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Some Properties of the $(F_o - F_c)$-Synthesis

BY W. COCHRAN

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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It is shown that a Fourier synthesis whose coefficients are the differences of observed and calculated structure factors has a number of properties which make it useful for accurate crystal-structure analysis. The use of this synthesis for the refinement of atomic co-ordinates and temperature-factor parameters is discussed and its equivalence to certain other methods is demonstrated.

1. Introduction and notation

The name 'error synthesis' was introduced by Bunn to denote a Fourier series whose coefficients are the differences of observed and calculated structure factors. This synthesis proved valuable in establishing the crystal structure of sodium benzyl penicillin (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949). Essentially the same Fourier synthesis has been used as a means of locating the hydrogen atoms of a crystal structure by Finbak & Norman (1948), and by the writer (Cochran, 1951). A closely related method was in fact used by Brindley & Wood (1929) in an investigation of the structure of the chlorine ion. In this paper we shall not be concerned with the use of the error synthesis to establish the broad features of a crystal structure, but rather with its use in the final stages of a structure analysis. Here the name '$(F_o - F_c)$-synthesis' is more appropriate, as the synthesis may show details which are not errors, but actual features of the crystal structure, for instance, hydrogen atoms or bonding electrons. It will be shown in succeeding sections that the $(F_o - F_c)$-synthesis has a number of properties which make it more useful than the F_o-synthesis normally used in crystal-structure investigations.

In order to effect an economy in writing certain equations, and to simplify the notation, we shall consider a centrosymmetric structure referred to orthogonal axes. Where a different result holds for a structure lacking a centre of symmetry, this will be pointed out.

We define

$x_i = x, y, z$; $a_i = a, b, c$; $h_i = h, k, l$ according as $i = 1, 2$ or 3.

x_{ji} = the x_i co-ordinate of the jth atom.

f_j = the scattering factor of the jth atom.

$\Theta = 2\pi \sum\limits_i \dfrac{h_i x_i}{a_i}$.

$s = 2\sin\theta/\lambda$.

F_o = observed structure factor.

F_c = calculated structure factor $= 2\sum\limits_j f_j \cos\Theta_j$.

ρ = electron density $= \dfrac{1}{V}\sum\limits_N F\cos\Theta$.

$D = \dfrac{1}{V}\sum\limits_N (F_o - F_c)\cos\Theta$.

$(\rho)_j$ = the value of ρ at the point (x_{j1}, x_{j2}, x_{j3}).

$\sum\limits_N$ denotes a triple sum over all h_i.

$\sum\limits_n$ denotes a triple sum over all h_i contained in a limited region of reciprocal space.

2. Use of the $(F_o - F_c)$-synthesis to refine atomic co-ordinates

While the electron density in a centrosymmetric crystal is given by

$$\rho = \frac{1}{V}\sum_N F\cos\Theta,$$

the density measured in practice is

$$\rho_0 = \frac{1}{V}\sum_n F_o\cos\Theta,$$

where the notation serves to emphasize that the measured structure factors are subject to experimental error, and that the series contains only n of the N terms of appreciable magnitude. Atomic co-ordinates taken as the maxima of ρ_0 are subject to systematic error because of the termination of the series, and those obtained by minimizing

$$\phi = \sum_n w(F_o - F_c)^2 \tag{2·1}$$

must be more accurate. The relations between this function and Fourier syntheses have been discussed in papers by the writer (Cochran, 1948), Booth (1948) and Cruickshank (1949, 1950).

These relations receive a simple interpretation in terms of the $(F_o - F_c)$-synthesis. The condition that ϕ should be a minimum with respect to the co-ordinates of the jth atom is $\partial\phi/\partial x_{ji} = 0$.

Now
$$\frac{\partial\phi}{\partial x_{ji}} = \frac{8\pi}{a_i}\sum_n (F_o - F_c)\, w f_j h_i \sin\Theta_j \tag{2·2}$$

from (2·1) and the definition of F_c.

