Acta Cryst. (1965). **18**, 541

A Rapid Method for Refining a Structure by Differential Synthesis

By Surendra Nath Srivastava

Physics Department, University of Allahabad, Allahabad, India

(*Received* 25 *May* 1964 *and in revised form* 1 *July* 1964)

The labour involved in 6–7 cycles of three-dimensional differential synthesis, for the complete refinement of even a simple structure, is quite formidable when only a desk calculator is available. In the present paper it has been shown that it is only necessary to refine the structure by the first cycle and a number of sub-cycles. Sub-cycle refinement can be finished in much shorter time as compared with the time required to carry out a complete three-dimensional differential synthesis. Planning the calculation as suggested here has the further advantage that values of electron densities and their derivatives at the atomic positions can also be evaluated without an undue amount of calculation.

Introduction

After the preliminary refinement of the structure by Fourier synthesis has been completed, other methods are employed to improve upon the structure and to obtain more accurate parameters. One such method is differential synthesis, in which for an orthogonal set of axes the shifts of the coordinates are given by the expression

$$\Delta x = -\frac{\delta \varrho / \delta x}{\delta^2 \varrho / \delta x^2} \quad (1)$$

and similar expressions for y and z coordinates.

Even for simple structures the calculations are quite tedious when attempted on desk calculators. For example, when only 1000 structure factors are used for refining the positions of 10 atoms (*i.e.* 30 parameters) as many as 30×1000 trigonometric terms have to be evaluated. Trigonometric terms can be evaluated more conveniently when expressed in the form of products of terms like $\begin{smallmatrix}\sin\\ \cos\end{smallmatrix} 2\pi hx/a$ *etc.* and thus 30,000 trigonometric terms would be obtained by computing more than 30,000 products. Each such term is further multiplied by the appropriate value of $F_o(hkl)$, *i.e.* 30,000 more products are calculated, that is a total of 60,000 products. Further, when $\cos 2\pi(hx/a+ky/b+lz/c)$ is expanded in terms of products of $\begin{smallmatrix}\sin\\ \cos\end{smallmatrix} 2\pi hx/a$ *etc.* there would result eight terms and for each separate term there would be 60,000 products to be computed. Some simplification, however, results by taking advantage of certain relationships among the structure factors for individual space groups, but still the order of products to be evaluated is a few hundred thousand. Thus if one to two thousand products are evaluated per day on a desk calculator the total work would involve a few months labour for its completion.

Generally complete shifts are not obtained just in one cycle of refinement but the coordinates approach more and more towards the accurate values in successive cycles. 6–7 cycles are quite often performed before the refinement is taken to be completed, and thus the total amount of labour on desk calculators is quite formidable. For the purpose of calculations suggested below, the refined coordinates are obtained in one cycle plus a number of sub-cycles. A second cycle of calculations is again done to check the accuracy of parameters obtained from the first cycle and its sub-cycles.

Theory

The utility of sub-cycles will become quite evident if we consider a physical picture of a spherically symmetric atom. For brevity we shall only consider the refinement of the x coordinate of an atom and the discussion can be similarly extended to other coordinates. We shall also take the axes to be orthogonal to make the discussion more simple. Let the assumed position of an atom be (x, y, z) while its accurate position is (X, Y, Z). If we move along a line passing through $(0, y, z)$ and parallel to the x axis then the electron density would show a peak value at (X,y,z). If we similarly move along a different line parallel to the x axis we shall again obtain a peak when the x coordinate$=X$. The height of the peak would go on increasing with the closeness of the line to the atom, but the position of the peak would remain at $x=X$ for each line. This statement will be true so long as the atoms are assumed to be spherically symmetric and the axes as orthogonal. Even when these conditions are not strictly fulfilled, the resulting refined coordinate will be very close to the true value, because the refinement is already started from the stage when the atomic shifts are expected to be quite small, *i.e.* we are in the neighbourhood of the true atomic positions. Hence it is justifiable to let the y and z coordinates remain fixed (as assumed in the first cycle) and the x coordinate only is refined subsequently. The refined value of x is then again fed into the calculations (y and z unaltered) and this cycle is called a sub-cycle. This process of iteration is continued until the x coordinate of one atom is completely refined and then the x coordinates of other atoms are refined one by one. A similar procedure is adopted for refining the y and z parameters of all the atoms.

