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Weighting of the Least-Squares and Steepest-Descents Methods in the Initial Stages of the Crystal-Structure Determination

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The behaviour of the methods of steepest descents and least squares in the initial stages of the crystal-structure determination, when the differences between the assumed and the correct positions of the atoms are large, depends on the choice of the weighting function. Various simple laws are assumed for the weights, and the 'efficiency of convergence' is calculated for the case of known signs of the observed F's; only the power law is found to be suitable. It is shown that only for weighting which corresponds to a large 'artificial temperature factor' is there a unique solution for large displacements; the overlapping of atomic peaks is also discussed in detail. Analysis of these two effects leads to the determination of the optimum value for the exponent in the power law. Curves are drawn from which the corrections to be applied to the calculated displacements can be obtained for one-, two-, and three-dimensional summations.

Introduction

The methods of least squares and steepest descents, when applied to the refinement of crystal structures, converge rapidly only when the assumed structure is fairly near the correct one. When the differences between the assumed and the correct positions of the atoms are large, the application becomes increasingly difficult, especially in a structure with many atoms.

Cochran (1948*a*) showed that the steepest-descents and any similar method ceases to converge when the corresponding Patterson peaks of the assumed and the true structure no longer overlap. This difficulty can be overcome by adjusting an artificial converging-factor, which spreads the peaks out so that they do overlap; the more effectively they overlap the better the convergence will be. However, a limit to the differences between the assumed and the correct atomic positions is imposed by the presence of the neighbouring atoms. The assumed atomic position will in general refine towards the nearest correct position; we can, therefore, take the upper limit of the errors in the atomic positions as being one-half of the mean interatomic distance in the structure (or projection) considered, i.e. 0·5–1·0 Å. Within this limit, the errors in the *fractional coordinates* can be considered small ($< 0{\cdot}1$ for a cell edge of 10 Å), whereas the total error in $2\pi Hx/a$, for instance, can be quite large if H is large. The convergence of the refinement in this case is of interest in the crystal-structure problem, and will be discussed below. Two conflicting requirements have to be considered: (*a*) large overlap of pairs of actual and assumed peaks improves the convergence, and (*b*) this also causes increased overlap of different atomic peaks, thus making the solutions indefinite.

In order to apply successfully the least-squares and steepest-descents methods where they are most needed, i.e. in the initial stages of the determination of complex crystal structures, it is necessary to build a detailed theory of weighting and convergence covering all aspects of the problem. This paper is limited to a discussion of the relations between the efficiency of convergence and the method of weighting for centric structures, assuming that the signs of the structure factors are known and the experimental errors negligible. The results must therefore be regarded as being of restricted validity and as one aspect of the much wider problem, which it is hoped to treat in further papers. It is, however, pertinent to remark that, as far as can be seen, the over-all efficiency of convergence in the general case can be expressed as a product of individual efficiencies (due to various causes), each of which is substantially independent of the others. Thus the present results, as far as they go, are useful in the general problem.

1. Harmonic method of analysis

Qurashi (1949) has shown that the optimum rate of convergence of successive approximations by steepest descents to the final structure is obtained when the n-dimensional R-contours are equi-axial; a con-

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sideration of the necessary conditions gives for the approximate corrections

$$\varepsilon(x_j) = \left(\sum_{hkl} W^2(\varphi_o-\varphi_c)\frac{\partial\varphi_c}{\partial x_j}\right)\Big/\left(\sum_{hkl} W^2\left(\frac{\partial\varphi_c}{\partial x_j}\right)^2\right), \quad (1)$$

where φ is a suitable function of the atomic parameters, x_j. The case of $\varphi \equiv F$ is important, and all other practical cases reduce to this with a suitable choice of weight, W. As the above formula follows from the least-squares solution by neglecting the small cross-product terms, the results proved below for $\varepsilon(x_j)$ will in general hold for the least-squares solution. For discussing the convergence, it is useful to analyze the discrepancies, (F_o-F_c), for harmonic components; in this way, we can obtain exact expressions for the errors in the atomic coordinates, and compare them with the approximate corrections given by equation (1).