Now consider

$$D_j = \frac{1}{V}\sum_n (F_o - F_c)\, w f_j \cos\Theta,$$

from which

$$\left(\frac{\partial D_j}{\partial x_i}\right)_j = -\frac{2\pi}{a_i V}\sum_n (F_o - F_c)\, w f_j h_i \sin \Theta_j. \qquad (2\cdot3)$$

Comparison of (2·2) and (2·3) gives

$$4V\left(\frac{\partial D_j}{\partial x_i}\right)_j = -\frac{\partial \phi}{\partial x_{ji}}. \qquad (2\cdot4)$$

It follows that ϕ is a minimum with respect to atomic co-ordinates when D_j has zero slope at atomic centres. If we take $w = 1/f_j$,

$$\phi \rightarrow \phi_j = \sum_n \frac{1}{f_j}(F_o - F_c)^2, \qquad (2\cdot5)$$

while $$D_j \rightarrow D = \frac{1}{V}\sum_n (F_o - F_c)\cos \Theta = \rho_o - \rho_c. \qquad (2\cdot6)$$

In the case where trial atomic co-ordinates do not minimize ϕ_j, but are close to those which do result in a minimization, simple geometrical considerations give

$$\Delta x_{ji} = -\left(\frac{\partial D}{\partial x_i}\right)_j \Big/ C(\rho_c)_j, \qquad (2\cdot7)$$

where $C(\rho_c)$ denotes the curvature of ρ_c. The identity of the correction (2·7) with that derived by Qurashi (1949) from a different point of view follows from equation (2·8) of Cruickshank (1950).

We note that minimization of ϕ_j, as defined by (2·5), results in co-ordinates which do not depend on the $(N-n)$ terms omitted from the corresponding $(F_o - F_c)$-synthesis. When, therefore, atomic co-ordinates have been obtained which result in zero slope at the corresponding points of D, these co-ordinates are free from series-termination errors, except in so far as the scattering factors used to calculate the F_c's may be incorrect.

Methods of correcting results obtained from an F_o-synthesis for series termination have been given by Booth (1946) and van Reijen (1942). It is not difficult to show that these methods are equivalent to the use of the $(F_o - F_c)$-synthesis.

3. Rate of convergence

The question whether the use of the $(F_o - F_c)$-synthesis will minimize ϕ_j more, or less, rapidly than other methods, will now be briefly considered. From the identity of the corrections given by Qurashi's method and by the $(F_o - F_c)$-synthesis, it follows that the two are identical as regards rate of convergence. Cruickshank (1950) has shown that the rate of convergence of the normal Fourier method, with corrections for series termination by Booth's method, is approximately the same as that of the least-squares method. It follows from the equivalence of the $(F_o - F_c)$-synthesis to the normal Fourier method plus Booth corrections, that the rate of convergence of the $(F_o - F_c)$-synthesis is approximately the same as that of the method of least squares. Cruickshank's conclusion that if a structure does not have a centre of symmetry, and if none of its projections are centrosymmetrical, the corrections given by the F_o-synthesis should be doubled to allow for phase-angle lag, can also be shown to apply to the $(F_o - F_c)$-synthesis. We can, in fact, generalize (2·7) and take

$$\Delta x_{ji} = -t\left(\frac{\partial D}{\partial x_i}\right)_j \Big/ C(\rho_c)_j,$$

where $t = 1$ if the structure is centrosymmetrical, $1 < t < 2$ if the structure is not centrosymmetrical but certain of its projections are (Schomaker & Shoemaker, private communication), and $t = 2$ if the structure is not centrosymmetrical and is not centrosymmetrical in any of its projections (Cruickshank, 1950).

4. Refinement of atomic scattering factors

We shall assume that the scattering factors of atoms at rest can be correctly obtained without reference to X-ray measurements. In the crystal lattice, allowance is made for thermal vibration and zero-point energy by taking

$$f_j = f_{0j}\exp\left[-s^2\{u_j n_{j1}^2 + v_j n_{j2}^2 + w_j n_{j3}^2\}\right]. \qquad (4\cdot1)$$

This equation expresses the fact that in general surfaces of constant f_j in reciprocal space are ellipsoids. The quantities u_j, v_j and w_j are constants, while n_1, n_2, n_3 are the direction cosines of $\mathbf{s}$ referred to the axes of this ellipsoid, which may be called the 'ellipsoid of thermal vibration'. If the thermal vibration of the jth atom is isotropic, the ellipsoid becomes a sphere and $f_j = f_{0j}\exp[-m_j s^2]$. If the thermal vibration of an atom is not isotropic in the $a_1 a_2$ plane, curves of constant f_j in the $a_1^* a_2^*$ plane of the reciprocal lattice are ellipses with major and minor axes in the direction of minimum and of maximum thermal vibration respectively, i.e.

