Acta Cryst. (1952). **5**, 511

On the Relations between Fourier and Least-Squares Methods of Structure Determination

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(*Received* 6 *October* 1951)

A criterion for determining atomic coordinates in the Fourier method, applicable to resolved or unresolved peaks, is introduced. The full equations for coordinate refinements according to this criterion are shown to have an exact similarity with the normal equations of least squares for the function $R = \Sigma w(|F_o|-|F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes for reflexions $h(= h, k, l)$, $w(h)$ is a weight function, and the sum is taken over the observed orders h. A criterion for finding atomic coordinates from the Patterson density leads to refinement equations which are similar to the normal equations for the function $R_2 = \Sigma w''(|F_o|^2-|F_c|^2)$, where $w''(h)$ is another weight function. Both centrosymmetric and non-centrosymmetric space groups are considered. Approximate forms of the equations and the relationship of this work to earlier work by Booth, Cochran, and Cruickshank are discussed.

Notation

Throughout this paper the suffices r, s, t and u refer to atoms or atomic positions, while the suffices i, j and k refer to any of the three coordinate directions; thus x_{tk} denotes the kth coordinate of atom t.

The following notation is not explained in the text:

a_i	Length of ith axis of unit cell.
f_r	Scattering factor of atom r.
F_c	Calculated structure factor.
F_o	Observed structure factor.
h_i	Plane index.
α	Calculated phase angle.
θ	$2\pi(\sum_i h_i x_i/a_i)$; $(i = 1, 2, 3)$.
θ_r	$2\pi(\sum_i h_i x_{ri}/a_i)$.
$\sum_3$	Finite triple summation over all planes observed.

1. Introduction

Cochran (1948*a*, *b*) showed that the coordinates of atom r which minimize

$$\varphi = \sum_3 \frac{1}{f_r}(|F_o|-|F_c|)^2 \qquad (1\cdot1)$$

are the same as those given by the Fourier series for the electron density

$$\varrho = \frac{1}{V}\sum_3 |F| \cos(\theta-\alpha) \qquad (1\cdot2)$$

when this is corrected for finite summation and peak overlapping. Similarly coordinates found by minimizing

$$R = \Sigma w(|F_o|-|F_c|)^2 \qquad (1\cdot3)$$

are the same as those found from the Fourier series

$$\varrho^r = \frac{1}{V}\sum_3 w' f_r |F| \cos(\theta-\alpha)\,. \qquad (1\cdot4)$$

For the final stages of structure refinement, Cruickshank (1950) pointed out an approximate equality between the normal equations of least squares (Hughes, 1941) and the equations governing the determination of coordinates from differential Fourier syntheses.

All these results were derived on the assumption that the peaks representing the atoms were resolved. In the present communication this restriction is removed, and a modified Fourier method capable of dealing with resolved or unresolved peaks is described, the equations of which are shown to have an exact similarity with the normal equations. Centrosymmetric space groups are treated in § 2, and non-centrosymmetric space groups in § 3.

In § 4 we shall consider the relations between minimizing

$$\Sigma w''(|F_o|^2-|F_c|^2)^2 \qquad (1\cdot5)$$

and a method working on the Patterson density.

The condition that φ, (1·1), is a minimum implies (Cruickshank, 1949, (2·3)) that the slopes at atom r of the observed and calculated electron densities, ϱ_o and ϱ_c, are equal. This consequence of the least-squares condition is a possible criterion to adopt for determining coordinates in the Fourier method, if we wish to correct for finite series and peak overlapping effects. The criterion is applicable to unresolved as well as to resolved peaks. We shall call the Fourier method using this criterion the modified Fourier method. In some circumstances it leads to the same coordinates as Booth's (1945, 1946) back-correction method; this is discussed in § 2·4.

2. Centrosymmetric space groups

2·1. *Equations of the modified Fourier method*

In this section we shall derive the equations for small coordinate refinements in the modified Fourier method for centrosymmetric space groups.

The conditions we wish to satisfy are that the slopes in the x_i direction at the position of atom r of the observed and calculated electron densities shall be equal, for all i and r. We denote this by

$$\left(\frac{\partial\varrho_o}{\partial x_i}\right)_r=\left(\frac{\partial\varrho_c}{\partial x_i}\right)_r. \tag{2·1}$$

The problem is to move the independent parts of the calculated structure so that these conditions are satisfied. If we have a set of trial coordinates, differing only by small amounts from the correct set, we can obtain the set of refinements ε_{sj}, to the jth (x, y or z) parameter of atom s by equating the zeroth- and first-degree terms of the multivariate Taylor expansions of the two sides of (2·1). Thus

$$\begin{aligned}\left(\frac{\partial\varrho_o}{\partial x_i}\right)_r+\sum_j\varepsilon_{rj}\left(\frac{\partial^2\varrho_o}{\partial x_j\partial x_i}\right)_r\\=\left(\frac{\partial\varrho_c}{\partial x_i}\right)_r+\sum_j\varepsilon_{rj}\left(\frac{\partial^2\varrho_c}{\partial x_j\partial x_i}\right)_r+\sum_{s,j}\varepsilon_{sj}\frac{\partial}{\partial x_{sj}}\left(\frac{\partial\varrho_c}{\partial x_i}\right)_r,\end{aligned} \tag{2·2}$$

