has been very successful in the two-dimensional refinement of the structure of conichalcite, $CaCu(AsO_4)OH$ (Qurashi & Barnes, in the press). For this mineral, only a few, relatively weak, reflections,

forbidden in *Pnma*, were observed, namely, eight $0kl$ for which $k+l=2n+1$, and nine $hk0$ for which $h=2n+1$. By ignoring these reflections, however, the principal features of the structure were first established in *Pnma* (Qurashi & Barnes, 1954). Small displacements of some of the metal and oxygen atoms from *Pnma* positions then were deduced from the ΔP syntheses and anti-symmetrical Fourier syntheses based on data for the forbidden reflections alone. Modification of the atomic coordinates by these shifts gave immediate improvement in R for all observed reflections in the three principal zones; for the most important zone, R was reduced from 0·22 to 0·12. Knowledge of these small shifts made successful refinement of the structure possible by standard methods in the true space group $P2_12_12_1$.

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Molecular Shapes of Thianthrene and Related Heterocyclic Compounds

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From data so far accumulated on three-membered heterocyclic compounds derived by replacing anthracene *meso* CH groups by atoms A and B, it is pointed out that molecules are planar if both A and B are any of C, N or O, but folded if at least one of A and B is S, Se or Te. This difference is explained by taking account of d orbitals in S and S-like atoms. The folding of the molecule is due to the 'natural' valency angle of a S atom, as was pointed out by Lynton & Cox in the case of thianthrene. The folding angle is not much affected in α and β thianthrene dioxide and thianthrene tetraoxide.

Introduction

Many kinds of three-membered heterocyclic compounds are derived if either or both of two anthracene *meso* CH groups are replaced by other kinds of atoms or atomic groups. Crystal structures of these compounds have been thoroughly or partly analysed by various authors, and enough data seem to have already been accumulated to allow us to discuss some essential characteristic features of atomic bondings in these compounds. Especially interesting is the fact that some molecules are planar whereas others are

folded, and it is interesting to explain such features in terms of electron configuration.

The crystal structure of thianthrene was fully analysed by X-ray diffraction and its molecule was found to be folded on the S–S line, so that the two benzene rings lie in two planes at an angle of 128° (Lynton & Cox, 1956; Rowe & Post, 1958). The folded molecular structure was also reported for two isomers of thianthrene dioxide (Fig. 1, 2) (Hosoya & Wood, 1957; Hosoya, 1958a) and on thianthrene tetraoxide or diphenylene disulphone (Fig. 3) (Hosoya, 1958b). Di-