$$f_j = f_{0j}\exp\{-s^2[u_j\cos^2(\omega - \beta_j) + v_j \sin^2(\omega - \beta_j)]\}, \qquad (4\cdot2)$$

where β_j is the angle which the direction of maximum thermal vibration makes with the a_1 axis. We shall consider only this two-dimensional case in detail, as results for the general case are obtainable, though at greater length, by the application of the same principles. It is convenient at this point to express two-dimensional F_o- and $(F_o - F_c)$-syntheses in terms of polar co-ordinates (r, ψ), r being measured from an atomic centre. For instance,

$$\rho_c = \frac{1}{A}\sum_n F_c \cos 2\pi\left[\frac{h_1}{a_1}(x_{j1} + r\cos\psi) + \frac{h_2}{a_2}(x_{j2} + r\sin\psi)\right].$$

Then $$\frac{\partial \rho_c}{\partial r} = -\frac{2\pi}{A}\sum_n F_c\left(\frac{h_1}{a_1}\cos\psi + \frac{h_2}{a_2}\sin\psi\right)\sin\Theta$$

$$= -\frac{2\pi}{A}\sum_n F_c s\cos(\omega - \psi)\sin\Theta, \qquad (4\cdot3)$$

and $$\frac{\partial^2 \rho_c}{\partial r^2} = -\frac{4\pi^2}{A}\sum_n F_c s^2\cos^2(\omega - \psi)\cos\Theta, \qquad (4\cdot4)$$

with corresponding results for $\partial D/\partial r$ and $\partial^2 D/\partial r^2$.

Here (s, ω) are the polar co-ordinates of the point (h_1, h_2) in the reciprocal lattice (see Fig. 1).

The condition for ϕ_j to be a minimum with respect to u_j is

$$0=\frac{\partial\phi_j}{\partial u_j}=-\sum_n\frac{2}{f_j}(F_o-F_c)\frac{\partial F_c}{\partial u_j}-\sum_n\frac{2}{f_j^2}(F_o-F_c)^2\frac{\partial f_j}{\partial u_j}.$$

The second term on the right-hand side corresponds merely to the change in ϕ_j produced by a change in the weighting factor $1/f_j$; it is the first term which reflects the change in the fit between F_o and F_c resulting from a change in u_j. Consequently we treat $1/f_j$ as a constant in the differentiation and take

$$\begin{aligned}\frac{\partial\phi_j}{\partial u_j}&=-\sum_n\frac{2}{f_j}(F_o-F_c)\frac{\partial F_c}{\partial u_j}\\&=4\sum_n(F_o-F_c)s^2\cos^2(\omega-\beta_j)\cos\Theta_j.\end{aligned}\qquad(4\cdot5)$$

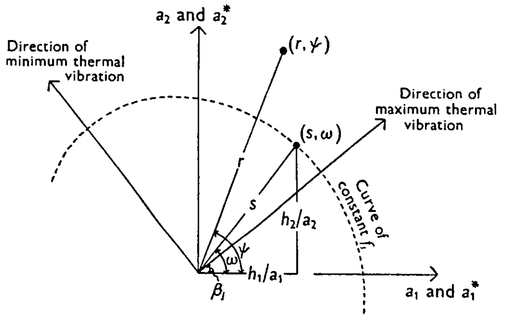

Fig. 1. Superposition of a_1a_2 and $a_1^*a_2^*$ planes to show that

$$\frac{h_1}{a_1}\cos\psi+\frac{h_2}{a_2}\sin\psi=s\cos(\omega-\psi).$$

The second step follows from (4·2) and the definition of F_c. Comparing (4·5) with

$$\left(\frac{\partial^2D}{\partial r^2}\right)_j=-\frac{4\pi^2}{A}\sum_n(F_o-F_c)s^2\cos^2(\omega-\psi)\cos\Theta_j,$$

the result analogous to (4·4), we obtain

$$\frac{\partial\phi_j}{\partial u_j}=-\frac{A}{\pi^2}\left(\frac{\partial^2D}{\partial r_1^2}\right)_j.\qquad(4\cdot6)$$

Similarly, $$\frac{\partial\phi_j}{\partial v_j}=-\frac{A}{\pi^2}\left(\frac{\partial^2D}{\partial r_2^2}\right)_j,$$

and $$\frac{\partial\phi_j}{\partial\beta_j}=-\frac{A}{\pi^2}(v_j-u_j)\left(\frac{\partial^2D}{\partial r_1\partial r_2}\right)_j.$$

