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The Use of the P_O Function in Structure Analysis

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New Patterson functions, P_E and P_O functions, are presented. For example, $P_{E,h}(x, y, z)$ contains only $|F(hkl)|^2$'s with h = even, and $P_{O,h}(x, y, z)$ only those with h = odd. The former corresponds to a structure derived from the original one by dividing each atom into halves and translating one half of each atom by $\frac{1}{2}\mathbf{a}$, while the latter corresponds to a structure derived by a similar operation, but in this case the translation $\frac{1}{2}\mathbf{a}$ is antisymmetric. P_E is of no use in actual structure analysis, but P_O may be used successfully in some cases. The possible use of P_O in structure analysis is considered, and its use is illustrated by applying it to the determination of the parameters x, y of the oxygen atom in tetragonal KH_2PO_4.

Let us consider a structure whose electron-density distribution is given by $\varrho(x, y)$. (For brevity a two-dimensional structure is considered, but the following discussion is valid in three dimensions also.) Dividing each atom into halves, we can, from this, derive two kinds of structures by two kinds of translations. One is derived by translating one half of each atom by $\frac{1}{2}\mathbf{a}$, or $\frac{1}{2}\mathbf{b}$, or $\frac{1}{2}(\mathbf{a}+\mathbf{b})$ and leaving the other half at its original position. As a result of each of these three translations, it follows that $F(hk)$'s with h = odd, or $F(hk)$'s with k = odd, or $F(hk)$'s with $h+k$ = odd vanish respectively, while those with h = even, or with k = even, or with $h+k$ = even remain unchanged. The Fourier series representing the electron density and the Patterson function for each of these three structures can therefore be deduced by using Fourier coefficients $F(hk)$ and $|F(hk)|^2$ with h = even, or k = even, or with $h+k$ = even which are to be observed with the original structure. We shall designate these electron-density functions and Patterson functions by $\varrho_{E,h}$, $\varrho_{E,k}$, $\varrho_{E,h+k}$ and $P_{E,h}$, $P_{E,k}$, $P_{E,h+k}$ respectively.

The other kind of structure is derived by an antisymmetric translation $\frac{1}{2}\mathbf{a}$, or $\frac{1}{2}\mathbf{b}$ or $\frac{1}{2}(\mathbf{a}+\mathbf{b})$ (Cochran, 1952), changing the sign of charge density of one half of each atom which is translated and leaving that of the counterpart unchanged. As a result of each of these translations, it follows that $F(hk)$'s with h = even, or with k = even, or with $h+k$ = even vanish, respectively, while those with h = odd, or k = odd, or $h+k$ = odd remain unaffected. For these three structures we have $\varrho_{O,h}$, $\varrho_{O,k}$, $\varrho_{O,h+k}$ and $P_{O,h}$, $P_{O,k}$, $P_{O,h+k}$.

The possible use of P_O in structure analysis is now to be considered. $\varrho_{E,h+k}$ and $\varrho_{O,h+k}$ derived from ϱ having, for example, the plane group symmetry *pgg* (Fig. 1(*a*)) are shown in Fig. 2(*a*) and Fig. 3(*a*). $\varrho_{E,h+k}$ has the plane group symmetry *cmm* and $\varrho_{O,h+k}$ the plane group symmetry p'_cgg, one of the forty-six black and white plane groups (Alexander & Herrmann, 1928, 1929; Weber, 1929; Shubnikov, 1940, 1946; Cochran, 1952; Mackay, 1957). Fig. 1(*b*) shows the ordinary Patterson function P for ϱ, which contains all Fourier coefficients $|F(hk)|^2$'s observed with the original structure. If we construct a Patterson function containing Fourier coefficients $|F(hk)|^2$'s with $h+k$ = even alone, we obtain $P_{E,h+k}$ (Fig. 2(*b*)) which corresponds to $\varrho_{E,h+k}$. On the other hand, a Patterson function which contains Fourier coefficients $|F(hk)|^2$'s