For a centro-symmetrical structure containing n atoms per half unit cell, we have:

$$F_{hkl} = 2\sum_{j=1}^{n} f_j \cos v_j = 2f\sum_j N_j \cos v_j ,$$

where

$$v_j = 2\pi(hx_j/a+ky_j/b+lz_j/c) , \quad f = \sum_j f_j/n, \quad N_j = f_j/f .$$

To a good approximation, the ratio $f_j/f = N_j$ is independent of h, k, l in the ranges of $\sin\theta/\lambda$ usually encountered (c.f. Harker & Kasper, 1948). If the values of the parameters assumed for an approximate structure are $x_{jc}, y_{jc}, z_{jc}, \ldots$; $N_{jc}, \ldots$, and the actual values (in the correct structure) are $x_{jo}, y_{jo}, z_{jo}, \ldots$; $N_{jo}, \ldots$, we can write:

$$v_{jo} = v_{jc}+\delta v_j; \text{ and } N_{jo} = N_{jc}+\delta N_j ,$$

where

$$\delta v_j = 2\pi(h\delta x_j/a+k\delta y_j/b+l\delta z_j/c) .$$

We now obtain:

$$F_c = 2f\sum_j N_{jc}\cos v_{jc}$$

and

$$F_o = 2f\sum_j N_{jo}\cos v_{jo}$$
$$= 2f\sum_j (N_{jc}+\delta N_j)(\cos v_{jc}\cos\delta v_j-\sin v_{jc}\sin\delta v_j) ,$$

whence

$$(F_o-F_c) = 2f\sum_j N_{jc}\{\cos v_{jc}(\cos\delta v_j-1)-\sin v_{jc}\sin\delta v_j\}$$
$$+2f\sum_j \delta N_j\{\cos v_{jc}\cos\delta v_j-\sin v_{jc}\sin\delta v_j\} . \quad (2)$$

If we apply to this expression the principles of harmonic analysis, the procedure is to multiply both sides of (2) by $\cos v_{ic}$ or $\sin v_{ic}$, weighted by a suitably chosen weight, and to sum over a sufficiently large number of terms.

The multiplication by a cosine leads to expressions useful for refinement of the scattering factors, multiplication by a sine to refinement of atomic coordinates.

It is to be noted that:

$$\partial F_c/\partial x_j = -2f.2\pi(h/a)N_{jc}\sin v_{jc} ,$$
$$\partial F_c/\partial N_{jc} = 2f\cos v_{jc} .$$

It follows that multiplication of both sides of (3) by the derivatives of F_c is equivalent to the multiplication by sine or cosine.

In order to lessen the typographical effort we shall use the following symbols:

$$WF_c = \varphi, \quad W(F_o-F_c) = \Delta\varphi ,$$
$$\sin v_{jc} = S_j, \quad \cos v_{jc} = C_j, \quad N_{jc} = N_j ,$$
$$\sin\delta v_j = s_j, \quad \cos\delta v_j = c_j, \quad Wf = w ,$$
$$\sum_{hkl} = \sum_3 .$$

We have from (1),

$$\varepsilon(x_j) = \frac{\sum_3 \Delta\varphi\frac{\partial\varphi}{\partial x_j}}{\sum_3\left(\frac{\partial\varphi}{\partial x_j}\right)^2} . \quad (3)$$

Also, we can write (2) as

$$\Delta\varphi = 2w\sum_j [N_j\{C_j(c_j-1)-S_js_j\}+\delta N_j\{C_jc_j-S_js_j\}] . \quad (3a)$$

Multiplying both sides of this expression by:

$$\partial\varphi/\partial x_i = -4\pi w(h/a)N_iS_i$$

we obtain:

$$\Delta\varphi\,\partial\varphi/\partial x_i = -8\pi w^2(h/a)N_i\sum_j [N_j\{S_iC_j(c_j-1)-S_iS_js_j\}$$
$$+\delta N_j\{S_iC_jc_j-S_iS_js_j\}] . \quad (4a)$$

Further we have

$$(\partial\varphi/\partial x_i)^2 = 16\pi^2w^2(h^2/a^2)N_i^2S_i^2 . \quad (4b)$$

