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Some Ideas on the Deconvolution of the Patterson Function

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If a minimum function is computed from overlap on a single-weight peak in the Patterson function, the resultant map will, ideally, show a single image of the structure. However it is difficult to locate single-weight peaks in practice and overlap on a multiple peak produces several heavily-overlapped parallel images of the structure.

The procedure described in this paper is as follows: (i) A minimum function is constructed from a multiple peak. (ii) The Fourier coefficients of the minimum function are found and, from these and the observed intensities, a map is computed which shows by what vectors the several images in the maximum function are displaced. (iii) The minimum function is displaced by the vectors found in (ii) and the minimum function of the result gives an approximation to the structure.

An application to a model structure is described and possible developments of the method are indicated.

Introduction

It has long been known that from an ideal, completely resolved Patterson function it would be possible to reconstruct the original structure (for detailed bibliography see Buerger, 1959). As an alternative to determining atomic coordinates one could use such a Patterson function to compute the phases of the structure factors (Hauptman & Karle, 1962) and so solve the structure in this way.

A procedure which is often successful is the application of the minimum-function method, particularly if the structure contains a fairly heavy atom or if symmetry allows a multiple-overlap function to be examined. However, when the atoms are more or less equal and symmetry gives no assistance, the usefulness of the method is very much reduced. Theoretically, for a centrosymmetric structure, if the minimum function is to show just a single image of the structure then the superposition vector should have single weight; that is to say it should be a resolved inversion peak. For a non-centrosymmetric structure superposition on a resolved single-weight peak yields the structure plus an image inverted through a centre of symmetry. The practical difficulties are that single weight peaks are not easy to find – they are concealed by chance overlap and also by fluctuations due to errors in the observed data – and that, in any case, the minimum function will contain a large number of other peaks which will confuse the resultant map.

If the overlap is carried out on a multiple peak, say of multiplicity n, then for a centrosymmetric structure there will be n parallel images while for a non-centrosymmetric structure there will be n parallel images with n parallel images inverted through a centre of symmetry. This may be seen readily for a non-centrosymmetric structure in Fig. 1, which shows a non-centrosymmetric structure, its Patterson function, and the results of overlapping on a single and on a threefold peak.

The method described here will show how to derive information from a multiple-peak overlap. This idea was first put forward by one of us (M.M.W.) in 1964* and a similar idea has independently been given by Simonov (1965). However the technique used by us differs in many ways from that suggested by Simonov and our method will now be described.

Preliminary ideas

The essence of the method proposed here is that one deliberately chooses a multiple peak for the overlap. The type of peak sought is one that is reasonably sharp and preferably of not too great a magnitude, say three to five times that of a single-weight peak.

The result of such an overlap is shown in Fig. 1(*d*) which is the result of overlapping on a threefold peak for a non-centrosymmetric structure. The three parallel images are shown in outline; three parallel images centrosymmetrically related to those outlined may also be discerned. If the vector displacements of the three parallel images were known and if a minimum function was formed with three of the figures 1(*d*) displaced by these vectors then, ideally, a single image of the structure should result.

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The first method tried for determining the vectors between the parallel images was to compute the self-convolution of the minimum function – the Patterson function of the minimum function so to speak. It was expected that this would strongly show the vectors between the parallel images and that, if these could be recognized, it should be simple to deduce the displacements of which they were the vector set.

To test this idea, structure factors were computed for the structure shown in Fig. 1 taking the atoms to be equal and with scattering factors given by the Forsyth & Wells (1959) constants for chlorine.

The corresponding Patterson function is shown in Fig. 2 and the peak chosen for the minimum-function overlap is indicated. The minimum function from this overlap is shown in Fig. 3; the Fourier coefficients of this function were calculated by a sampling method and the squares of these used to compute the self-convolution of the minimum function (Fig. 4). From the weight of the peak X in Fig. 2 it seemed that there should be three parallel images of the structure in Fig. 3 but it was not possible to interpret anything in Fig. 4 as due to a vector set of three points. It seemed that the lack of resolution of Fig. 4 was due to the presence of a large number of vectors other than those due to complete displacements of the structure.

