Short Communications

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Phase determination and zero points in the Patterson function. (Remarks on the paper "Direct determination of phases by the use of linear equations between structure factors" by P. Main and M. M. Woolfson.)

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It has been demonstrated independently by Main & Woolfson (1962, 1963) and by us (Hoppe, 1962; Anzenhofer & Hoppe, 1962; Hoppe, Anzenhofer & Huber, 1962; Anzenhofer, 1963) that phase-determining procedures can be established which make use of regions in the Patterson function with insignificant density ('zero points'). It is interesting to note that both groups of methods use the same kind of information. The physical evidence, however, extracted from this information and used as a basis for phase determination is entirely different. It is surprising that two different direct techniques may be derived from the same information.

This note gives a short comparison of the principles of both methods. The abbreviations 'Method *A*' (M. & W.) and 'Method *B*' (A. & H.) will be used.

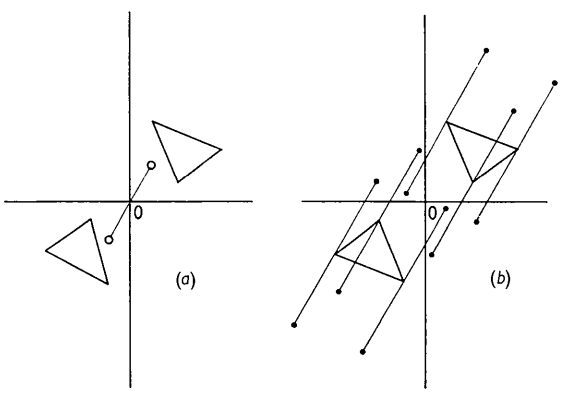

Fig. 1. The different physical evidence extracted from the zero points of the Patterson function in methods *A* and *B*. In (*a*) (method *A*) a zero point means there is no electron density in the positions marked by the two white circles. In (*b*) (method *B*) the same zero point means there is no electron density in the positions marked by black dots.

Following *A*, a zero point in the Patterson function (position **r**) of a centrosymmetrical structure means there can be no significant electron density at a distance $\pm\frac{1}{2}\mathbf{r}$ from the origin. Following *B*, a zero point in the Patterson function at the same position **r** means there can be no significant electron density at a distance $\pm\mathbf{r}$ from every atom in the structure. In *B* there is no restriction to centrosymmetrical structures. (Compare Fig. 1).

A establishes a unique correlation between a zero point in the Patterson function and a single zero point in the electron-density function. *B* establishes a correlation between a zero point in the Patterson function and *N* points (*N* = number of atoms in the unit cell) of electron density zero in the structure. *B* correlates *N*-times as many electron density zero points with the Patterson zero points as does *A*. However, the positions of the points of zero electron density after method *A* are fixed in the unit cell, whereas the points of zero electron density in method *B* are only known in relation to the (unknown) structure.

If one takes into account these fundamental differences, the fact is not surprising that both methods were developed in different mathematical forms.

In *A*, a product will be formed between the electron density of the structure and the (known) *M* function. This product is equal to the electron density. In *B*, a product will be formed between the electron density and the shifted electron density ('shift product method'). This product equals zero for all points in the unit cell. Both methods now make use of the corresponding convolutions in reciprocal space; they lead to linear equations which can be solved to get information about the signs of the structure factors. It is important to note that in *A* one of the two convoluted functions in reciprocal space is known in amplitude and phase. This is the reason why signs of single structure factors appear as unknowns in the set of linear equations. It is therefore possible to solve the equations directly for absolute signs (in the structure invariant group. or for relative signs in the other parity groups). In *B* the variables are the phases between double products of structure factors, because both convoluted functions are unknown in phase. The basic results of *B* are the relative phases of the terms of the Sayre sums

$$\sum_{\mathbf{h}'} F_{\mathbf{h}'} F_{\mathbf{h}-\mathbf{h}'} .$$

It is, therefore, necessary to use a special scheme for the reduction of the double-product phases to phases of single structure factors. This necessity intrinsically complicates method *B* more than *A*. However, our experience, while investigating a not-too-simple organic-structure determination (23 light atoms in the asymmetric unit), has shown that it is not difficult to find the single phases, if a sufficient number of double-product phases has been determined. It may be mentioned that normally our single phase will be checked by several double-product indications. In comparison with method *A* method *B* seems to operate with smaller sets of linear equations for the same set of structure

factors. This can be explained by the fact that the number of equations in A equals the number of structure factors, while in B this number equals the number of zero points. This might be important in practice with regard to the necessary computer time.