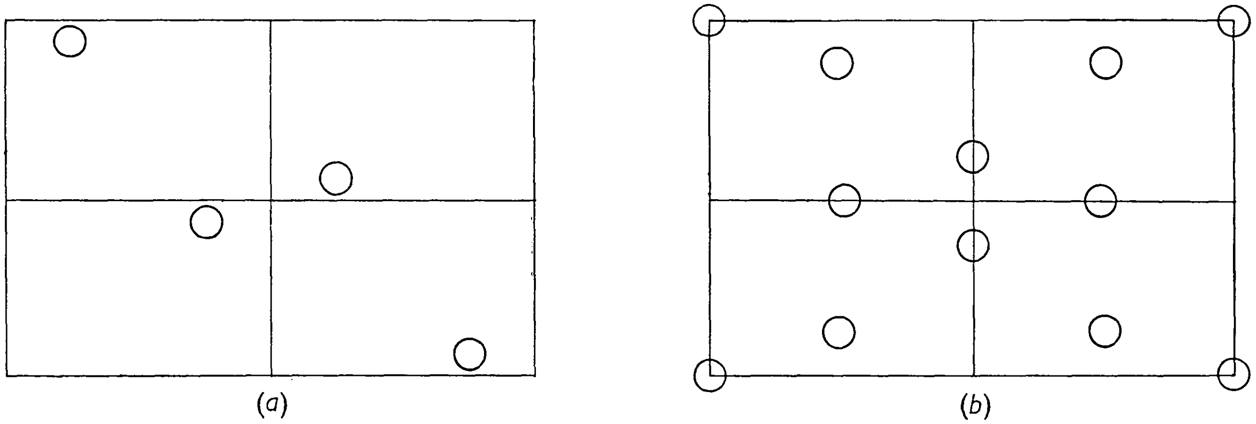
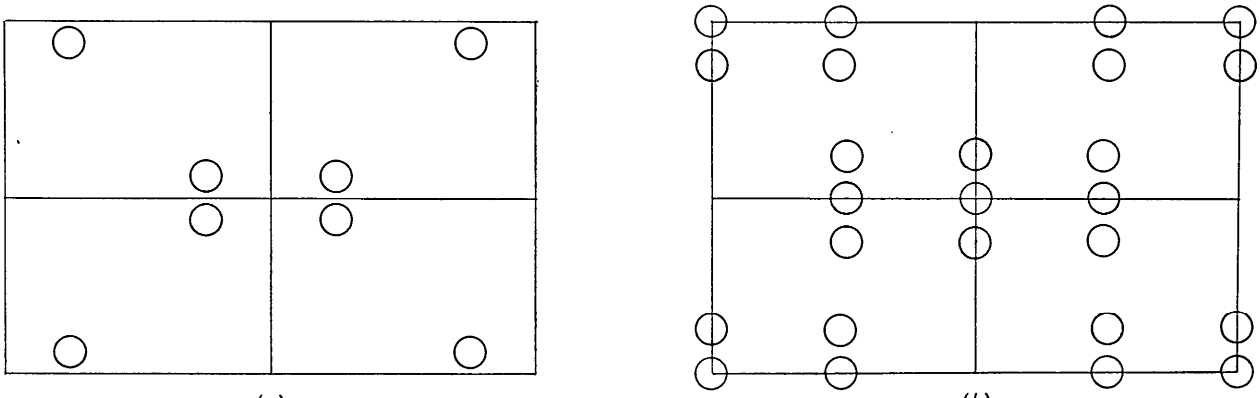
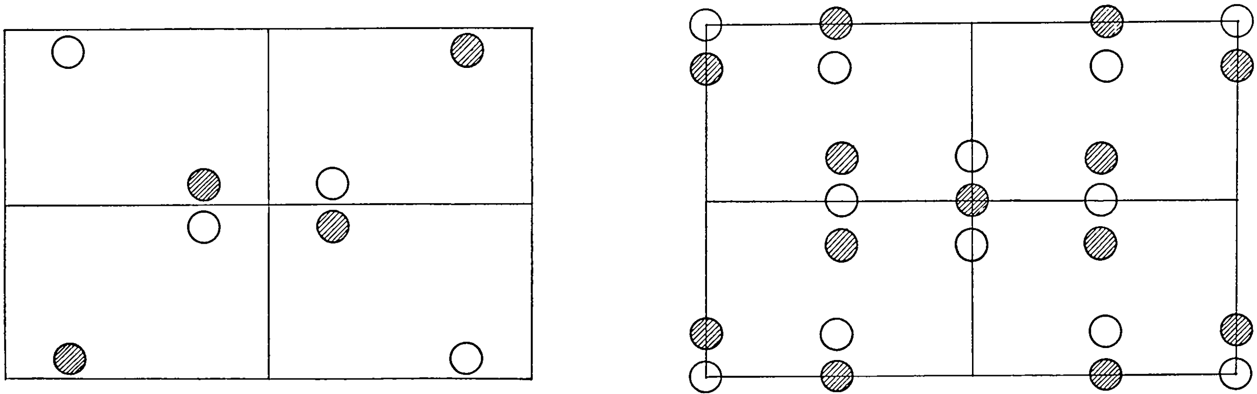