The plan of the calculations to be made is as follows. The electron density $\varrho(xyz)$ for a centrosymmetric structure is given by

$$\varrho(xyz) = \sum_h \sum_k \sum_l \frac{F(hkl)}{V} \cos 2\pi \left(\frac{hx}{a}+\frac{ky}{b}+\frac{lz}{c}\right).$$

This can also be expressed as

$$\varrho(zyz) = \sum_h \sum_k \sum_l F(hkl)\ P(ky, lz) \cos 2\pi \frac{hx}{a} - Q(ky, lz) \sin 2\pi \frac{hx}{a}, \quad (2)$$

where the P's and Q's are appropriate trigonometric functions of ky and lz, which take different forms for different space groups, when similar types of terms are combined to shorten the calculations. For brevity we can further write

$$\varrho(xyz) = \sum_h R_h(y, z) \cos 2\pi \frac{hx}{a} - \sum_h S_h(y, z) \sin 2\pi \frac{hx}{a}, \quad (3)$$

where

$$R_h(y, z) = \sum_k \sum_l F(hkl)\ P(ky, lz)$$

and

$$S_h(y, z) = \sum_k \sum_l F(hkl)\ Q(ky, lz)$$

for a fixed value of h, y and z. Differentiating the electron density with respect to x we obtain

$$\frac{\delta\varrho}{\delta x} = -\frac{2\pi}{a} \sum R_h(y, z) h \sin 2\pi \frac{hx}{a} - \frac{2\pi}{a} \sum S_h(y, z) h \cos 2\pi \frac{hx}{a}. \quad (4)$$

Values of $R_h(y, z)$ and $S_h(y, z)$ are evaluated for each value of h and for every (y, z) coordinate of all the atoms. $\delta\varrho/\delta x$ can then be easily obtained with the help of equation (4), which is only a single summation.

$\delta^2\varrho/\delta x^2$ can also be obtained by differentiating equation (3) twice with respect to x. Thus

$$\frac{\delta^2\varrho}{\delta x^2} = -\frac{4\pi^2}{a^2} \sum R_h(y, z) h^2 \cos 2\pi \frac{hx}{a} + \frac{4\pi^2}{a^2} \sum_h S_h(y, z) h^2 \sin 2\pi \frac{hx}{a}. \quad (5)$$

Expression (5) is again a single summation and can be easily evaluated giving the value of $\delta^2\varrho/\delta x^2$. Δx can then be easily obtained with the help of expression (1) after evaluating $\delta\varrho/\delta x$ and $\delta^2\varrho/\delta x^2$ as indicated above. The new value of x is again substitued in equations (4) and (5) and then with the help of equation (1) Δx is again obtained. This is called the first sub-cycle; it would be followed by second and subsequent sub-cycles until Δx became negligibly small. Since the calculations of sub-cycles require only a single summation, a number of sub-cycles can be calculated in a single day, whereas in the routine way of refinement a number of months are required to complete a single cycle.

It is likely that the coordinates obtained in the first cycle and its sub-cycles may not be sufficiently refined on account of anisotropy, non-orthogonality of the axes, changes of phases due to coordinate shifts, series termination errors and errors in the calculations. It would, therefore, be always preferable to do complete calculations for a second cycle starting from the coordinates obtained from the first cycle and its sub-cycles. It is interesting to note that the method was utilized in refining the structure of anthrone and none of the above factors was found to affect seriously the refinements of the coordinates, excellent agreement being found between the results of the sub-cycles of the first cycle and those of the second cycle. In a few cases an appreciable discrepancy was also found between the two sets of results. But it was always traced back to some error which crept into the calculations. Thus the second cycle is mainly used as a check against likely errors of calculations. The maximum difference between a coordinate input to the first cycle and the corresponding coordinate output from the last sub-cycle of the first cycle was 0·065 Å, and the order of difference between these two sets of input and output coordinates was in the neighbourhood of 0·03 Å for most of the parameters of the atoms. The maximum difference between a coordinate input to the second cycle and the corresponding coordinate output, in cases where no error was made in the previous calculation, was 0·013 Å, whereas in most cases this difference was of the order of 0·003 Å.

This way of calculation has a further advantage, that it affords the electron density values to be computed with the help of expression (3). Once the values of $R_h(y, z)$ and $S_h(y, z)$ are evaluated, the values of electron densities can be computed for any number of points along a line parallel to the x-axis and passing through $(0, y, z)$. The computation of electron density at any point on that line would only involve a single summation. A little modification of expression (3), by differentiating it with respect to x would also similarly yield, with the same ease, the values of first and higher derivatives of electron density at any point along the line parallel to [100].

The author is very grateful to Prof. H. Lipson for his useful discussions while he was at Calcutta, India, and to Prof. K. Banerjee for his encouragement.