This note should conclude with some more general remarks. As methods A and B are based on different physical principles, it might be worth while to use both methods in centrosymmetrical structures in parallel, or to combine them. Furthermore, the distinguishing features of the methods in comparison with the squaring methods should be emphasized. There is no restriction whatsoever on the shape of the electron-density functions. There may be overlap (in projections), different weights of the atoms, *etc.* The last remark concerns the philosophy behind the methods. They have some common features with the heavy-atom and image-seekind methods in spite of their otherwise fundamental physical difference. All three techniques are based on certain information which first has to be extracted from the Patterson function. This information consists of the heavy-atom–heavy-atom peak in the heavy-atom technique, of the positions of single-weight Patterson peaks in the image-seeking methods, or, in the third case, of the positions of Patterson zero points in the methods discussed in this note. There is, however, one essential point in favour of the new methods. It is well known that it is sometimes very difficult to extract the necessary Patterson information for the initial steps of the first two methods. On the other hand, it is quite easy to find zero regions in a Patterson map or to use a simple computer program in connection with the phase-determining procedure.

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On minimum receiving apertures in single crystal diffractometry.

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In conjunction with a study of systematic errors in integrated intensity measurements (Ladell & Spielberg, 1963), we have derived the minimum dimensions of the receiving aperture required for both the 2:1 and ω-scan methods for crystals of circular cross section. A derivation of the minimum dimensions of the receiving aperture has already been reported by Alexander and Smith (1962) in a similar study, but our results for the case of a point source of monochromatic radiation incident upon a 'perfect' crystal of circular aperture do not agree with those reported. This case is of theoretical importance because (unlike the case of a crystal of negligible size) the requisite minimum aperture is a function of θ, the Bragg angle. Any attempt to evaluate the systematic error due to the use of a receiving aperture less than the minimum dimension must take this θ dependence into account.

We place our crystal of radius r (Fig. 1) at the origin of a Cartesian coordinate system (designated $X'Y'$) and the point source at the coordinates $(-1, 0)$. Let σ measure deviation from the Bragg angle θ as the crystal is rotated counterclockwise. When $\sigma = 0$ diffraction takes place all along the diameter of the circular cross section which is collinear with the X' axis and the central diffracted ray is shown terminating at the coordinates $(\cos 2\theta, \sin 2\theta)$, at which point we place the center of the receiving aperture of the detector. When the crystal is rotated through an angle σ, an incident beam from $(-1, 0)$ proceeds along line I. Diffraction takes place along the chord formed by the part of line I intercepted by the circular cross section; the leading edge of the diffracted beam is denoted by line II and the trailing edge of the beam is denoted by line III. Line IV is normal to the central diffracted ray passing through $(\cos 2\theta, \sin 2\theta)$ and coincides with the trace of the detector in the plane of the drawing. In this derivation, for simplicity, the detector and point source are equidistant from the crystal. (The same analytic method can be employed to consider the case of unequal distances).

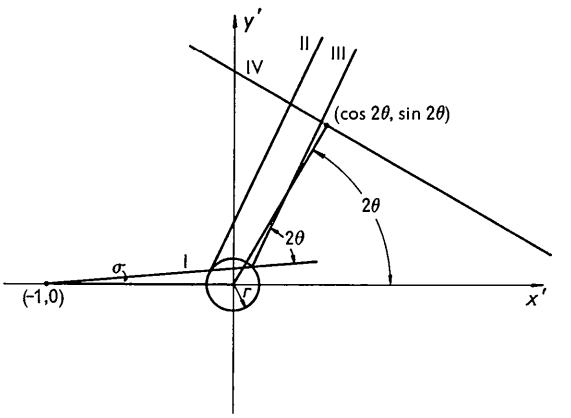

Fig. 1. Schematic of geometric construction used to derive the dimensions of minimum receiving apertures.