It should be noted that no approximations were used in deriving equation (4a); it represents an exact equation,* which can, in principle, be solved for s_i and c_i, and therefore for the unknowns $\delta x_i, \delta y_i, \delta z_i, \delta N_i$. We can effect a very considerable simplification by summing these expressions over hkl, if the summation is over a spherical annulus in reciprocal space and the unit cell is nearly orthogonal (cf. Cruickshank, 1950). Remembering that, when the number of terms is large compared with the number of unknowns, and there is not much overlapping of the atomic peaks,

$$\overline{S_iC_j} = \overline{S_iS_j} = \overline{C_iC_j} = 0 \quad \text{for} \quad i \neq j ,$$
$$\overline{S_iC_i} = 0, \qquad \overline{S_iS_i} = \overline{C_iC_i} = \tfrac{1}{2} ,$$

we have

$$\left.\begin{aligned}\sum_3 \Delta\varphi\,\partial\varphi/\partial x_i &= 4\pi\sum_3 w^2(h/a)N_i^2s_i ,\\ \sum_3(\partial\varphi/\partial x_i)^2 &= 8\pi^2\sum_3 w^2(h^2/a^2)N_i^2 .\end{aligned}\right\} \quad (5)$$

* On multiplication by $\partial\varphi/\partial N_i$ expressions are obtained for δN_i.

From (5) and (3), we thus obtain

$$\varepsilon(x_i) = \frac{\sum_3 w^2(h/a)s_i}{2\pi \sum_3 w^2h^2/a^2} = \frac{2\pi\delta x_i \sum_3 w^2(h/a)\delta x_i s_i}{4\pi^2 \sum_3 w^2[(h/a)\delta x_i]^2}, \quad (6)$$

with two similar expressions for $\varepsilon(y_i)$ and $\varepsilon(z_i)$.

These expressions represent the correction-vector ε in three-dimensional space and its relation to the atomic displacement vector, defined by its three components δx_i, δy_i, δz_i. In practice, the latter is unknown and it need not even be parallel to the vector ε. The above equations are therefore valuable for determining the atomic positions of an approximate structure when the structure is so far from the correct one that the linear approximation of the steepest-descents formula does not hold. The general displacement can be simplified by suitable transformation of co-ordinates into a displacement along the x axis only, without loss of generality of the resulting conclusions. We have then in the new co-ordinates system $\delta x_i \neq 0$, $\delta y_i = 0$, $\delta z_i = 0$, and we can write

$$\varepsilon(x_i) = \frac{\sum_3 w^2(h/a) \sin 2\pi(h/a)\delta x_i}{2\pi \sum_3 w^2h^2/a^2},$$

$$\varepsilon(y_i) = \frac{\sum_3 w^2(k/b) \sin 2\pi(h/a)\delta x_i}{2\pi \sum_3 w^2k^2/b^2},$$

$$\varepsilon(z_i) = \frac{\sum_3 w^2(l/c) \sin 2\pi(h/a)\delta x_i}{2\pi \sum_3 w^2l^2/c^2}.$$

From these equations it can be seen that the two vectors are parallel when the summations are carried out over a region of reciprocal space symmetrical about the origin. When this condition is fulfilled, in the expressions for $\varepsilon(y_i)$ and $\varepsilon(z_i)$ there will be terms which cancel in pairs, so that

$$\varepsilon(y_i) = 0, \quad \varepsilon(z_i) = 0,$$

and the two vectors are parallel, differing only in their magnitudes. The ratio of these two vectors will be designated by η; it represents the 'efficiency' of the modified steepest-descents formula (1) under the particular conditions.* In the following part of the paper an attempt will be made to determine the behaviour of η. We have, in the transformed system,

$$\eta = \varepsilon(x_i)/\delta x_i = \frac{2\pi \sum_3 w^2(h/a)\delta x_i \sin 2\pi(h/a)\delta x_i}{4\pi^2 \sum_3 w^2(h^2/a^2)\delta x_i^2}. \quad (7)$$

In this expression, the only function that contains k and l is the weight w. We can therefore sum over k and l first, and write

$$\sum_{kl} w^2 = \psi.$$

Writing

$$2\pi(h/a)\delta x_i = u,$$

we obtain

$$\eta = \frac{\sum_h \psi u \sin u}{\sum_h \psi u^2}.$$

If the summation proceeds by sufficiently small steps, it can be replaced with sufficient approximation by integration (e.g. with $\delta x_i/a = 0{\cdot}1$, the error in η is $\sim 0{\cdot}01$), and we can therefore write:

$$\eta^* = 2\int_{+u_0}^{+U} \psi u \sin u\, du \Big/ 2\int_{+u_0}^{+U} \psi u^2 du.$$