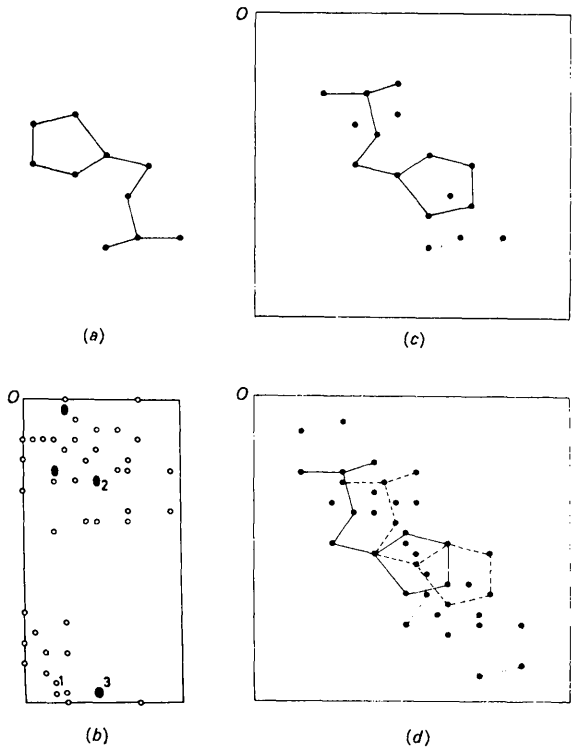

Fig. 1. (*a*) A point non-centrosymmetric structure. (*b*) One asymmetric unit of the Patterson function. The symbols for double and treble peaks are indicated. Other peaks are single. (*c*) The superposition function on the single peak shown in (*b*). (*d*) The superposition on the threefold peak shown in (*b*). Three parallel images are shown and inverted images are also present.

A modified procedure

In an ideal situation there will be a number, M, of parallel images of the structure in the minimum function. However the images will appear with some distortion of the relative weights of the atoms. In what follows we shall assume that the minimum function shows several 'true' images of the structure and accept the fact that deviations from this idealized situation will affect the strength of the conclusions which we draw.

We first take the case of a centrosymmetric structure. The minimum function will show M parallel images whose centres of symmetry can be taken to be at $\pm \mathbf{R}_1$,

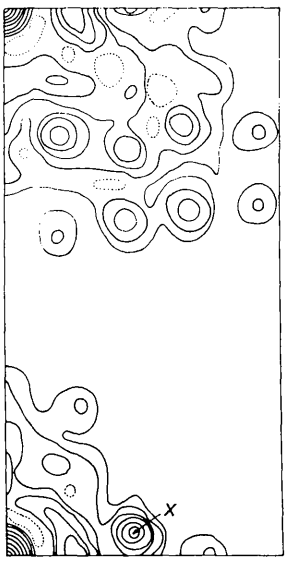

Fig. 2. A computed Patterson function for the structure shown in Fig. 1(*a*).

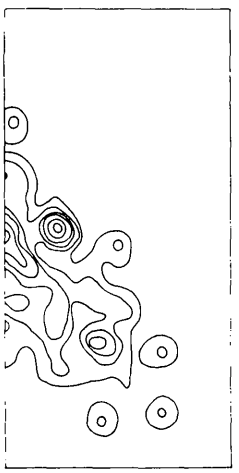

Fig. 3

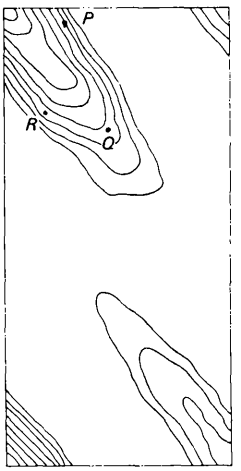

Fig. 4

Fig. 3. The minimum function from overlap on the peak X in Fig. 2.

Fig. 4. The self-convolution of the minimum-function map shown in Fig. 3. Inter-image vectors should occur at the positions P, Q and R.

$\pm \mathbf{R}_2 \ldots \pm \mathbf{R}_{M/2}$ and with weights proportional to W_1, $W_2 \ldots W_{M/2}$. Let us assume that the 'atom' j of image m is of such a form that its Fourier transform for a particular reciprocal space vector $\mathbf{s}$ is given by

$$\varepsilon_j = K_s W_m f_j$$

where K_s is a constant for all atoms and f_j is the normal scattering factor for the atom j.

The hth Fourier coefficient of the minimum function is given by

$$\psi_{\mathbf{h}} = K_s \sum_{m=1}^{M} \sum_{j=1}^{N} W_m f_j \cos 2\pi \mathbf{h} \,.\, (\mathbf{r}_j + \mathbf{R}_m) \qquad (1)$$

which, since the vectors $\mathbf{R}$ exist in pairs of the form $\pm \mathbf{R}$, may be rewritten as

$$\psi_{\mathbf{h}} = 2K_s \sum_{m=1}^{\frac{1}{2}M} W_m \cos 2\pi \mathbf{h} \,.\, \mathbf{R}_m \sum_{j=1}^{N} f_j \cos 2\pi \mathbf{h} \,.\, \mathbf{r}_j \qquad (2)$$

or

$$\psi_{\mathbf{h}} = 2K_s F_{\mathbf{h}} \sum_{m=1}^{\frac{1}{2}M} W_m \cos 2\pi \mathbf{h} \,.\, \mathbf{R}_m \,. \qquad (3)$$

Hence

$$\varphi_{\mathbf{h}} = \frac{\psi_{\mathbf{h}}}{K_s F_{\mathbf{h}}} = 2 \sum_{m=1}^{\frac{1}{2}M} W_m \cos 2\pi \mathbf{h} \,.\, \mathbf{R}_m \qquad (4)$$

and $\varphi_{\mathbf{h}}$ is seen to be the hth Fourier coefficient of a set of points of weights W_m at $\pm \mathbf{R}_m$.