Fig. 1. (*a*) $\varrho(x, y)$, (*b*) $P(x, y)$.



(a) (b)

Fig. 2. (a) $\varrho_{E,h+k}(x, y)$, (b) $P_{E,h+k}(x, y)$.



(a) (b)

Fig. 3. (a) $\varrho_{O,h+k}(x, y)$, (b) $P_{O,h+k}(x, y)$. Shaded circles represent negative value.

with $h+k$ = odd alone, corresponds to $\varrho_{O,h+k}$ (Fig. 3(*b*)). In contrast with P and P_E both of which are positive everywhere, P_O contains negative pits as well as positive peaks. The number of peaks in P_E or that of peaks and pits in P_O is increased as compared with that in P, so that, in general, there seems to be no advantage in using P_E and P_O. In the case of P_O, however, the antisymmetric character of the translation causes interactions between some atoms to be depressed or those involving atoms at particular positions to disappear completely. There arise therefore cases in which P_O can be interpreted rather easily and gives us useful information on the structure. An obvious case is a structure which contains, in addition to light atoms in general positions, heavy atoms in special positions, for example, (0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$) in the structure shown in Fig. 1(*a*). For this structure $P_{O,h+k}$ contains only interatomic vectors between light atoms, those between heavy atoms themselves and between light and heavy atoms disappearing entirely, and its interpretation leads to the determination of the positions of some of the light atoms. If there are atoms on the *a* or *b* axis in the above structure, the interactions due to these atoms also disappear completely.

As an example of the use the P_O function, let us apply it to the determination of the parameters x, y of the oxygen atom in potassium dihydrogen phosphate (West, 1930). This structure is indeed very simple, but it serves as an illustration of the usefulness of the P_O function. The positions and the signs of charge density of oxygen atoms derived by the antisymmetric translation $\frac{1}{2}$a from the (001) projection of this structure are shown in Fig. 4(*a*), from which it can be seen that a line synthesis along the *a* axis, $P_{O,h}(x, 0)$, will give the desired parameters. $P_{O,h}(x, 0)$ is antisymmetric with respect to the point $x = \frac{1}{4}$ and is shown in Fig. 4(*b*) over the range from $x = 0$ to $x = \frac{1}{4}$. From the positions of the peak and pit we obtain the parameter values $x = 0{\cdot}067$ and $y = 0{\cdot}143$ (using the data of West), which are to be compared with the values $x = 0{\cdot}081$ and $y = 0{\cdot}144$ given by West. The disagreement in the x parameter may be attributed to the displacement of the position of the pit in $P_{O,h}(x, 0)$ due to the presence of the peak at $x = 0{\cdot}214$ as well as a series-termination error. Patterson (1935) used the same structure as an example of the application of the Patterson function and gave Patterson projections on (001) and [100] in Fig. 5 and Fig. 6 of his paper respectively. In comparison