where the left-hand side gives the value of $\partial\varrho_o/\partial x_i$ at a point distant (ε_{rx}, ε_{ry}, ε_{rz}) from the trial position of atom r, and on the right hand side the first two terms give $\partial\varrho_c/\partial x_i$ near r and the third group of terms allows for the changes in $(\partial\varrho_c/\partial x_i)_r$ due to changing all the parameters by ε_{sj}. In this last group of terms we may regard ϱ_c either as a function of the independent parameters x_{sj} (or ε_{sj}), or as a function of all the atomic coordinates x_{sj}, these being related in sets by symmetry. In the former case the summation $\sum\limits_{s,j}$ is over only the independent parameters; in the latter case the summation is over all the atomic coordinates, and we have relations between the ε_{sj}'s, e.g. $\varepsilon_{sj}=-\varepsilon_{tj}$, for atoms s and t related by the centre of symmetry. Unless otherwise stated it will be convienient to regard ϱ_c as a function of the independent parameters. If, for the given set of trial coordinates, we denote by ϱ_s the calculated electron density of atom s and those atoms related to s by symmetry, we may write the coefficient of ε_{sj} in (2·2) as

$$\frac{\partial}{\partial x_{sj}}\left(\frac{\partial\varrho_s}{\partial x_i}\right)_r, \tag{2·3}$$

since $\varrho_c=\sum\limits_s\varrho_s$. Denoting by F_s that part of F_c due to atom s and those atoms related to s by symmetry, the series for (2·3) is

$$-\frac{1}{V}\frac{2\pi}{a_i}\sum_3 h_i\frac{\partial F_s}{\partial x_{sj}}\sin\theta_r. \tag{2·4}$$

There is an equation like (2·2) for each independent direction at each independent atom, hence we may obtain a set of simultaneous linear equations which determine the parameter refinements ε_{sj}.

The omission of the second group of terms from each side of (2·2) gives equations determining the parameters from the conditions that the slopes of the observed and calculated electron densities are to be equal at the trial positions of the atoms. We shall call these equations,

$$\left(\frac{\partial\varrho_o}{\partial x_i}\right)_r=\left(\frac{\partial\varrho_c}{\partial x_i}\right)_r+\sum_{s,j}\varepsilon_{sj}\frac{\partial}{\partial x_{sj}}\left(\frac{\partial\varrho_s}{\partial x_i}\right)_r, \tag{2·5}$$

the equations of the modified differential Fourier method, using the word differential to indicate that the equations are correct only for small refinements.

Usually the terms omitted from (2·2) are not of importance. In § 2·3 we shall consider the approximate forms of the equations (2·5) which may be used in practice.

2·2. *The normal equations of least squares*

In this section we shall transcribe the normal equations for least squares into a form rather similar to (2·5). We shall consider the function

$$R=\sum w(F_o-F_c)^2, \tag{2·6}$$

where w is the weight of each independent plane, the summation is over the independent planes observed, and we omit the moduli signs as compared with (1·3) as the F's are all real. The normal equations for R, (2·6), are of the type

$$\sum_{s,j}c_{ri,\,sj}\varepsilon_{sj}=b_{ri}, \tag{2·7}$$

where

$$b_{ri}=\sum w(F_o-F_c)\frac{\partial F_c}{\partial x_{ri}},$$

and

$$c_{ri,\,sj}=\sum w\frac{\partial F_c}{\partial x_{ri}}\frac{\partial F_c}{\partial x_{sj}},$$

the summations being over independent planes.

We can take the summations over all planes observed, that is the independent planes and those related to them by symmetry, by putting

$$w'p=w, \tag{2·8}$$

where p is the number of planes related by symmetry. Further, if q is the number (including atom r) of atoms related to atom r by symmetry, $\partial F_c/\partial x_{ri}=\partial F_r/\partial x_{ri}$ is a sum of a number of terms of the type

$$\pm\frac{2\pi}{a_i}h_if_r\sin\theta,$$

so that, using the symmetry, we may write

$$b_{ri}=-q\frac{2\pi}{a_i}\sum_3 w'f_rh_i(F_o-F_c)\sin\theta_r, \tag{2·9}$$

and

$$c_{ri,\,sj} = -q\frac{2\pi}{a_i}\sum_3 w'f_r h_i \frac{\partial F_s}{\partial x_{sj}}\sin\theta_r\,. \qquad (2{\cdot}10)$$

Introducing a weighted electron density

$$\varrho^r = \frac{1}{V}\sum_3 w'f_r F\cos\theta\,,$$

derived from the ordinary finite-series electron density by weighting each term by a factor $w'f_r$, we can write the normal equations in the form

$$\left(\frac{\partial\varrho^r_o}{\partial x_i}\right)_r = \left(\frac{\partial\varrho^r_c}{\partial x_i}\right)_r + \sum_{s,j}\varepsilon_{sj}\frac{\partial}{\partial x_{sj}}\left(\frac{\partial\varrho^r_s}{\partial x_i}\right)_r, \qquad (2{\cdot}11)$$

which is obtained by comparing (2·10) with (2·4) and dividing by qV.

This differs from the modified differential Fourier equation (2·5) only by the presence of the weighting factor $w'f_r$ in each term of the various series. Comparison of (2·5) and (2·11) demonstrates the formal similarity between the equations of the modified differential Fourier method and the normal equations.

If all the atoms have the same or similar scattering factors, then by choosing $w' = 1/f_r$ the normal equations become identical with the modified differential Fourier equations; or conversely, retaining the proper w', the normal equations are identical with the Fourier equations for weighted electron densities ϱ^r. If the atoms have different f's, on choosing $w' = 1/f_r$ or using weighting factors $w'f_r$, the only identical corresponding equations are those involving derivatives evaluated at atom r or at atoms with the same or similar scattering factors as r. This last point is important theoretically, for it shows that despite their remarkable similarities the least-squares and modified Fourier methods are fundamentally distinct. However, it will appear from the discussion of the approximate forms of the equations for complete three-dimensional summation that, with appropriate weighting factors, coordinates found by both methods are approximately the same.