The values of η can be obtained as a series if we substitute for the sine its development:

$$\sin u = u - \frac{1}{3!}u^3 + \frac{1}{5!}u^5 - \ldots.$$

Then

$$\eta = 1 - \frac{1}{3!}G_3 + \frac{1}{5!}G_5 - \ldots,$$

where

$$G_p = \int \psi u^{p+1} du \Big/ \int \psi u^2 du.$$

The solution depends on the particular value of the weighting function and on the boundaries chosen. In the following we shall discuss three typical forms of weighting function, namely:

$$(1)\ \psi = d^n, \quad (2)\ \psi = \exp(-2\sigma/d),$$
$$(3)\ \psi = \exp(-\sigma^2/d^2),$$

where $d \equiv d_{hkl}$, $\sigma \equiv$ constant.

2. The one-dimensional case

The problem becomes particularly simple in the one dimension as $\psi = w^2$. A wide variety of weighting functions might be preferred for one reason or another. We first assume that the weights obey a power law $w^2 = h^{-n}$, which is logical since the errors $(|F_o - F_c|/f)$ vary roughly as h; another reason for selecting this function is its simplicity. We have then $\psi \sim u^{-n}$ and therefore

$$G_p = \frac{\int u^{p-n+1} du}{\int u^{2-n} du} = \frac{3-n}{p-n+2} U^{p-1} \quad \text{for} \quad n < 3,$$

* η is seen to be the efficiency of the linear approximation in the practical least-squares method, and in a sense measures its difference from the Fourier-synthesis method.

* U corresponds to the highest index used in the summation, and u_0 to the lowest index. When the integrals are rapidly convergent at the lower limit, u_0 can be replaced by zero without appreciable error in η.

and the efficiency

$$\eta_1(n) = 1-\frac{1}{3!}\frac{3-n}{5-n}U^2+\frac{1}{5!}\frac{3-n}{7-n}U^4-\dots ,$$

where the upper limits of integration are given by $U \simeq 2\pi(H/a)\delta x_i$, where H is the highest Miller index occurring in the summation.

In some cases, the series can be expressed in terms of trigonometric or other functions. In one-dimension and for n a whole number, we have (putting $u_0 = 0$),

$$\eta_1(0) \simeq \frac{3}{U^3}(\sin U - U\cos U) \quad \text{for} \quad n = 0,$$

$$\eta_1(1) \simeq \frac{2}{U^2}(1-\cos U) \quad \text{for} \quad n = 1,$$

$$\eta_1(2) \simeq \frac{\mathrm{Si}(U)}{U} \quad \text{for} \quad n = 2,$$

where $\mathrm{Si}(U)$ is the sine integral $\int_0^U \frac{\sin u}{u}\,du$, which is easily obtained numerically from the tables. It should be noted that for $n \geqq 3$, in order to avoid singularity at $u = 0$, the approximate $\int_0^U$ is to be replaced by the exact $\int_{u_0}^U$, where the lower limit, $u_0 \simeq 2\pi\frac{h_0-\frac{1}{2}}{a}\delta x_i$,* depends on the lowest index h_0 used in the summation. Writing

$$\Phi = u_0/U \simeq (h_0-\tfrac{1}{2})/H ,$$

(where h_0 and H are the minimum and the maximum index, respectively) we have

$$G_3 = \frac{\Phi^2-1}{2\log\Phi}U^2 \quad \text{for} \quad n = 3,$$

$$G_3 = \frac{2\log\Phi}{1-1/\Phi^2}U^2 \quad \text{for} \quad n = 5 \quad \text{and}$$

$$G_3 = \frac{(3-n)\,1-\Phi^{5-n}}{(5-n)\,1-\Phi^{3-n}}U^2 \quad \text{for all other } n .$$

Similar expressions are obtained for the higher coefficients of the expansion. In order to judge the effect of Φ on η, the coefficient G_3/U^2 is plotted in Fig. 1 as a function of n for $\Phi \to +0$ and for $\Phi = 1/20$, the latter value being likely to occur in practice ($h_0 = 1$, $H \simeq 10$).

