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The Convergence of the Least-Squares and Fourier Refinement Methods

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A comparison is made between the atomic co-ordinate corrections given in structure refinement by the least-squares and Fourier methods. For centrosymmetric structures the same corrections, when less than about 0·10 A., are given by both methods. A modified form of the Fourier method is suggested to allow for phase-angle refinement in non-centrosymmetric structures, which is equivalent to the least-squares method when the corrections are small.

1. Introduction

Qurashi (1949) has shown how the convergence of the method of steepest descents (Booth, 1947*a*, *b*) may be improved, successive parameter corrections being identical with those given in successive refinements by the (linear) least-squares method (Hughes, 1941). By using Cochran's (1948*a*, *b*) relationship between the least-squares and Fourier methods Booth (1948) showed that in a map of $(\rho_o-\rho_c)$, the difference of the observed and calculated electron densities, the directions of greatest ascent at the positions used to calculate the structure factors, F_c, are the same as the directions in which the atoms would be moved by his method of steepest descents, and that the gradients at these points are proportional to the magnitudes of the vector corrections given by his method.

The purpose of the present paper is to extend these results by examining the connexion between the corrections given by the least-squares (or improved steepest-descents) and Fourier methods. A direct connexion will be established between the two methods for the final stages of refinement, though this takes slightly different forms for centrosymmetric and non-centrosymmetric structures, which we shall consider separately. A number of results and some notation will be taken from a paper (Cruickshank, 1949) on the accuracy of the least-squares method, which will be referred to as paper A.

The object of the least-squares and steepest-descents methods is to find parameters for which some function of the observed and hypothetical structures is a minimum. We shall consider two closely related functions,

$$R=\sum_3 w_1(|F_o|-|F_c|)^2, \qquad (1\cdot1)$$

where $\sum_3$ is a summation over the independent planes observed *and* those planes dependent on them because of symmetry, w_1 is the weight given to each observation, and F_o and F_c are the observed and calculated structure factors; and

$$\phi=\sum_3 \frac{1}{f_r}(|F_o|-|F_c|)^2, \qquad (1\cdot2)$$

f_r being the scattering factor of the rth atom. (A structure will have as many ϕ functions as it has different kinds of atoms.)

We shall define the p density as

$$p_o=\frac{1}{V}\sum_3 w_1 f_r |F_o| \cos(\theta-\alpha_c), \qquad (1\cdot3)$$

and

$$p_c=\frac{1}{V}\sum_3 w_1 f_r |F_c| \cos(\theta-\alpha_c), \qquad (1\cdot4)$$

where α_c is the calculated phase angle and

$$\theta=2\pi\sum_j (h_j x_j/a_j) \quad (j=1,2,3).$$

As in A we assume that:

(A 2) the shapes of the observed and calculated peaks of the electron (or the p) density near corresponding maxima are the same; and

(A 3) the peaks are resolved and the finite-series corrections small.

In the form involving ϕ and the electron density ρ, Cochran's result is that the co-ordinates of the rth atom which minimize ϕ (with the scattering factor of this atom) are the same as those given by the Fourier series for ρ_o, when corrected for finite summation and peak overlapping by ρ_c. A similar relationship holds between R and the p density.

2. Centrosymmetric structures

2·1. *Refinement corrections*

We shall take F as the signed structure factor, omitting the phase angle α.

Let F_c be calculated for a trial configuration of the structure, then in the (linear) least-squares method applied to ϕ there are v normal equations to determine the small corrections $\epsilon_1, \epsilon_2, \ldots, \epsilon_m, \ldots, \epsilon_v$ to the co-ordinate parameters. These equations for different m are of the type

$$\sum_{n=1}^{v} c_{mn}\epsilon_n=\sum_3 \frac{1}{f_r}\left(\frac{\partial F_c}{\partial x_m}\right)(F_o-F_c), \qquad (2\cdot1)$$

where

$$c_{mn}=c_{nm}=\sum_3 \frac{1}{f_r}\left(\frac{\partial F_c}{\partial x_m}\right)\left(\frac{\partial F_c}{\partial x_n}\right), \qquad (2\cdot2)$$

and $(\partial F_c/\partial x_m)$ is evaluated for the parameters of the trial configuration.

