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An analytical method of dealing with unresolved peaks in Fourier projections. By D. M. BURNS,
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When the electron density of a crystal is projected on to a plane, it often happens that the separation of two projected atoms is so small that they give rise to only one compound peak, which is more or less elongated in the direction of separation of the constituent atoms. This problem is often attacked in the following way. From well-resolved peaks in the same projection, an atomic profile is obtained, and two such profiles are summed, for various separations of their peaks, until the resultant profile resembles most closely the profile of the observed, compound peak, taken parallel to the line of centres. The present note describes an analytical method of dealing with the problem in the special case of two identical atoms which is less laborious and which uses the computed electron-density values in the neighbourhood of the compound peak in a more systematic way.

Suppose the constituent atoms to be situated at the points P_1 and P_2 , giving rise to a resultant peak at P_0 , the mid-point of the line joining P_1 and P_2 . Let the co-ordinates of P_0 , P_1 , and P_2 be (x_0, y_0) , (x_1, y_1) and (x_2, y_2) respectively, referred to rectangular axes. Let it be assumed that each of the constituent atoms can be adequately represented by a Gaussian function

$$\rho(r) = \rho_0 \exp[-pr^2]. \quad (1)$$

Then the resultant electron density at a point (x, y) is given by

$$\rho(x, y) = \rho_0 \exp[-p\{(x-x_1)^2 + (y-y_1)^2\}] + \rho_0 \exp[-p\{(x-x_2)^2 + (y-y_2)^2\}]. \quad (2)$$

If the separation of the constituent peaks be written 2Δ , then

$$\left. \begin{aligned} x_1 &= x_0 + \Delta_x, & y_1 &= y_0 + \Delta_y, \\ x_2 &= x_0 - \Delta_x, & y_2 &= y_0 - \Delta_y, \end{aligned} \right\} \quad (3)$$

where Δ_x , Δ_y are the components of Δ , and the expression for the electron density becomes

$$\rho(x, y) = 2\rho_0 \exp[-p\{(x-x_0)^2 + (y-y_0)^2 + \Delta^2\}] \times \cosh 2p\{(x-x_0)\Delta_x + (y-y_0)\Delta_y\}. \quad (4)$$

Taking natural logarithms of both sides, there results

$$\ln \rho(x, y) = \text{Const.} - p(x-x_0)^2 - p(y-y_0)^2 + \ln \cosh 2p\{(x-x_0)\Delta_x + (y-y_0)\Delta_y\}. \quad (5)$$

Now,

$$\ln \cosh u = u^2/2 - u^4/12 + \dots \quad (6)$$

Hence, retaining only the first term in the expansion, (5) becomes

$$\ln \rho(x, y) = \text{Const.} - p(1 - 2p\Delta_x^2)(x-x_0)^2 - p(1 - 2p\Delta_y^2)(y-y_0)^2 + 4p^2\Delta_x\Delta_y(x-x_0)(y-y_0), \quad (7)$$

from which it is evident that, to this degree of approximation, the contours of constant $\ln \rho$ are ellipses with centre $P_0(x_0, y_0)$. The eccentricity of these ellipses is given by the simple expression

$$\varepsilon = \sqrt{(2p)\Delta}. \quad (8)$$

The procedure to be adopted is as follows. The natural logarithms (or numbers proportional to them) of the nine electron-density values nearest the compound peak are fitted by an elliptic paraboloid, and the peak co-ordinates (x_0, y_0) , the eccentricity (ε) and the angle (θ) which the major axis of the ellipse makes with the positive direction of the x axis are obtained. A systematic procedure for doing all this in the general case, where the electron density has been computed at the points of a non-rectangular mesh, has been described in detail by Ladell & Katz (1954).^{*} The value of Δ is then calculated from (8), the values of Δ_x and Δ_y are obtained from Δ and the value of θ , and finally the co-ordinates of the constituent peaks are found from (3), using the calculated peak co-ordinates (x_0, y_0) . Using an electric desk calculating machine the whole process takes about half-an-hour.

It may be pointed out that it is not strictly speaking necessary to use the logarithms of the electron-density values. If the right-hand side of equation (2) is expanded and terms of the second and higher order are neglected, equations (7) and (8) can still be obtained, but the approximation is decidedly inferior.

This point was demonstrated by setting up two Gaussian atoms with $p = 5$, and computing the resultant electron density at nine points of a square mesh of side 0.2 Å. The calculation was performed for two different values of the peak separation, namely 0.212 Å and 0.576 Å, with the line of centres randomly oriented with respect to the mesh in each case. For identical Gaussian atoms, the critical separation, i.e. the separation below which they appear as one peak, is given by $\sqrt{(2/p)}$, which, for $p = 5$, amounts to 0.632 Å. Using logarithmic values and proceeding as detailed above, the method gave 0.210 Å and 0.544 Å; using the electron-density values directly gave 0.166 Å and 0.504 Å. The superiority of the logarithmic method is obvious.