There is also a set of least-squares equations corresponding to (2·2) obtained from the complete multivariate Taylor expansions of $\partial R/\partial x_{ri}$, namely,

$$\sum w(F_o-F_c)\frac{\partial F_c}{\partial x_{ri}} + \sum_j\varepsilon_{rj}\sum w(F_o-F_c)\frac{\partial^2 F_c}{\partial x_{ri}^2} - \sum_{s,j}\varepsilon_{sj}\sum w\frac{\partial F_c}{\partial x_{ri}}\frac{\partial F_c}{\partial x_{sj}} = 0\,. \qquad (2{\cdot}12)$$

2·3. *Approximate equations*

We have seen how both the modified Fourier and least-squares methods lead to sets of simultaneous equations, (2·5) and (2·7), in the refinement parameters. We shall now show that it is often unnecessary to compute in detail all the terms of these equations, and that the set of equations in all the parameters often approximately reduces to sets of equations in one or a few parameters. For convienience we shall discuss the modified Fourier method; the corresponding discussion for least squares can be obtained by replacing ϱ's by ϱ^r's.

The problem is to determine which coefficients,

$$\frac{\partial}{\partial x_{sj}}\left(\frac{\partial\varrho_s}{\partial x_i}\right)_r = -\frac{1}{V}\frac{2\pi}{a_i}\sum_3 h_i\frac{\partial F_s}{\partial x_{sj}}\sin\theta_r\,, \qquad (2{\cdot}4)$$

of the ε_{sj}'s in (2·5) are large. As a first step towards this we reinterpret these coefficients; a reinterpretation which is itself of interest.

In this section we shall rigourously adopt the rule that x_{sj} denotes one of the independent parameters of the structure, and that, if t is one of the atoms related to s by symmetry, x_{tk} denotes the kth coordinate of atom t, and that differentiation of any function with respect to x_{tk} does not imply changes in the coordinates of any other atom, whether related to s by symmetry or not.

We have already remarked in § 2·1 that in (2·2), and thus also in (2·5), we could have treated the x_{sj}'s either as independent parameters or as atomic coordinates; hitherto we have adopted the former point of view, but if we now adopt the latter point of view, but adhere to the notation just defined, we can write (2·5) as

$$\left(\frac{\partial\varrho_o}{\partial x_i}\right)_r = \left(\frac{\partial\varrho_c}{\partial x_i}\right)_r + \sum_s\sum_t\sum_k\varepsilon_{tk}\frac{\partial}{\partial x_{tk}}\left(\frac{\partial\varrho_t}{\partial x_i}\right)_r, \qquad (2{\cdot}13)$$

where

$$\varrho_t = \frac{1}{V}\sum_3 f_t\cos(\theta-\theta_t)\,,$$

is the finite-series electron density due to atom t alone, and the summation over t includes all atoms related to s by symmetry, so that the triple summation over s, t and k includes all the coordinates of all the atoms in the unit cell.

Now

$$\frac{\partial}{\partial x_{tk}}\left(\frac{\partial\varrho_t}{\partial x_i}\right)_r = -\left(\frac{\partial^2\varrho_t}{\partial x_i\partial x_k}\right)_r; \qquad (2{\cdot}14)$$

substituting this in the second group of terms on the right-hand side of (2·13) gives an expression for the change of slope of ϱ_c at r, which is the same as we should have derived from a geometrical point of view, from which, regarding ϱ_c as the sum of the ϱ_t's of all the atoms in the unit cell, the change of slope of ϱ_c is equal to minus the sum of the displacements of all the atoms multiplied by the respective second derivatives of the atomic densities evaluated at r.

Further

$$\varepsilon_{tk} = \varepsilon_{sj}\frac{\partial x_{tk}}{\partial x_{sj}}\,; \qquad (2{\cdot}15)$$

where we remark that $\partial x_{tk}/\partial x_{sj} = 0$ for $j \neq k$ in a monoclinic space group, say, but $= \pm 1$ for a cubic space group.

Thus the coefficient (2·4) of ε_{si} in (2·5) may be

written
$$-\sum_t\sum_k\frac{\partial x_{tk}}{\partial x_{sj}}\left(\frac{\partial^2\varrho_t}{\partial x_i\partial x_k}\right)_r. \qquad (2\cdot16)$$

It is also possible to obtain this result directly from (2·4), thus checking that the alternative treatments of (2·2) are equivalent. For
$$\begin{aligned}F_s&=f_s\sum_t\cos\theta_t\\&=f_s\sum_t\cos\,(2\pi\sum_k h_kx_{tk}/a_k)\,.\end{aligned}$$

Hence
$$\frac{\partial F_s}{\partial x_{sj}}=-f_s\sum_t\sum_k 2\pi\frac{h_k}{a_k}\frac{\partial x_{tk}}{\partial x_{sj}}\sin\theta_t\,.$$

Substituting this in (2·4), we again reach (2·16) on noticing that
$$\begin{aligned}&\sum_t\frac{\partial x_{tk}}{\partial x_{sj}}\sin\theta_t\sin\theta_r\\&=\sum_t\tfrac{1}{2}\frac{\partial x_{tk}}{\partial x_{sj}}(\cos\,(\theta_t-\theta_r)-\cos\,(\theta_t+\theta_r)) \qquad (2\cdot17)\\&=\sum_t\frac{\partial x_{tk}}{\partial x_{sj}}\cos\,(\theta_t-\theta_r)\,,\end{aligned}$$
since the space group is centrosymmetric, and $\partial x_{tk}/\partial x_{sj}=-\partial(-x_{tk})/\partial x_{sj}$.

For simplicity supposing for the moment that $\partial x_{tk}/\partial x_{sj}=0$ for $j\neq k$, we may note that (2·16) is not equal to $-(\partial^2\varrho_s/\partial x_i\partial x_j)_r$, where $\varrho_s=\sum_t\varrho_t$, for this is equal to $-\sum_t(\partial^2\varrho_t/\partial x_i\partial x_j)_r$, the term $\partial x_{tj}/\partial x_{sj}$ which may be ±1 not appearing.