Corresponding to A (3·6) we have approximately for a large summation (changing the notation slightly)

$$c_{rj,\,rj}=\frac{4\pi^2}{a_j^2}t^2\sum_3(h_j^2f_r/s), \tag{2·3}$$

where t is the number of atomic co-ordinates determined by symmetry from this one parameter, and s is the multiplicity of a plane. Similarly, for the term involving the i and j co-ordinates of the rth atom,

$$c_{ri,\,rj}=\frac{4\pi^2}{a_ia_j}t^2\sum_3(h_ih_jf_r/s). \tag{2·4}$$

This will be small as compared with (2·3) for a summation throughout a spherical region of reciprocal space when the sides a_i and a_j of the unit cell are orthogonal, but not necessarily otherwise. When the cross terms c_{mn} involve the parameters of different atoms, both $c_{qj,\,rj}$ and $c_{qj,\,ri}$ will be small as compared with (2·3). Thus the corrections to the three parameters of one atom are determined to a good approximation in a large summation by only three equations, which, using the usual indices h, k, l and co-ordinates x, y, z, may be written

$$\left.\begin{aligned}c_{hh}\epsilon_x+c_{hk}\epsilon_y+c_{hl}\epsilon_z&=C_h,\\ c_{hk}\epsilon_x+c_{kk}\epsilon_y+c_{kl}\epsilon_z&=C_k,\\ c_{hl}\epsilon_x+c_{kl}\epsilon_y+c_{ll}\epsilon_z&=C_l,\end{aligned}\right\} \tag{2·5}$$

where
$$C_h=\sum_3\frac{1}{f_r}\left(\frac{\partial F_c}{\partial x}\right)(F_o-F_c),\ \text{etc.} \tag{2·6}$$

By symmetry C_h consists of t equal sums, giving as by A (2·2),

$$C_h=-\frac{2\pi}{a}t\sum_3h(F_o-F_c)\sin\theta_r. \tag{2·7}$$

When $c_{ij}(i\neq j)$ is small the corrections are simply

$$\epsilon_j=C_j/c_{jj}, \tag{2·8}$$

which, with c_{jj} defined by (2·2), is the steepest-descent correction given by Qurashi as applied to ϕ.

In the ordinary process of Fourier refinement the co-ordinate corrections to the positions of one atom in a trial configuration may be obtained by using differential syntheses, the equations (Booth, 1946*b*) determining the corrections being

$$\left.\begin{aligned}A_{hh}\epsilon_x+A_{hk}\epsilon_y+A_{hl}\epsilon_z+A_h&=0,\\ A_{hk}\epsilon_x+A_{kk}\epsilon_y+A_{kl}\epsilon_z+A_k&=0,\\ A_{hl}\epsilon_x+A_{kl}\epsilon_y+A_{ll}\epsilon_z+A_l&=0,\end{aligned}\right\} \tag{2·9}$$

where
$$A_h=-\frac{2\pi}{aV}\sum_3hF\sin\theta_r, \tag{2·10}$$

and
$$A_{hk}=-\frac{4\pi^2}{abV}\sum_3hkF\cos\theta_r. \tag{2·11}$$

To allow for the effect of finite summation and peak overlapping we can solve (2·9) separately for both the 'observed' and 'calculated' structures, taking the differences as the corrections; or, assuming the observed and calculated A_{hk}, etc., to be approximately equal, we may write down a single set of equations taking A_{hk} as in (2·11) and

$$A_h=-\frac{2\pi}{aV}\sum_3h(F_o-F_c)\sin\theta_r, \tag{2·12}$$

but by (2·7)
$$A_h=C_h/tV, \tag{2·13}$$

and writing $F_c=\sum_r f_r\cos\theta_r$, we have approximately, as in A (3·11),

$$\begin{aligned}A_{hk}&=-\frac{1}{V}\frac{4\pi^2}{ab}\sum_3\frac{t}{s}hkf_r\\ &=-c_{hk}/\epsilon V\quad\text{by (2·3).}\end{aligned} \tag{2·14}$$