It is to be seen that for $n < 3$, the influence of Φ on G_3 is small. For $n \geqq 3$, $G_3 \to 0$ and therefore $\eta \to 1$ as $\Phi \to +0$; but by making n too large, only the low-index reflexions would remain effective, and our assumption that there is a sufficient number of terms compared with the number of unknown parameters would be violated. The case of large n is equivalent to the use of a large artificial temperature factor,

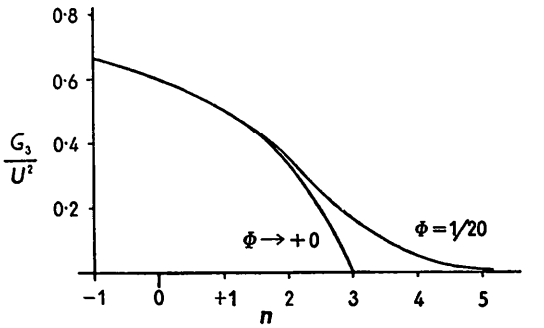

Fig. 1. Curves showing the influence of $\Phi \simeq (h_0-\frac{1}{2})/H$ on the coefficient of U^2 in the series expansion for η_1.

which would also spread the atomic peaks, and therefore increase the overlapping (cf. § 3 below).

For $n = 3$, we obtain

$$\eta_1(3) = -\frac{1}{\log\Phi}\left\{\frac{\sin u_0}{u_0}-\frac{\sin U}{U}+\mathrm{Ci}(U)-\mathrm{Ci}(u_0)\right\},$$

where

$$\mathrm{Ci}(x) = \int_\infty^x \frac{\cos u}{u}\,du .$$

For small u_0, $\mathrm{Ci}(u_0) = \log u_0+\gamma$, where $\gamma = 0{\cdot}5772$ is Euler's constant, so that

$$\eta_1(3) \fallingdotseq 1-\frac{1}{\log\Phi}\left\{1-\frac{\sin U}{U}+\mathrm{Ci}(U)-\log U-\gamma\right\}$$
$$= 1-1/(\log\Phi)\times f(U) .$$

The curves for η against U are plotted in Fig. 2 for

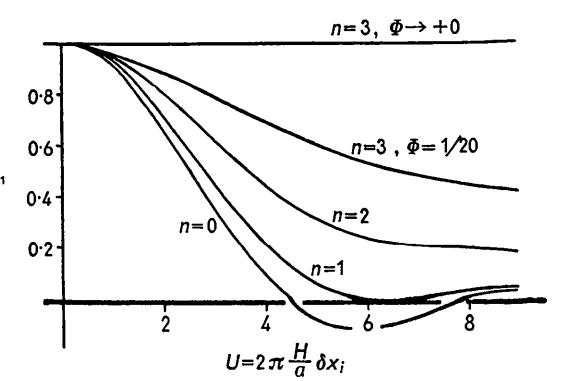

Fig. 2. Curves for the one-dimensional efficiency of convergence, η_1, as a function of $U = 2\pi(H/a)\delta x$.

integral values of n from 0 to 3. The exact shape of the curves, especially for $n < 3$ is only slightly dependent on the value of Φ; those in the figure have therefore been calculated with $\Phi = 0$, except for $n = 3$, when $\Phi = 1/20$ was assumed.

* For exact equivalence of the summations and integrals,

$$u_0 \simeq 2\pi\frac{\delta x_i}{a}\left(h_0-\tfrac{1}{2}+\tfrac{1}{12}\frac{n-2}{2h_0-1}\right), \quad U \simeq 2\pi\frac{H+\frac{1}{2}}{a}\delta x_i .$$

An important result of the presence of the lower limit, u_0, in the integrals deserves notice: in all cases, when U is sufficiently large, η ultimately becomes zero and then oscillates about zero with decreasing amplitude. If by R_1 we denote that value of $u_0 = U\Phi$ for which η first becomes zero, then R_1 gives the maximum radius of convergence of the steepest-descents (and least-squares) formula; approximate expressions for R_1 are given below for a one-dimensional summation with various values of n. (The results in two and three dimensions are similar if n is replaced by $n-1$ and $n-2$ respectively.)