The problem of determining which of the coefficients (2·4) are important is now one of finding which of the terms $(\partial^2\varrho_t/\partial x_i\partial x_j)_r$ are large. These terms are second derivatives of the density of atom t evaluated at the position of atom r. They will be small unless the finite series densities of atoms t and r overlap. We shall discuss the approximate values of the coefficients in detail for the cases of complete three-dimensional summation within a large reciprocal sphere, and of the corresponding two-dimensional summation.

Consider first the three-dimensional case. By complete summation within a large reciprocal sphere we imply that the limiting reciprocal radius is such that the value at the minimum interatomic distance of the finite series representing the electron density of any atom is small in comparison with the value at its atomic position of the series representing any other atom, and that no reflexions are omitted within this reciprocal sphere. In these circumstances all the terms $(\partial^2\varrho_t/\partial x_i\partial x_j)_r$ are negligible for $t\neq r$, and consequently the coefficients of all the $\varepsilon_{sj}(s\neq r)$ in (2·5) are negligible. If ϱ_r is the finite series representing atom r alone, the non-negligible part of the coefficient of ε_{rj} in (2·5) is
$$-\sum_k\frac{\partial x_{rk}}{\partial x_{rj}}\left(\frac{\partial^2\varrho_r}{\partial x_i\partial x_k}\right)_r=-\left(\frac{\partial^2\varrho_r}{\partial x_i\partial x_j}\right)_r,$$
since for $j\neq k$ either $\partial x_{rk}/\partial x_{rj}=0$, or, if not, $(\partial^2\varrho_r/\partial x_i\partial x_k)_r=0$.

Similarly the coefficient of ε_{ri} in (2·5) is $-(\partial^2\varrho_r/\partial x_i^2)_r$.

Consequently, in this three-dimensional case the approximate form of (2·5) is
$$\left(\frac{\partial\varrho_o}{\partial x_i}\right)_r=\left(\frac{\partial\varrho_c}{\partial x_i}\right)_r-\sum_j\varepsilon_{rj}\left(\frac{\partial^2\varrho_r}{\partial x_i\partial x_j}\right)_r. \qquad (2\cdot18)$$

Thus the set of equations (2·5), simultaneous in all the parameters, approximately reduces to independent sets of equations, each set involving only the parameters of one atom. These sets correspond to the equations discussed in an earlier paper (Cruickshank, 1950).

As a series,
$$-\left(\frac{\partial^2\varrho_r}{\partial x_i\partial x_j}\right)_r=\frac{1}{V}\frac{4\pi^2}{a_ia_j}\sum_3 h_ih_jf_r\,, \qquad (2\cdot19)$$
where the summation is over all planes within the reciprocal sphere (and thus includes any planes which may have been systematically absent in the original space group).

It often happens, for example for orthorhombic cells or for monoclinic cells with β nearly 90°, that $(\partial^2\varrho_r/\partial x_i\partial x_j)_r$ is negligible for $i\neq j$. In this case (2·18) becomes
$$\left(\frac{\partial\varrho_o}{\partial x_i}\right)_r=\left(\frac{\partial\varrho_c}{\partial x_i}\right)_r-\varepsilon_{ri}\left(\frac{\partial^2\varrho_r}{\partial x_i^2}\right)_r, \qquad (2\cdot20)$$
so that each parameter is determined from a single equation.

In the case of complete two dimensional summation within a reciprocal circle the terms $(\partial^2\varrho_t/\partial x_i\partial x_j)_r$ may not be negligible either if atom t, being related to r by symmetry, coincides with r in projection, or if atom t (not necessarily related to r by symmetry) overlaps atom r in the projection. In the former case the coefficient of ε_{ri} will be a simple multiple of
$$-\left(\frac{\partial^2\varrho_r}{\partial x_i\partial x_j}\right)_r=-\frac{1}{A}\frac{4\pi^2}{a_ia_j}\sum_2 h_ih_jf_r\,.$$

In the latter case it is necessary to compute fully either
$$-\left(\frac{\partial^2\varrho_t}{\partial x_i\partial x_j}\right)_r=\frac{1}{A}\frac{4\pi^2}{a_ia_j}\sum_2 h_ih_jf_r\cos\,(\theta_t-\theta_r)\,,$$
or the proper coefficient of ε_{sj}.

If none of the atoms related to s by symmetry overlap atom r in the projection the coefficient of ε_{sj} in (2·5) may be neglected. Thus the two-dimensional form of the set of equations like (2·5) approximately reduces to a set in which the only important cross terms arise from overlapping peaks, and this set may in fact break up into a number of independent sets of equations.

2·4. *Connection with Booth's back-correction method*

In Booth's (1945, 1946) back-correction method, corrections are found from a calculated synthesis based on the maxima of the final observed synthesis, using the displacements of the calculated synthesis with reversed signs as corrections. In the present notation, coordinate corrections to atom r are determined from three equations of the type

$$\left(\frac{\partial \varrho_o}{\partial x_i}\right)_r = \left(\frac{\partial \varrho_c}{\partial x_i}\right)_r - \sum_j \varepsilon_{rj} \left(\frac{\partial^2 \varrho_c}{\partial x_i \partial x_j}\right)_r . \tag{2·21}$$

(We have included the term $(\partial \varrho_o/\partial x_i)_r$ on the left-hand side, though it is actually zero, to clarify the relation of Booth's method to (2·5); as written, (2·21) is a generalization of Booth's method for any set of trial coordinates.) The conditions for the equivalence of Booth's method and the modified differential Fourier method are that the coefficient of ε_{sj} $(s \neq r)$ in (2·5) should be zero, and that the coefficient of ε_{rj} in (2·5) can be written as in (2·21). The discussion of § 2·3 shows that these conditions are approximately fulfilled for complete three-dimensional summation within a large reciprocal sphere, since then for $t \neq r$ $(\partial^2 \varrho_t/\partial x_i \partial x_j)_r$ is negligible and so $(\partial^2 \varrho_c/\partial x_i \partial x_j)_r = (\partial^2 \varrho_r/\partial x_i \partial x_j)_r$. The correct refinement to atom r is also given in the two-dimensional case if no other atom overlaps r.