From (2·13) and (2·14) we see that the sets of equations (2·5) and (2·9) are the same; thus for centrosymmetric structures the same corrections (when small) are given by the least-squares method and by the related Fourier method with correction for finite summation and peak overlapping.

Booth (1946*b*) has pointed out the very simple form which the equations (2·9) of the differential refinement method take when the peaks are spherically symmetrical. This also applies to the equivalent equations (2·5) of the least-squares method where, if the peaks are spherically symmetrical,

$$c_{hh}=c_{kk}=c_{ll}, \tag{2·15}$$

the other coefficients being of the type

$$c_{hl}=c_{hh}\cos\beta, \tag{2·16}$$

where β is the angle between the x and z axes. Further, these coefficients are approximately independent of the trial co-ordinates and need be calculated but once.

2·2. *Conditions for equivalence*

We shall now make a more detailed examination of the conditions under which the least-squares (or improved steepest-descents) and related Fourier methods give the same results.

The two methods will give different results, even when the assumptions (A 2) and (A 3) are true, if the corrections are large enough to cause substantial differences between the observed and calculated values of A_{hk}, etc., at the atomic positions of the hypothetical structure. This difference of results is lessened if the comparison is made between density maps (instead of differential syntheses) and least squares and is then due to the inaccuracy of the linear approximations in least squares (or in steepest descents to the assumption that ϕ is a second degree surface). If we assume (Costain, 1941; Booth, 1945, 1946*a*) that the atomic peaks of the electron density maps may be represented by

$$\rho(r)\propto\exp(-pr^2),$$

and take $p=5$, then for corrections of 0·14 A. there is roughly a 10 % difference between the estimates by least squares and electron-density maps. For p density maps and their corresponding least-squares function R a 10 % difference corresponds to a correction of about

0·20 A. (if $w_1=1$), these differences decreasing with p. Hence we may say roughly that the methods are equivalent for corrections less than 0·10 A.

2·3 *General comparison*

In the Fourier refinement method the signs of the F_o's in one stage are taken as those of the F_c's calculated for the atomic positions reached at the end of the previous stage. By assuming continuity in the partial derivatives of $|F_c|$ the least-squares and steepest-descents processes are also only able to change the signs of the F's in between refinement stages; for in fact the partial derivatives of $|F_c|$ are discontinuous when F_c changes sign. In the form in which we have written the least-squares equations without moduli in §2·1 the equivalent situation is that the sign of F_o can only be changed at the end of a stage when it is found that F_c is of a different sign for the new co-ordinates. Thus both the least-squares and Fourier methods are on the same basis as regards phase-sign changes.

We have already remarked that the least-squares method suffers from the inadequacy of its linear approximations when the corrections are large, so that we conclude that the least-squares method is only better than the Fourier method (taking the corrections as the differences of those given separately from ρ_o and ρ_c) when the peaks are unresolved.

This conclusion for centrosymmetric structures may be compared with those made for general structures by Booth (1948) at the end of his discussion on steepest descents and the Fourier method:

'The above discussion makes it clear that the normal Fourier refinement technique, in which the new atomic positions are taken to be those of the maxima of ρ_o, is incorrect, and that much better convergence would be obtained by taking as new co-ordinates those of the maxima in the $(\rho_o-\rho_c)$ space, although for the early stages of a determination this will still be much inferior to the true steepest-descent method.'

First, agreeing that it is incorrect to take the new atomic positions as the maxima of ρ_o (unless there is no peak overlapping in the ρ_c map), the new atomic positions in the final stages of refinement when the peaks are resolved will not be given by the maxima of $(\rho_o-\rho_c)$, but by taking as corrections the difference of those given separately from ρ_o and ρ_c (a procedure suggested by Booth (1945, 1946*a*) and which is what has been meant in this paper by the Fourier method).