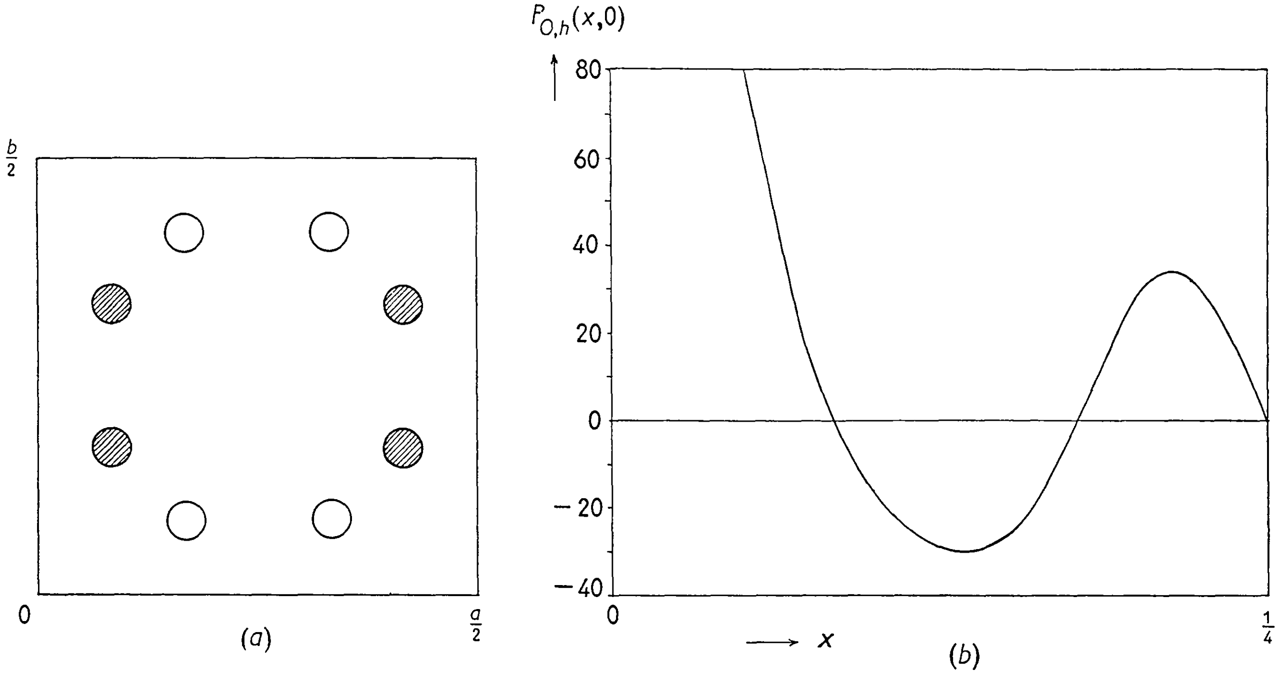


Fig. 4. (*a*) Positions and signs of charge density of oxygen atoms derived by the antisymmetric translation $\frac{1}{2}\mathbf{a}$ from the (001) projection of KH_2PO_4. Shaded circles represent negative value. (*b*) $P_{0,h}(x, 0)$.

with these figures, $P_{0,h}(x, 0)$ shows peaks and pits more clearly and enables us to determine their positions more definitely.

Independently of the author, Mr Y. Yamada devised the P_0 function from an analytical point of view and applied it successfully to a certain stage in the structure determination of ammonium bisulphate, giving an interesting example of its use. A detailed account of his work will be published elsewhere.

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