Unfortunately the condition of completeness is not always fulfilled in practice, for, although observations may be made for a spherical region of reciprocal space, many reflexions may be too weak to be recorded. These missing low-valued F's may make only a small difference to the value of the observed electron density at any point, but, though the peaks may be well resolved in the ordinary sense, it is no longer true that near atom r ϱ_c is nearly equal to ϱ_r, for in this latter series any omitted term is important.

If, despite $(\partial^2 \varrho_c/\partial x_i \partial x_j)_r = (\partial^2 \varrho_r/\partial x_i \partial x_j)_r$, none of the $(\partial^2 \varrho_t/\partial x_i \partial x_j)_r$ are large in comparison with $(\partial^2 \varrho_r/\partial x_i \partial x_j)_r$, then a first approximation to (2·5) still gives (2·18). In the series (2·19) terms corresponding to those accidentally unobserved must be omitted, but systematic absences must still be allowed for. To avoid including contributions corresponding to systematic absences outside the region of observation, this is most convieniently done by summing only for the planes actually observed but with appropriate multiples in the zones of systematic absences.

The above reasoning suggests that for the case of three-dimensional summation with accidental omissions the corrections given by Booth's method will be a little too small, but even augmented corrections will be not quite correct owing to the neglect of the cross terms of (2·5) in (2·18).

In the practical use of (2·5) it may be unnecessary to compute the series for $(\partial \varrho_o/\partial x_i)_r$ and $(\partial \varrho_c/\partial x_i)_r$, if difference $(\varrho_o - \varrho_c)$ maps (see e.g. Cochran, 1951) are being used, as $[\partial/\partial x_i(\varrho_o - \varrho_c)]_r$ may be interpolated from these. In part, the present paper is a contribution to the theory of difference maps. Also, if (2·21) is being used, it may suffice to use in place of the $(\partial^2 \varrho_c/\partial x_i \partial x_j)_r$, the $(\partial^2 \varrho_o/\partial x_i \partial x_j)_r$ which may be available by interpolation from the observed electron-density map.

3. Non-centrosymmetric space groups

3·1. *Equations of the modified Fourier method*

We must now allow for the variation of phase angles with changing coordinates. We shall keep to the convention that x_{sj} is one of the independent parameters, and that x_{tk} denotes a coordinate of an atom t related to s by symmetry. We shall use A and B to denote the real and imaginary parts of the structure factor, so that, in particular,

$$A_s = \sum_t f_s \cos \theta_t ; \quad B_s = \sum_t f_s \sin \theta_t . \tag{3·1}$$

α will denote the phase angle of F_c; $\alpha = \tan^{-1}(B/A)$. It will be convienient to state two results now:

$$\begin{aligned} \frac{\partial |F_c|}{\partial x_{sj}} &= \frac{\partial A_s}{\partial x_{sj}} \cos \alpha + \frac{\partial B_s}{\partial x_{sj}} \sin \alpha \\ &= -\sum_k \sum_t 2\pi \frac{h_k}{a_k} \frac{\partial x_{tk}}{\partial x_{sj}} f_s \sin (\theta_t - \alpha) ; \end{aligned} \tag{3·2}$$

$$\begin{aligned} \frac{\partial \alpha}{\partial x_{sj}} &= \frac{1}{|F_c|} \left(-\frac{\partial A_s}{\partial x_{sj}} \sin \alpha + \frac{\partial B_s}{\partial x_{sj}} \cos \alpha \right) \\ &= \sum_k \sum_t 2\pi \frac{h_k}{a_k} \frac{\partial x_{tk}}{\partial x_{sj}} \frac{f_s}{|F_c|} \cos (\theta_t - \alpha) . \end{aligned} \tag{3·3}$$

Corresponding to (2·2), the equation for small refinements is

$$\begin{aligned} &\left(\frac{\partial \varrho_o}{\partial x_i}\right)_r + \sum_j \varepsilon_{rj} \left(\frac{\partial^2 \varrho_o}{\partial x_j \partial x_i}\right)_r + \sum_{s,j} \varepsilon_{sj} \frac{\partial}{\partial x_{sj}} \left(\frac{\partial \varrho_o}{\partial x_i}\right)_r \\ &= \left(\frac{\partial \varrho_c}{\partial x_i}\right)_r + \sum_j \varepsilon_{rj} \left(\frac{\partial^2 \varrho_c}{\partial x_j \partial x_i}\right)_r + \sum_{s,j} \varepsilon_{sj} \frac{\partial}{\partial x_{sj}} \left(\frac{\partial \varrho_c}{\partial x_i}\right)_r . \end{aligned} \tag{3·4}$$

In this equation

$$\begin{aligned} \frac{\partial}{\partial x_{sj}} \left(\frac{\partial \varrho_o}{\partial x_i}\right)_r &= -\frac{1}{V} \frac{2\pi}{a_i} \sum_3 h_i |F_o| \frac{\partial}{\partial x_{sj}} \sin (\theta_r - \alpha) \\ &= \frac{1}{V} \frac{2\pi}{a_i} \sum_3 h_i |F_o| \cos (\theta_r - \alpha) \frac{\partial \alpha}{\partial x_{sj}} \end{aligned} \tag{3·5}$$

$$= \frac{1}{V} \sum_k \sum_t \frac{4\pi^2}{a_i a_k} \frac{\partial x_{tk}}{\partial x_{sj}} \sum_3 h_i h_k \frac{|F_o|}{|F_c|} f_s \cos (\theta_r - \alpha) \cos (\theta_t - \alpha) , \tag{3·6}$$

by (3·3).