Secondly, ignoring the general conclusion reached above, at the level of approximation assumed in §2·1, which treats the R or ϕ surfaces as of the second degree, the Fourier and least-squares (or improved steepest-descents) methods are equivalent. Booth has rightly concluded that in general his steepest-descents method and the Fourier method lead to different results, but it is his steepest-descents method, resolution of the peaks being assumed, which, for centrosymmetric structures at any rate, is the less efficient. Booth's formulae find the line of steepest descent on the ϕ surface at the point which represents the trial configuration, and estimate where ϕ is a minimum along that line; while Qurashi's steepest-descent method (to which the least-squares and, at this level of approximation, Fourier methods are equivalent) estimates directly where the ϕ surface has a minimum, descending, as it were, along the geodesic curve of steepest descent.

2·4. *Electron and p densities*

Connexions similar to those established above for ϕ and the electron density hold between R and the p density. Precise comments on whether the electron or p density gives the better rate of convergence are difficult to make, but as the peaks of the p density are more spread out than those of the electron density, it would seem that in the early stages of refinement, when resolution of the peaks is important, it would be better to use the electron density; while in the latter stages, when final accuracy is important, it would be better to use the p density. As the electron density yields other useful information besides the atomic co-ordinates, perhaps the best scheme would be to carry the refinement as far as possible with the electron density, and then to carry out a final refinement with the p density or least squares to get the most accurate co-ordinates. Another reason for only using the p density at the last stage is the slight complication that it involves different 'weights' f_r for different kinds of atoms.

3. Non-centrosymmetric structures

Much of §2 is also applicable to non-centrosymmetric structures; we shall therefore consider only changed aspects. For simplicity we shall assume a structure with no elements of symmetry.

3·1. *Modified differential synthesis*

Booth (1946*c*) has shown how the equations (2·9) of the differential Fourier method may be modified to refine phase angles as well as co-ordinates. After calculating the corrections given by (2·9) he introduces into each of the three equations (2·9) an extra term ΔA_h, ΔA_k, ΔA_l respectively, where

$$\Delta A_h=\frac{2\pi}{aV}\sum_3 h\,|F|\cos(\theta_r-\alpha)\,\epsilon_\alpha, \text{ etc.,} \qquad (3\cdot1)$$

ϵ_α being the change in the phase angle given by the first corrections. The revised equations then give a second set of corrections, from which new phase-angle changes can be calculated to use in a third set of equations, etc.

Assuming (A 2) and (A 3) and that all the corrections are small, we shall show that this iterative process has as its limit corrections which are twice those given by the original equations (2·9). If, as in §2·1, we assume that the observed and calculated A_{hk}, etc. and also ΔA_h are approximately equal, we may write down a single

set of equations for the difference of the 'observed' and 'calculated' corrections, taking A_h as in (2·12).

By Booth (1946*c*),

$$\epsilon_\alpha = \frac{1}{|F_c|}\sum_r f_r \cos(\theta_r - \alpha)\,\epsilon_{\theta r}, \tag{3·2}$$

where $$\epsilon_{\theta r} = 2\pi\left(h\frac{\epsilon_{xr}}{a} + k\frac{\epsilon_{yr}}{b} + l\frac{\epsilon_{zr}}{c}\right),$$

and $\epsilon_{xr}, \epsilon_{yr}, \epsilon_{zr}$ are the co-ordinate corrections from (2·9). Following our previous approach for large summations, ΔA_h is approximately given by

$$\Delta A_h = \frac{2\pi}{aV}\sum_3 h f_r \cos^2(\theta_r - \alpha)\,\epsilon_{\theta r}$$

$$= -\tfrac{1}{2}(A_{hh}\epsilon_{xr} + A_{hk}\epsilon_{yr} + A_{hl}\epsilon_{zr}) \tag{3·3}$$

