Short Communications

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X-ray analysis and the method of steepest descents.

By W. Cochran, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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It has been pointed out by Booth (1947 *a*, *b*) that the desirable features of any systematic form of crystal-structure determination are as follows:

(*a*) If the structure of a molecule is known, it should be possible to proceed from arbitrary co-ordinates specifying the position and orientation of the molecule in the unit cell to co-ordinates which are correct for each atom, within the limits imposed by considering the molecule as a rigid unit of known structure.

(*b*) Having done this it should be possible to determine more accurately individual atomic positions.

Booth has claimed that a solution to these problems is to be found in the method of 'steepest descents', which is in essence a method for systematically minimizing either

$$R_1=\sum_{hkl}\Big|\,|F_o|-|F_c|\,\Big|, \qquad (1)$$

or

$$R_2=\sum_{hkl}(F_o^2-F_c^2)^2, \qquad (2)$$

where F_o is an observed structure amplitude and F_c that calculated for an assumed structure. Of the two problems, that of determining the approximate position of the molecule is by far the more difficult, so that the discovery of a method by which this could be done, using only X-ray data, would represent a considerable advance. The following simple considerations show, however, that Booth's method does not provide a direct solution of problem (*a*).

The Patterson function (Patterson, 1935) of a structure is given by

$$P_o=\sum_{hkl}F_o^2\cos 2\pi\,(hx+ky+lz),$$

while that of any postulated structure which might form a starting-point for the 'steepest descents' technique is

$$P_c=\sum_{hkl}F_c^2\cos 2\pi(hx+ky+lz).$$

Hence it follows that

$$\int_V (P_o-P_c)^2\,dV\simeq\sum_{hkl}(F_o^2-F_c^2)^2=R_2, \qquad (3)$$

where $\int_V$ denotes an integration over the unit-cell volume. It follows that the 'direction of steepest descent' is the direction which minimizes most rapidly the integral (3).

Consider now a single atom specified by one co-ordinate, together with a second related to the first through the operation of a centre of symmetry at the origin, and assume that the electron density in this atom falls to zero within a distance r of its centre, which we may suppose fixed at the point x_0. The corresponding Patterson distribution is then centred at the point $2x_0$ and falls to zero in a distance $2r$. It will be seen that if one assumes for the atom of the postulated structure a co-ordinate outside the range $x_0\pm 2r$ the functions P_o and P_c nowhere overlap, except for the peaks at the origin whose coincidence corresponds to the fact that $F_c(0)$ is correct for all postulated structures. R_2 is therefore constant for values of x outside this range and there is thus no possibility of *systematically* finding the true co-ordinate, unless we choose to call trial and error a systematic method. Simple systems involving not more than three variables can be treated similarly, and it is found that over part of the range there may be no direction of steepest descent, while starting from other points one could be led to the correct value for one variable while that of the two others remained unknown, or to the correct difference between two variables while all three remained indefinite, etc. In dealing with a molecule consisting of several atoms, each specified by three co-ordinates, it is not possible to visualize R_2 as it is then a function in multidimensional space, but by thinking in terms of the vector space of the Patterson function, and remembering that steepest descents takes one in the direction which minimizes most rapidly $\int(P_o-P_c)^2\,dV$, one can see that unless one began with co-ordinates correct to within a distance about equal to an atomic diameter the correct result could not be obtained. It is interesting to note that by giving the molecule the correct orientation in the unit cell, but quite the wrong position, one already obtains a low value of R_2 because the intramolecular, although not the intermolecular vectors, of the true and postulated structures coincide.

In conclusion it may be said that there is little difference in principle between systematically minimizing R_2 and systematically accounting for each peak of the Patterson function in terms of the crystal structure. It would appear that if the structure is too complex for its Patterson diagram to be interpreted the 'steepest descents' technique cannot be expected to yield a solution.

References

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