Instead of writing

$$\begin{aligned} \frac{\partial}{\partial x_{sj}} \left(\frac{\partial \varrho_c}{\partial x_i}\right)_r = &- \frac{1}{V} \frac{2\pi}{a_i} \sum_3 h_i \frac{\partial A_s}{\partial x_{sj}} \sin \theta_r \\ &+ \frac{1}{V} \frac{2\pi}{a_i} \sum_3 h_i \frac{\partial B_s}{\partial x_{sj}} \cos \theta_r , \end{aligned} \tag{3·7}$$

it proves more useful to use the alternative expression

$$\frac{\partial}{\partial x_{sj}}\left(\frac{\partial \varrho_c}{\partial x_i}\right)_r = -\frac{1}{V}\frac{2\pi}{a_i}\sum_3 h_i \frac{\partial |F_c|}{\partial x_{sj}} \sin(\theta_r-\alpha)$$

$$+\frac{1}{V}\frac{2\pi}{a_i}\sum_3 h_i |F_c| \cos(\theta_r-\alpha)\frac{\partial \alpha}{\partial x_{sj}}, \qquad (3\cdot8)$$

where the second sum can be written in a form similar to (3·6).

If, as in (2·5), we form the equations to make the slopes of ϱ_o and ϱ_c equal at the trial positions, we simply omit the second group of terms on both sides of (3·4). Further, we may notice that for nearly correct positions the difference between (3·5) and the second part of (3·8) is small in comparison with the first part of (3·8). If we may neglect this difference, and omit the second groups of terms in (3·4), we have the equations

$$\left(\frac{\partial \varrho_o}{\partial x_i}\right)_r = \left(\frac{\partial \varrho_c}{\partial x_i}\right)_r - \sum_{s,j}\varepsilon_{sj}\frac{1}{V}\frac{2\pi}{a_i}\sum_3 h_i \frac{\partial |F_c|}{\partial x_{sj}}\sin(\theta_r-\alpha), \qquad (3\cdot9)$$

which we shall call the modified differential Fourier equations for non-centrosymmetric space groups.

3·2. *The normal equations of least squares*

We shall now consider the normal equations for the function

$$R = \Sigma w(|F_o|-|F_c|)^2 . \qquad (1\cdot3)$$

These are usually written

$$\sum_{s,j} c_{ri,\,sj}\varepsilon_{sj} = b_{ri}, \qquad (3\cdot10)$$

where

$$b_{ri} = \Sigma w(|F_o|-|F_c|)\frac{\partial |F_c|}{\partial x_{ri}},$$

and

$$c_{ri,\,sj} = \Sigma w \frac{\partial |F_c|}{\partial x_{ri}}\frac{\partial |F_c|}{\partial x_{sj}} .$$

By following through an argument similar to that used for centro-symmetric space groups, we find that (3·10) may be written

$$\left(\frac{\partial \varrho_o^r}{\partial x_i}\right)_r = \left(\frac{\partial \varrho_c^r}{\partial x_i}\right)_r - \sum_{s,j}\varepsilon_{sj}\frac{1}{V}\frac{2\pi}{a_i}\sum_3 w' f_r h_i \frac{\partial |F_c|}{\partial x_{sj}}\sin(\theta_r-\alpha), \qquad (3\cdot11)$$

which is the equation for the weighted electron density corresponding to (3·9).

If we consider the complete multivariate Taylor expansions of $\partial R/\partial x_{ri}$, as in (2·12), we add to (3·10) terms of the type

$$\varepsilon_{sj}\Sigma w(|F_o|-|F_c|)\frac{\partial^2 |F_c|}{\partial x_{sj}\partial x_{ri}} .$$

Expressed as functions of the weighted electron density these terms added to (3·11) give the equation corresponding to (3·4). Thus we see that the same relations which hold between the least-squares and modified Fourier methods for centrosymmetric space groups hold also for non-centrosymmetric space groups.

3·3. *Approximate equations*

Using (3·2), the coefficient of ε_{sj} in (3·9) may be written

$$\frac{1}{V}\frac{2\pi}{a_i}\sum_t\sum_k \frac{2\pi}{a_k}\frac{\partial x_{tk}}{\partial x_{sj}}\sum_3 h_i h_k f_s \sin(\theta_t-\alpha)\sin(\theta_r-\alpha) . \qquad (3\cdot12)$$

Now

$$\sum_t \frac{\partial x_{tk}}{\partial x_{sj}}\sin(\theta_t-\alpha)\sin(\theta_r-\alpha) \qquad (3\cdot13)$$

$$= \tfrac{1}{2}\sum_t \frac{\partial x_{tk}}{\partial x_{sj}}\cos(\theta_t-\theta_r) - \tfrac{1}{2}\sum_t \frac{\partial x_{tk}}{\partial x_{sj}}\cos(\theta_t+\theta_r-2\alpha) .$$

Thus the contribution of the first group of terms in (3·13) to the coefficient of ε_{sj} in (3·9) is

$$-\tfrac{1}{2}\sum_t\sum_k \frac{\partial x_{tk}}{\partial x_{sj}}\left(\frac{\partial^2 \varrho_t}{\partial x_i \partial x_k}\right)_r, \qquad (3\cdot14)$$

which is half the coefficient (2·16) of ε_{sj} in the corresponding equation (2·5) for centrosymmetric space groups, and so the discussion of the approximate value of (2·16) gives the approximate value of (3·14).