n	R_1
0	$4{\cdot}5\Phi(1-1{\cdot}5\Phi^3)$
1	$2\pi\Phi(1-\Phi)$
2	$1{\cdot}9_3\pm 2\Phi$
3	$2{\cdot}1_7\pm 1{\cdot}5\Phi^2$
$\ldots\infty$	$\ldots\pi$

It is apparent that for $n \leqq 1$, $R_1 \propto \Phi$, while for $n \geqq 2$, R_1 is approximately independent of Φ, and increases with increasing n to the limit π, which is set by the condition that $\sin u_0$ must not be negative. With $n = 3$, R_1 is about 70% of the theoretical limit; further increase in n will increase R_1 very slowly. Much the same values are obtained for R_1 when the original summations over hkl are considered instead of the integrals, which approximate to them.

It should be remembered that U is unknown at the beginning of the calculation, and it is necessary to rewrite the efficiency formulae in terms of $\varepsilon(x_i)$ or better in terms of $U_c = 2\pi(H/a)\varepsilon(x_i)$; they are shown graphically in Fig. 3. It is apparent that all cases with $n \leqq 2$ are unsatisfactory; with $n = 2$, the correct direction of shift is obtained for all practical U, but multiple solutions occur in certain ranges of U_c. For a unique solution, a satisfactory weighting-function should have $n \geqq 3$ (cf. curve for $n = 3$).

3. Overlapping atomic peaks in projection

As some overlapping usually occurs in one-, and two-dimensional projections, it is important to consider

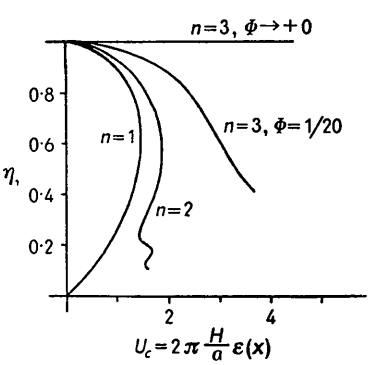

Fig. 3. Curves for the efficiency of convergence, η_1, plotted against the quantity $2\pi(H/a)\varepsilon(x)$, $\varepsilon(x)$ being obtained from the modified steepest-descents formula (1). The multiplicity of solutions for $n < 3$ is evident.

the appropriate modifications to formula (1) and the η-curves. Returning to the derivation of equation (6) from the exact equation (4a), it is apparent that when two atomic peaks overlap, the quantities $\overline{S_iS_j}$ and $\overline{C_iC_j}$ for the two atoms i and j will no longer be small, but will have a value depending on the distance (in projection) between the peaks and the extent of the summation $\sum_{1 \text{ or } 2}$. All other cross-product terms can be treated as before. Thus for the x coordinates of the overlapping atoms in a two-dimensional projection, we have, instead of (5),

$$\left.\begin{aligned} \sum_2 \Delta\varphi \frac{\partial\varphi}{\partial x_i} &= 4\pi \sum_2 w^2(h/a)(N_i^2 s_i + N_iN_j 2S_iS_j s_j)\,, \\ \sum_2 \Delta\varphi \frac{\partial\varphi}{\partial x_j} &= 4\pi \sum_2 w^2(h/a)(N_iN_j 2S_iS_j s_i + N_j^2 s_j)\,, \end{aligned}\right\} \quad (8a)$$

and

$$\sum_2 \left(\frac{\partial\varphi}{\partial x_i}\right)^2 = 8\pi^2 \sum_2 w^2(h^2/a^2)N_i^2\,,$$

$$\sum_2 \left(\frac{\partial\varphi}{\partial x_j}\right)^2 = 8\pi^2 \sum_2 w^2(h^2/a^2)N_j^2\,. \quad (8b)$$