In the above equations, r_1 and r_2 denote that r is measured in the directions $\psi=\beta_j$ and $\psi=\beta_j+\frac{1}{2}\pi$ respectively. It follows from these results that the correct choice of temperature-factor parameters, which makes

$$\frac{\partial\phi_j}{\partial u_j}=\frac{\partial\phi_j}{\partial v_j}=\frac{\partial\phi_j}{\partial\beta_j}=0,$$

results in zero curvature of D at the centre of the jth atom. This result might have been anticipated to some extent from the physics of the problem. More useful results are obtained when we consider how the values of u_j, v_j and β_j can be corrected from measurement of the curvature of D at atomic centres. We proceed as for the least-squares solution, and take

$$\sum_j\left(\frac{\partial F_c}{\partial u_j}\Delta u_j+\frac{\partial F_c}{\partial v_j}\Delta v_j+\frac{\partial F_c}{\partial\beta_j}\Delta\beta_j\right)=F_o-F_c.$$

There will be $\frac{1}{2}n$ such equations, corresponding to the $\frac{1}{2}n$ independent observations of F_o. The normal equations are formed by multiplying each such equation throughout by each of $\frac{1}{f_j}\frac{\partial F_c}{\partial u_j}$, etc., in turn, and adding the $\frac{1}{2}n$ separate equations in each case. This gives three equations of which the first is

$$\begin{aligned}\sum_{\frac{1}{2}n}\frac{1}{f_j}\left(\left(\frac{\partial F_c}{\partial u_j}\right)^2\Delta u_j+\frac{\partial F_c}{\partial u_j}\frac{\partial F_c}{\partial v_j}\Delta v_j+\frac{\partial F_c}{\partial u_j}\frac{\partial F_c}{\partial\beta_j}\Delta\beta_j\right)\\=\sum_{\frac{1}{2}n}\frac{1}{f_j}(F_o-F_c)\frac{\partial F_c}{\partial u_j}.\end{aligned}\qquad(4\cdot7)$$

Clearly $\sum\limits_{\frac{1}{2}n}$ can be replaced by our customary $\sum\limits_n$ throughout. The non-occurrence of terms $\frac{\partial F_c}{\partial u_j}\frac{\partial F_c}{\partial u_{j'}}$ with $j\neq j'$, is explained by the fact that such terms may be neglected if the atoms are well enough resolved to satisfy

$$\sum_n f_jf_{j'}s^4\cos\Theta_j\cos\Theta_{j'}\ll\sum_n f_j^2s^4\cos^2\Theta_j.$$

Using a number of results such as

$$\left(\frac{\partial^4\rho_c}{\partial r_1^4}\right)_j=\frac{32\pi^4}{A}\sum_n f_js^4\cos^4(\omega-\beta_j)\cos^2\Theta_j$$

and

$$\left(\frac{\partial^2D}{\partial r_1^2}\right)_j=-\frac{4\pi^2}{A}\sum_n(F_o-F_c)s^2\cos^2(\omega-\beta_j)\cos\Theta_j,$$

the normal equations (4·7) reduce exactly to

$$\left.\begin{aligned}\left(\frac{\partial^4\rho_c}{\partial r_1^4}\right)_j\Delta u_j+\left(\frac{\partial^4\rho_c}{\partial r_1^2\partial r_2^2}\right)_j\Delta v_j&=4\pi^2\left(\frac{\partial^2D}{\partial r_1^2}\right)_j,\\\left(\frac{\partial^4\rho_c}{\partial r_1^2\partial r_2^2}\right)_j\Delta u_j+\left(\frac{\partial^4\rho_c}{\partial r_2^4}\right)_j\Delta v_j&=4\pi^2\left(\frac{\partial^2D}{\partial r_2^2}\right)_j,\\(u_j-v_j)\left(\frac{\partial^4\rho_c}{\partial r_1^2\partial r_2^2}\right)_j\Delta\beta_j&=2\pi^2\left(\frac{\partial^2D}{\partial r_1\partial r_2}\right)_j.\end{aligned}\right\}\qquad(4\cdot8)$$