Apart from the basic approximation involved in the neglect of higher-order terms in the expansion of $\ln \cosh u$, the method in practice is subject to errors from the following sources:

(i) Inapplicability of the Gaussian form (1), either due to an inaccurate knowledge of the parameter p , or due to a lack of spherical symmetry in the atom. With regard to the first, it is probable that the best value of p is to be obtained, not by taking sections through well-resolved peaks in the projection, but by computing the finite Hankel transform of the appropriate atomic scattering curve, since the concept of 'well-resolved peak' is not at all precise. With regard to the second, it is clear that any appreciable degree of non-sphericity in the atoms will invalidate the procedure entirely.

(ii) Errors in the computed values of the electron density due to errors in the observed structure factors. This affects the determination of the constants of the

^{*} In this paper there is an error in equation (3) giving the values of the constants in the elliptic paraboloid. There the value of C is given as $\frac{1}{4}(g-4sA)/t$, whereas it ought to read $\frac{1}{4}(g-8sA)/t$.

elliptic paraboloid by the method of Ladell & Katz, which in turn affect the determination of (x_0, y_0) , ϵ , and θ .

(iii) The influence of the other peaks in the projection on the electron-density values in the vicinity of the compound peak. If a reliable atomic profile has been obtained, as mentioned under (i) above, then this effect may be corrected for.

The basic approximation involved in the method can, of course, be improved by including additional terms in the expansion of $\ln \cosh u$; but taking into account only

the next term, namely $-u^4/12$, and dealing only with the simple case in which the electron density has been computed at the points of a square mesh, the required correction term to equation (8) is much too cumbersome to be of any practical value. In any event, in view of the other sources of error present, it is doubtful whether any such attempt at correcting (8) would be worth while.

References

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An X-ray investigation of air-dried lysozyme chloride crystals. II: correction. By ROBERT B. COREY, *California Institute of Technology,* Pasadena, California, U.S.A.*, JERRY DONOHUE, *University of Southern California, Los Angeles, California, U.S.A.*, KENNETH N. TRUEBLOOD, *University of California, Los Angeles, California, U.S.A.*, and KENNETH J. PALMER, *Western Utilization Research Branch,† Albany, California, U.S.A.*

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If the Wilson (1942) method of obtaining the scale factor is to give a reliable value, the Patterson peak at the origin must not contain any contributions arising from the spreading out of near-by peaks. In an earlier communication (Corey, Donohue, Trueblood & Palmer, 1952), which dealt with the interpretation of the Patterson function of air-dried lysozyme chloride, we described briefly a procedure for modifying the Wilson method for application to cases in which a very large temperature factor results in a considerable overlapping of peaks arising from short interatomic distances with the Patterson peak at the origin. The procedure, of course, involves the estimation of the total height contributed by these peaks at the origin in Patterson space. Our attention has been called (Crick, 1953) to an error in our treatment. It is the purpose of this note to correct this error, to restate the problem, and to indicate a method for its possible solution. Since our original treatment contained several minor ambiguities with regard to notation, we now define the following terms:

R = distance from the center of a Patterson peak to the origin.

$P_{ij}(r)$ = height of a Patterson peak (due to atoms i and j) at a distance r from the center of the peak (spherical symmetry assumed).

$P(u, v, w)$ = value of Patterson function at point (u, v, w) .

Thus the height of the Patterson peak at the origin is the sum of two terms:

$$P(0, 0, 0) = \sum_i P_{ii}(0) + \sum_i \sum_j P_{ij}(R).$$

As before,

$$P_{ij}(r) = Z_i Z_j (2\pi/B)^{3/2} \exp[-2\pi^2 r^2/B],$$

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so that

$$\sum_i P_{ii}(0) = (2\pi/B)^{3/2} \sum_i Z_i^2,$$

and

$$\sum_i \sum_j P_{ij}(R) = (2\pi/B)^{3/2} \bar{Z} \sum_i Z_i \int_0^\infty \exp[-2\pi^2 x^2/B] dN(x),$$

where $N(x)$ is a function which gives the number of atoms within a distance x of each atom. Our previous treatment was in error in that $N(x)$ was assumed to be uniform (equal to $0.25x^3$), that $N(x)dx$ was used instead of $dN(x)$, and that $\sum_i Z_i^2$ was used in place of the always

smaller $\bar{Z} \sum_i Z_i$. Since the value of the Patterson function at the origin is also given by

$$P(0, 0, 0) = \frac{1}{V} \sum_{hkl} k |F'_{hkl}|^2 + \frac{1}{V} |F'_{000}|^2,$$

where F'_{hkl} are the observed relative structure factors, and k is the scale factor, we may equate the two expressions, and solve for k , provided that both $N(x)$ and B can be evaluated from other considerations. $N(x)$ can, in principle, be obtained from a (non-uniform) radial distribution function derived from some appropriate model.

The function $N(x)$ must be evaluated for values of x extending from zero to a maximum value beyond which there is no significant overlap of the $P_{ij}(R)$ with $P(0, 0, 0)$. If B is small, as for ordinary crystals, there is no overlap; if B is large, then the maximum value of x will be so great that the function $N(x)$ may be, in practice, difficult to evaluate. The accuracy of the scale factor will depend upon the accuracy with which B and $N(x)$ have been estimated.

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