Since the sign of $F_{\mathbf{h}}$ is unknown so is the sign of $\varphi_{\mathbf{h}}$ so that we cannot determine the set of points $\mathbf{R}$ by means of a Fourier synthesis. However, in general M is a small number and a Fourier synthesis with coefficients $\varphi_{\mathbf{h}}^2$, which will show the vector set of the points $\mathbf{R}$, should not be too difficult to interpret.

The situation is somewhat different for a non-centrosymmetric structure. With the structure related to some point, P, as origin the real and imaginary parts of the structure factor of index $\mathbf{h}$ are given by

$$A_{\mathbf{h}} = \sum_{j=1}^{N} f_j \cos 2\pi \mathbf{h} \,.\, \mathbf{r}_j$$

$$B_{\mathbf{h}} = \sum_{j=1}^{N} f_j \sin 2\pi \mathbf{h} \,.\, \mathbf{r}_j \,.$$

The minimum function will show $\frac{1}{2}M$ images of the structure whose representative points, P, are displaced by $\mathbf{R}_1 \ldots \mathbf{R}_{M/2}$ from the centre of symmetry of the map and another $\frac{1}{2}M$ images produced by inversion through the centre of symmetry.

The Fourier coefficient of index $\mathbf{h}$ for this map will be given by

$$\psi_{\mathbf{h}} = 2K_s \sum_{m=1}^{\frac{1}{2}M} \sum_{j=1}^{N} W_m f_j \cos 2\pi \mathbf{h} \,.\, (\mathbf{r}_j + \mathbf{R}_m) \,, \qquad (5)$$

which yields on expansion

$$\psi_{\mathbf{h}} = 2K_s \left\{ A_{\mathbf{h}} \sum_{m=1}^{\frac{1}{2}M} W_m \cos 2\pi \mathbf{h} \,.\, \mathbf{R}_m - B_{\mathbf{h}} \sum_{m=1}^{\frac{1}{2}M} W_m \sin 2\pi \mathbf{h} \,.\, \mathbf{R}_m \right\}$$

$$= 2K_s |F_{\mathbf{h}}| \sum_{m=1}^{\frac{1}{2}M} W_m \cos (2\pi \mathbf{h} \,.\, \mathbf{R}_m + \alpha_{\mathbf{h}}) \,, \qquad (6)$$

where $\alpha_{\mathbf{h}}$ is the phase of $F_{\mathbf{h}}$ referred to an origin at P.

Squaring both sides of this equation we find

$$\varphi_{\mathbf{h}}^2 = \frac{\psi_{\mathbf{h}}^2}{K_s^2 |F_{\mathbf{h}}|^2} = 2 \sum_{m=1}^{\frac{1}{2}M} \sum_{n=1}^{\frac{1}{2}M} W_m W_n \cos [2\pi \mathbf{h} \,.\, (\mathbf{R}_m + \mathbf{R}_n) + 2\alpha_{\mathbf{h}}] + 2 \sum_{m=1}^{\frac{1}{2}M} \sum_{n=1}^{\frac{1}{2}M} W_m W_n \cos 2\pi \mathbf{h} \,.\, (\mathbf{R}_m - \mathbf{R}_n) \,. \qquad (7)$$

It is clear that a Fourier summation whose hth Fourier coefficient equals $\varphi_{\mathbf{h}}^2$ will give strong peaks at points such as $\mathbf{R}_m - \mathbf{R}_n$. There will also be a general background due to the first term on the right hand side of (7), so that only half the total weight of the peaks is concentrated in the peaks we wish to know. The map for the non-centrosymmetric case should therefore be more difficult to interpret in terms of being a vector set of the displacements $\mathbf{R}$. However, as we shall see, such an interpretation was possible in the case of a model structure.

Testing the modified procedure

The values of $\psi_{\mathbf{h}}$ had been computed from the minimum function of the model structure and the values of $\varphi_{\mathbf{h}}^2$, as given in equation (7), could be found. To do this it was not necessary to know in advance the function K_s. It was sufficient to multiply the values of $\psi_{\mathbf{h}}^2/|F_{\mathbf{h}}|^2$ by an empirically determined function of $\mathbf{s}$, which removed any systematic fall-off with increasing $\mathbf{s}$. However some care is needed at this stage particularly if the value of $|F|$ is low. For one thing the experimental errors in measuring F will be proportionately higher for a small $|F|$, but more important than this is the effect on the value of $\psi_{\mathbf{h}}$ of deviations from the idealized situation postulated in the previous section.