The approximate contribution of the second group of terms in (3·13) is more difficult to assess. We shall consider several particular cases:

First, suppose that we are dealing with a two-dimensional projection which is centrosymmetric. Then $2\alpha = 0$ or 2π, and so, by the same argument as followed (2·17), this second group of terms makes another contribution to the coefficient of ε_{sj} equal to (3·14), giving the same total as we derived in the centrosymmetric theory.

In the case of a three-dimensional summation for the triclinic space group with no centre of symmetry, and for a structure not dominated by any heavy atom, we may expect that any of the sums

$$\sum_3 h_i h_k f_s \cos(\theta_t+\theta_r-2\alpha) \qquad (3\cdot15)$$

will be small since some cosine terms are likely to be positive and some negative.

For a three-dimensional summation for a space group which is centrosymmetric in certain projections we may again expect that, excluding the summations for these projections, the sums (3·15) over the general planes will be small. Accordingly, for example, in the space group $P2_1$ for complete three-dimensional summation we may expect that the coefficient of ε_{ri} in (3·9) will be approximately

$$\frac{1}{2}\frac{1}{V}\frac{4\pi^2}{a_i^2}\sum_3 n h_i^2 f_r , \qquad (3\cdot16)$$

where $m = 1$ for the general hkl reflexions, and $m = 2$ for $h0l$ (and $m = 2$ for the $0k0$ planes observed if the systematic absences are excluded from the summation).

Thus we see that for no symmetry the coordinate refinements for non-centrosymmetric space groups are twice those for centrosymmetric space groups, while if the structure is centered in certain projections the refinements are of intermediate value. The above appears to be the theoretical basis of the 'n shift rule' introduced by Shoemaker, Donohue, Schomaker & Corey (1950).

4. The Patterson density

4·1. *Equations of the modified Patterson method*

In § 1 we introduced as a criterion for the determination of atomic coordinates the condition that the slopes of the observed and calculated electron densities should be equal at the atomic positions. We can introduce a similar criterion for determining atomic coordinates from the Patterson density: namely, that the slopes of the observed and calculated Patterson densities should be equal at the interatomic vectors.

If u and r denote atoms, we may express this symbolically as

$$\left(\frac{\partial P_o}{\partial x_i}\right)_{u-r} = \left(\frac{\partial P_c}{\partial x_i}\right)_{u-r}, \tag{4·1}$$

where P_o is the observed Patterson density

$$P_o = \frac{1}{V} \sum_3 |F_o|^2 \cos\theta ,$$

and P_c is the calculated Patterson density

$$P_c = \frac{1}{V} \sum_3 |F_c|^2 \cos\theta .$$

As in the modified Fourier method, we can derive equations for small parameter refinements. Corresponding to (2·5) we may derive the equation

$$\left(\frac{\partial P_o}{\partial x_i}\right)_{u-r} = \left(\frac{\partial P_c}{\partial x_i}\right)_{u-r} + \sum_{s,j} \varepsilon_{sj} \frac{\partial}{\partial x_{sj}} \left(\frac{\partial P_c}{\partial x_i}\right)_{u-r}, \tag{4·2}$$

where

$$\frac{\partial}{\partial x_{sj}} \left(\frac{\partial P_c}{\partial x_i}\right)_{u-r} = -\frac{1}{V} \frac{2\pi}{a_i} \sum_3 2h_i |F_c| \frac{\partial |F_c|}{\partial x_{sj}} \sin(\theta_u - \theta_r) . \tag{4·3}$$

Now there are more criteria of the type (4·1) than there are independent parameters, and accordingly the complete set of equations of the type (4·2) for all atoms u and r will be inconsistent. One way of getting only as many equations as there are parameters is to take the equations of type (4·2) for fixed r and sum them over all atoms u in the unit cell.

4·2. *The normal equations of least squares*

We now consider the normal equations for the function

$$R_2 = \Sigma w''(|F_o|^2 - |F_c|^2)^2 , \tag{1·5}$$

(for correct weighting $w'' = w/|F_o|^2$).

The normal equations corresponding to (2·7) are

$$\Sigma w''(|F_o|^2 - |F_c|^2)|F_c| \frac{\partial |F_c|}{\partial x_{ri}} = \sum_{s,j} \varepsilon_{sj} \Sigma 2w''|F_c|^2 \frac{\partial |F_c|}{\partial x_{sj}} \frac{\partial |F_c|}{\partial x_{ri}} . \tag{4·4}$$

The relation between this equation and that derived from (4·2) by summing over u can be seen as follows. Introduce a weighted Patterson density

$$P^{ur} = \frac{1}{V} \sum_3 w''' f_u f_r F^2 \cos\theta , \tag{4·5}$$

where $w'''p = w''$, p being the number of planes related by symmetry. Corresponding to (4·2) we may write

$$\left(\frac{\partial P_o^{ur}}{\partial x_i}\right)_{u-r} = \left(\frac{\partial P_c^{ur}}{\partial x_i}\right)_{u-r} + \sum_{s,j} \varepsilon_{sj} \frac{\partial}{\partial x_{sj}} \left(\frac{\partial P_c^{ur}}{\partial x_i}\right)_{u-r} . \tag{4·6}$$

If we sum the equations of this type for given r over all atoms u in the unit cell, we get the equation

$$\begin{aligned} &\frac{1}{V} \Sigma w'''(|F_o|^2 - |F_c|^2)|F_c| \frac{2\pi}{a_i} h_i f_r \sin(\theta_r - \alpha) \\ &= -\frac{1}{V} \sum_{s,j} \varepsilon_{sj} \sum_3 2w'''|F_c|^2 \frac{\partial |F_c|}{\partial x_{sj}} \frac{2\pi}{a_i} h_i f_r \sin(\theta_r - \alpha) . \end{aligned} \tag{4·7}$$

This equation is equivalent to (4·4) by the same argument as showed (2·11) equivalent to (2·7). Thus, from the weighted Patterson densities we have derived an equation for small coordinate refinements which is the same as the least-squares normal equation for the function R_2.

