Short Communications

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Location of atomic centres in an electron-density synthesis. By HELEN D. MEGAW, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

When a structure is to be refined by successive electron-density syntheses, it is desirable to have a simple, accurate and objective method for locating the centre of a peak. A method proposed by Booth (1948) is commonly used; it consists in fitting a parabola to three points of known electron density lying on a line drawn through the peak. The accuracy is not sufficient for late stages of refinement, because the approximation of a parabola to a peak of arbitrary shape is only good close to the maximum; the usual intervals of 1/60 or 1/120 of the cell edge represent too coarse a scan. For this reason many authors prefer least-squares methods, or more elaborate mathematical interpolation.

There is, however, a better way of using the Fourier map, based on Booth's postulate (1946) of a Gaussian atom: that the electron density near the centre of any atom is represented, to a good approximation, by $A \exp(-pr^2)$. The validity of this for the present purpose was confirmed by Megaw (1952) in applying the method to afwillite; it holds good within about 0·5 Å of the peak. For such an atom,

$$\log_e \varrho = \text{const.} - pr^2;$$

hence a plot of $\log \varrho$ against r is a parabola whose shape depends only on p, a constant for the atom in the particular conditions of the synthesis. Further, any projection or section of a Gaussian atom gives a parabola of the same shape, differing only in the value of the constant A: this is true also of the distribution along a line not passing through the peak, if r is measured from the maximum on the line. Hence if a parabola is fitted to any three points on a line passing near the peak, it suffices to determine the position and height of the maximum on the line, and the value of p.

In practice, a series of parabolas are drawn on tracing paper for likely values of p, on some convenient scale of r. The logarithms of the density at three points such as A, B, C (see Fig. 1) 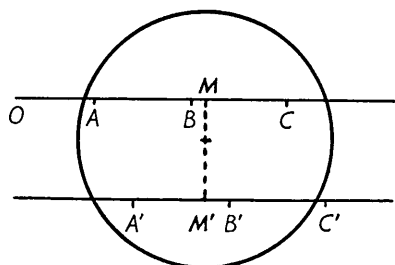are plotted against distance, measured on the same scale, from some arbitrary origin O, and a parabola is fitted to them; suppose its maximum is at M. This is repeated for the line A', B', C', using the same parabola; let the maximum be at M'. Then the centre of the atom must lie on MM'. Repetition with a second pair of lines, not parallel to the first, gives another line intersecting MM', and their intersection is the centre of the atom. A third pair of lines is used as a check, and the triangle enclosed by the three locating lines estimates the accuracy with which the position of the centre can be determined from the synthesis. Care must be taken, of course, that the diagrams are drawn on such a large scale that graphical errors are unimportant. This can very conveniently be done by using paper prepared for electron-density maps and taking 10 divisions to represent 1.

It has been assumed that the atom, in section or projection, has circular symmetry. This implies that MM' must be perpendicular to BC and $A'B'$, and hence departures from circular symmetry can be detected from the diagram. One interesting fact was noticed when the method was applied to afwillite (Megaw, 1952): at an early stage of refinement, when the atoms were not circular, and the locating lines were not perpendicular to the lines of section, they nevertheless enclosed only a small triangle between them. This suggests that the method is empirically useful even when the conditions are far from ideal.

The advantages of this method are its simplicity, its 'direct relation to the Fourier synthesis and the fact that it carries its own internal check and does not lose any accuracy inherent in the synthesis. A scan at intervals of 0·2 Å gives sufficient data, making subdivision into 1/120ths unnecessary, except for very large cells. Since three points on a line determine p, the accuracy with which the same parabola fits all lines across a given atom serves as a test of the basic assumption as well as of the accuracy of the synthesis. Misfits due to random background fluctuations or departures of the atoms from circular symmetry are sources of error which cannot be eliminated by any procedure for finding the centre, and it is a virtue of the method that it shows how far they influence the result.

The same method can be adapted for interpolating points from which to plot the contours of an atom.

Fig. 1.

References

BOOTH, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.
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