These are not convenient for practical application. However, if u_j and v_j are not very different,

$$\left(\frac{\partial^4\rho_c}{\partial r_1^4}\right)_j\doteqdot\left(\frac{\partial^4\rho_c}{\partial r_2^4}\right)_j\doteqdot3\left(\frac{\partial^4\rho_c}{\partial r_1^2\partial r_2^2}\right)_j\doteqdot\frac{6\pi^4}{A}\sum_n\bar{f}_js^4,$$

where $$\bar{f}_j=f_{0j}\exp[-\tfrac{1}{2}s^2(u_j+v_j)].$$

Hence $$\Delta u_j\doteqdot\frac{A\{3(\partial^2D/\partial r_1^2)_j-(\partial^2D/\partial r_2^2)_j\}}{4\pi^2\sum\limits_n\bar{f}_js^4},$$

$$\Delta v_j\doteqdot\frac{A\{3(\partial^2D/\partial r_2^2)_j-(\partial^2D/\partial r_1^2)_j\}}{4\pi^2\sum\limits_n\bar{f}_js^4}.$$

If the thermal vibration is isotropic,

$$\Delta m_j=\frac{A(\partial^2D/\partial r^2)_j}{2\pi^2\sum\limits_n f_js^4}.\qquad(4\cdot9)$$

From the third of the normal equations (4·8), it may be deduced that when $\Delta\beta_j=0$, or $u_j=v_j$, the directions of principal curvature of D at the centre of the jth atom are the directions of maximum and of minimum thermal vibration of this atom. $\Delta\beta_j=0$ corresponds to the correct choice of β_j; $u_j=v_j$ corresponds to the assumption of an isotropic scattering factor.

These results may be extended to the three-dimensional case, and it is found that if an isotropic scattering factor is used in calculating the F_c's, the directions of principal curvature of D at the centre of the jth atom are the directions of the axes of the corresponding 'ellipsoid of thermal vibration', while

$$\Delta u_j=\frac{3V\{4(\partial^2D/\partial r_1^2)_j-(\partial^2D/\partial r_2^2)_j-(\partial^2D/\partial r_3^2)_j\}}{8\pi^2\sum_n f_j s^4},$$

with strictly analogous formulae for Δv_j and Δw_j.

5. The effect of errors of scale

So far it has been assumed that the calculated and observed structure factors are on the same absolute scale. In practice this will not always be the case, since the F_o's are often measured in arbitrary units and subsequently scaled by comparison with the F_c's. Any error of scale will interfere very seriously with attempts to find the correct temperature-factor parameters. In the case where the scattering factors are isotropic, we can allow for a possible error of scale by taking

$$f_j=f_{0j}(1-K)\exp[-m_js^2],$$

where K is the same for all atoms. Proceeding as in previous sections, the corrections ΔK and Δm_j required to minimize ϕ_j are found to be given by

$$\sum_n f_j\Delta K+\sum_j\left\{\sum_n f_js^2\right\}\Delta m_j=-\tfrac{1}{2}\sum_n\frac{1}{f_j}F_c(F_o-F_c), \quad (5\cdot1a)$$

$$\sum_n f_js^2\Delta K+\sum_n f_js^4\Delta m_j=\frac{A}{2\pi^2}\left(\frac{\partial^2D}{\partial r^2}\right)_j. \quad (5\cdot1b)$$

(We are again considering a two-dimensional example.) If $\Delta K=0$, (5·1b) reduces to (4·9). Equation (5·1a) involves the Δm_j's of all atoms, but (5·1b) involves only one at a time. Consequently by measuring $\partial^2D/\partial r^2$ at each atomic centre, and evaluating the right-hand side of (5·1a), the equations can be solved for ΔK and all Δm_j's.

Equation (5·1b) serves to emphasize that only by including observations corresponding to large values of s, so that $\sum_n s^4f_j$ becomes comparable with, or greater than, $\sum_n s^2f_j$, can accurate values of the Δm_j's be obtained.

We may also note that the establishment of the correct scale of the scattering factors of *individual* atoms requires, if

$$f_j=f_{0j}(1-K_j)\exp[-m_js^2], \quad \frac{\partial\phi_j}{\partial K_j}=0.$$

Using the definition of ϕ_j (2·5) and of D (2·6), this reduces to $(D)_j=0$.

In short, the correct choice of scale, atomic coordinates and atomic scattering-factor parameters results in $D=0$, $\partial D/\partial r=0$ and $\partial^2D/\partial r^2=0$ at each atomic centre.

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