If all the atoms have the same scattering factor, then by choosing $w''' = 1/f^2$ the normal equations are identical with the corresponding unweighted Patterson refinement equations. If the atoms have different f's then there is no choice of w''' which makes any of the corresponding equations identical.

An important question is the comparison between the coordinates determined by least squares from R, (1·3), and R_2, (1·5).

The conditions $\partial R/\partial x_{ri} = 0$ are

$$\Sigma w(|F_o| - |F|_c) \frac{\partial |F_c|}{\partial x_{ri}} = 0 , \tag{4·8}$$

and the conditions $\partial R_2/\partial x_{ri} = 0$ are

$$\Sigma w(|F_o|^2 - |F_c|^2)|F_c| \frac{\partial |F_c|}{\partial x_{ri}} = 0 . \tag{4·9}$$

If we choose $w'' = w/|F_o|^2$, (4·9) becomes

$$\Sigma w \left((F_o| \frac{|F_c|}{|F_o|} - |F_c| \frac{|F_c|^2}{|F_o|^2} \right) \frac{\partial |F_c|}{\partial x_{ri}} = 0 . \tag{4·10}$$

Thus different coordinates will be found by both methods, though, since $|F_c|/|F_o|$ is nearly unity for small errors ΔF, (4·10) confirms the expectation that the two sets of coordinates are approximately the same.

4·3. *Approximate equations*

Comparison of (4·7) with (3·9) shows that in the coefficient for ε_{sj} each term of the series in (4·7) is $w'''|F_c|^2 f_r$ times the corresponding term in (3·9). Accordingly, similar trigonometric manipulation to that used in § 3·3 is applicable to the coefficient of ε_{sj} in (4·7).

Corresponding to (3·14), we find that the first part of the coefficient of ε_{sj} in (4·7) is equal to

$$-\tfrac{1}{2}\sum_{t}\sum_{k} 2\,\frac{\partial x_{tk}}{\partial x_{sj}}\left(\frac{\partial^2 P_c^{rs}}{\partial x_i \partial x_k}\right)_{t-r}. \qquad (4·11)$$

The terms $(\partial^2 P_c^{rs}/\partial x_i \partial x_k)_{t-r}$ are second derivatives of a weighted Patterson density evaluated at the interatomic vector between t and r. In comparison with the term for $t = r$, which gives a second derivative of the origin peak, the terms for $t \neq r$ will be small, unless we are considering a projection in which t either overlaps or coincides with r.

As in § 3·3, if the structure is centrosymmetric the terms corresponding to the second group in (3·13) give a further contribution to the coefficient of ε_{sj} equal to (4·11).

Thus the theory of the approximation of (4·7) is rather similar to the theory of the approximation of (3·9) and (2·5), so that in the approximate form of the normal equations for R_2 cross terms only arise in two-dimensional problems where the atoms overlap or coincide.

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Desordre Unidimensionnel dans SiC et son Influence sur les Intensites Diffractées des Rayons X

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(*Reçu le* 18 *décembre* 1951)

The theory is developed of the X-ray scattering by SiC crystals of the usual 4-, 6- and 15-layer types, which show order in two translation directions but disorder in the third direction. A '4-layer influence' for the 4- and 6-layer types, and a '6-layer influence' for the 15-layer type is postulated. Furthermore, it is put forward that four layers can never be arranged in a hexagonal close-packed way, and five layers never in a cubic way. The description of the disorder then needs one parameter α or two parameters α and β. The intensity of diffraction is expressed in terms of two quantities x_n and C_n, which themselves depend upon α (or α and β), where α (α and β) is (are) the probability(s) that a fifth (seventh) layer continues a cubic arrangement of the 4 (6) preceding layers. The line widths and displacements of the positions of certain reflexion maxima depend on the degree of order. Numerical data and comparision with experimental results will be communicated later.

1. Introduction

Jagodzinski & Laves (1948) ont introduit le terme 'ordre défectueux unidimensionnel' (*eindimensionale Fehlordnung*) pour les cristaux qui présentent un ordre parfait dans deux directions de translations, mais un désordre dans la troisième. Les travaux de Landau (1937) et Lifschitz (1937, 1939) nous ont montré comment il fallait aborder le problème du calcul de l'intensité des rayons X diffractés par de tels cristaux. Hendricks & Teller (1942) et Wilson (1942) ont calculé quelques cas spéciaux où il n'y a pas d'action réciproque entre les diverses couches. Ces auteurs se sont occupés également des cristaux hexagonaux et cubiques, qui présentent des irrégularités dans la succession des couches dans le sens de l'empilement compact. Ils ont postulé une influence des deux dernières couches, c'est-à-dire chaque nouvelle couche est conditionnée par les deux précédentes. On dit alors, en employant la notation de Jagodzinski (1949*a*, *b*, *c*), que le rayon d'action des forces ordonnantes est $s = 2$. Ce dernier a étendu la méthode de Wilson et a résolu ainsi le problème pour un empilement compact où l'on postulerait $s = 3$. En même temps il attira l'attention sur le fait que cette méthode pourrait encore être étendue aux cas où s aurait une valeur supérieure; mais qu'on se heurterait alors à de graves difficultés d'ordre mathématique.

Nous présenterons la solution pour un cas spécial de $s = 4$, applicable aux cristaux de SiC avec une périodicité 4 et 6, et un cas spécial de $s = 6$, ap-