$$= \tfrac{1}{2}A_h \quad \text{by (2·9).} \tag{3·4}$$

Thus the equations for the second set of corrections ϵ'_{xr}, etc., which are of the type

$$A_{hh}\epsilon'_{xr} + A_{hk}\epsilon'_{yr} + A_{hl}\epsilon'_{zr} + A_h + \Delta A_h = 0,$$

reduce to $$A_{hh}\epsilon'_{xr} + A_{hk}\epsilon'_{yr} + A_{hl}\epsilon'_{zr} + \tfrac{3}{2}A_h = 0. \tag{3·5}$$

Hence $$\epsilon'_{xr} = \tfrac{3}{2}\epsilon_{xr}, \text{ etc.}$$

The new value of ΔA_h is now

$$\Delta A'_h = -\tfrac{1}{2}(A_{hh}\epsilon'_{xr} + A_{hk}\epsilon'_{yr} + A_{hl}\epsilon'_{zr}) \tag{3·6}$$

$$= \tfrac{3}{4}A_h,$$

leading to $$\epsilon''_{xr} = \tfrac{7}{4}\epsilon_{xr}, \text{ etc.}$$

Continuing this process we find that the limit is a set of corrections which are twice those given originally by (2·9).

This suggests that when the co-ordinate corrections are small, the corrections given by the Fourier method for non-centrosymmetric structures should be doubled to allow for phase-angle correction.

3·2. *Least-squares refinement corrections*

Corresponding to (2·2) we have, if m and n refer to the x and y co-ordinates of the rth atom,

$$c_{mn} = \sum_3 \frac{1}{f_r}\left(\frac{\partial|F_c|}{\partial x}\right)\left(\frac{\partial|F_c|}{\partial y}\right)$$

$$= \sum_3 4\pi^2\frac{hk}{ab} f_r \sin^2(\theta_r - \alpha)$$

$$= \frac{1}{2}\frac{4\pi^2}{ab}\sum_3 hk f_r, \quad \text{as in (2·4)}$$

$$= -\tfrac{1}{2}VA_{hk}, \quad \text{as in (2·14).} \tag{3·7}$$

Corresponding to (2·7),

$$C_h = -\frac{2\pi}{a}\sum_3 h(|F_o| - |F_c|)\sin(\theta_r - \alpha)$$

$$= VA_h, \quad \text{by (2·12).} \tag{3·8}$$

If we now compare (2·5) and (2·9), we see that the corrections given by the least-squares equations are twice those given by the ordinary differential Fourier method. Thus the same corrections are given by the least-squares method and the Fourier method when modified as in § 3·1 to allow for phase-angle refinement.

3·3. *Discussion*

As with centrosymmetric structures the identity of correction by least-squares and the (now modified) Fourier methods holds only for small corrections.

Though the least-squares equations now allow for phase-angle variation, further refinement will be necessary if the corrections ϵ_{xr} are so large that they apparently make values of $|F_c|$ at the new co-ordinates negative, i.e. if

$$|F_c(\text{initial})| + \sum_r \frac{\partial|F_c|}{\partial x_r}\epsilon_{xr} < 0. \tag{3·9}$$

A further effect of large corrections will be to render the linear approximations of the method inadequate. On the other hand, the ordinary Fourier method is able to refine phase angles only in between stages, though when the corrections are small phase-angle changes may be allowed for by taking double the ordinary corrections, as in § 3·1. This process, however, is not valid when the corrections are large. The Fourier method is also unsatisfactory when the peaks are unresolved. Thus though the least-squares and modified Fourier methods give the same corrections when these are small, it is difficult to compare them when the corrections are large.

A possibility in practice, when using Fourier methods for *non-centrosymmetric* structures, would be to take the differences of the corrections given for ρ_o and ρ_c by the ordinary Fourier method as corrections until these are less than 0·10 A., and thereafter to use double corrections.

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