We can see from equation (7) that the maximum possible value of the right hand side is

$$\varphi_{\max}^2 = \left(\sum_{m=1}^{M} W_m \right)^2 . \qquad (8)$$

It follows then that the maximum value of $\psi_{\mathbf{h}}$ should be such that $\varphi_{\mathbf{h}}$ does not exceed $\varphi_{\max}$ and hence if $|F_{\mathbf{h}}|$ is small the value of $\psi_{\mathbf{h}}$ should be correspondingly small. In such a case deviations of $\psi_{\mathbf{h}}$ from the idealized value can lead to very distorted values of $\varphi_{\mathbf{h}}$. It was concluded that the way to remove the worst effects of this situation was to exclude any terms from the synthesis for which $|F_{\mathbf{h}}|$ was below some limit; in this particular case the criterion for exclusion was

$$|F_{\mathbf{h}}|^2 \leq 0{\cdot}01 \, F_o^2 \,. \qquad (9)$$

Unfortunately the exclusion of small values of $|F_{\mathbf{h}}|$ does not exclude only small values of $\varphi_{\mathbf{h}}$ but, since M is always a small number and the number of data is comparatively large, the partial Fourier summation should show the peaks of the vector set reasonably well.

The summation is shown in Fig. 5. The indicated vectors were interpreted as due to the set of points A, B, C. It should be noted that the interpretation in this case corresponded to a non-centrosymmetric set of

points; if we had been dealing with a centrosymmetric structure the set would have to be centrosymmetric.

A multiple superposition of the map shown in Fig. 3 on the points *A*, *B* and *C* was computed and the minimum function (Fig. 6) showed the structure quite clearly although with some spurious peaks.

Possible extensions of the method

An obvious step in a method of this type is to work with three-dimensional data. The greater resolution of the Patterson function would give much higher discrimination in the overlap functions. It has been found that the quality of the Patterson function or, what amounts to the same thing, of the observed data, severely affects the efficiency of the process. This is presumably due to the loss of small peaks by the superposition of the random errors of the poor data, and once a peak is lost the minimum function process can do nothing to restore it. An attempt can be made to remedy some of the loss at the last stage of the process, when a multiple superposition is made, by taking the second smallest value of the overlapped functions instead of the minimum.

In practice, whatever one does, the final map will not be a perfect representation of the structure. The relative heights of the atom images will be awry and indeed some of the atoms may disappear altogether. False peaks will also appear and, indeed, it may be impossible to fit a model to the resultant map with any degree of confidence. However, in the centrosymmetric case, such a map may still be useful for sign determination if the 'signal to noise' ratio is sufficiently high. The Fourier coefficients (ξ's) of the map would tend to give an indication of sign for the F's and the probability of having a correct sign would be expected to vary with $F \times \xi$ (Woolfson, 1956). In fact the weighting scheme proposed by Woolfson could well be used to compute a trial Fourier synthesis and this would probably be the best one could do in the circumstances.

This work was started when we were both members of the Physics Department of the College of Science and Technology, Manchester and we must acknowledge the splendid service provided by the Manchester University Computing Laboratory Atlas computer during this period. We are grateful to the Scientific Research Council on two counts – for the services of their Atlas Computer Laboratory and also for a research grant to enable us to complete this and, we hope, other projects of a similar nature.

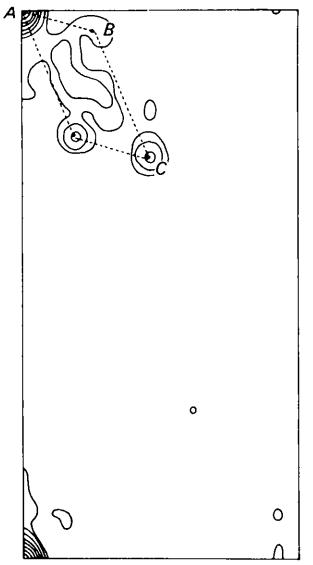

Fig. 5. The modified convolution function. The vectors shown are due to the set of points *A*, *B*, *C*.

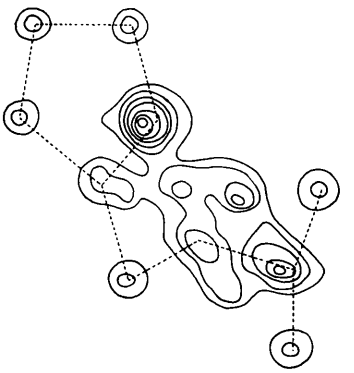

Fig. 6. The final superposition map.

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