It is clear that the extra term in (8a) corresponds to the cross-product term $\sum_2 W^2 \frac{\partial F}{\partial x_i}\cdot\frac{\partial F}{\partial x_j}$ in the least-squares solution, and could be evaluated as such if s_i and s_j were small. Writing $\overline{S_iS_j}$ for the average of S_iS_j over the reflexions in a small range $d\theta$ of Bragg angles, and putting

$$(\sum_2 N_i^2 w^2(h/a)s_i)/(\sum_2 N_i^2 w^2 h^2/a^2) = 2\pi\delta x_i \times \eta_i\,,$$
$$(\sum_2 N_j^2 w^2(h/a)s_j)/(\sum_2 N_j^2 w^2 h^2/a^2) = 2\pi\delta x_j \times \eta_j\,,$$

we have from (8a) and (8b)

$$\varepsilon(x_i) = \eta_i\delta x_i + \eta_j\delta x_j \times \frac{N_j}{N_i}(\sum_2 N_iN_j w^2(h/a)2\overline{S_iS_j}s_j)/(\sum_2 N_iN_j w^2(h/a)s_j),$$

$$\varepsilon(x_j) = \eta_j\delta x_j + \eta_i\delta x_i \times \frac{N_i}{N_j}(\sum_2 N_iN_j w^2(h/a)2\overline{S_iS_j}s_i)/(\sum_2 N_iN_j w^2(h/a)s_i).$$

Remembering that $N_i/N_j = f_i/f_j$, and putting

$$\frac{\sum_2 N_iN_j w^2(h/a)2\overline{S_iS_j}s_i}{\sum_2 N_iN_j w^2(h/a)s_i} = \frac{\sum_2 w^2(h/a)2\overline{S_iS_j}s_i}{\sum_2 w^2(h/a)s_i} = \alpha_i\,,$$

with a similar expression for α_j, we have

$$\varepsilon(x_i) = \eta_i\delta x_i + (f_j/f_i)\alpha_j.\eta_j\delta x_j\,,$$
$$\varepsilon(x_j) = \eta_j\delta x_j + (f_i/f_j)\alpha_i.\eta_i\delta x_i\,,$$

which give on solution and simplification,

$$\delta x_i = \frac{\varepsilon(x_i)}{\eta_i}\left(1-\alpha_j\frac{f_j}{f_i}\frac{\varepsilon(x_j)}{\varepsilon(x_i)}\right)\Big/(1-\alpha_i\alpha_j)\,, \qquad (9)$$

and symmetrically for δx_j. This should be compared with the corresponding formula for no overlap, namely

$$\delta x_i = \varepsilon(x_i)/\eta_i\,.$$

It is seen that the only new quantities involved are α_i and α_j. Now

$$\begin{aligned}2\overline{S_iS_j} &= 2\,\overline{\sin 2\pi\{(h/a)x_i+(k/b)y_i\}\sin 2\pi\{(h/a)x_j+(k/b)y_j\}}\\ &= \overline{\cos 2\pi\{(h/a)(x_i-x_j)+(k/b)(y_i-y_j)\}}\\ &\qquad -\overline{\cos 2\pi\{(h/a)(x_i+x_j)+(k/b)(y_i+y_j)\}}\\ &= \cos 2\pi\delta/d-0 = \cos 2\pi\delta/d\,,\end{aligned}$$

where δ is the distance in projection between the atoms, and d is the mean inter-planar spacing in the narrow annulus in reciprocal space over which the averaging is carried out. We are justified in averaging S_iS_j separately because in general there is no correlation between δx_i, δy_i, etc., and δ, and therefore between s_i and S_iS_j. Thus

$$\begin{aligned}\alpha_i &= \Big(\sum_2 w^2(h/a)\cos 2\pi(\delta/d)\sin 2\pi(h/a\,\delta x_i+k/b\,\delta y_i)\Big)\Big/\\ &\qquad \Big(\sum_2 w^2 h/a\sin 2\pi(h/a\,\delta x_i+k/b\,\delta y_i)\Big)\\ &\simeq \Big(\sum_2 w^2(h^2/a^2)\cos 2\pi\delta/d\Big)\Big/\Big(\sum_2 w^2h^2/a^2\Big)\,, \qquad (10)\end{aligned}$$

since δx_i, δy_i, etc., are usually smaller than δ; this approximation makes $\alpha_i = \alpha_j = \alpha$.* For the one-dimensional case, we have, on putting $2\pi(h/a)\delta = u(\delta)$,

$$\begin{aligned}\alpha &= \frac{\sum_1 w^2u^2(\delta)\cos u(\delta)}{\sum_1 w^2u^2(\delta)}\\ &\simeq \left(\int_{u_0(\delta)}^{U(\delta)} w^2u^2\cos u\,du\right)\Big/\left(\int_{u_0(\delta)}^{U(\delta)} w^2u^2\,du\right)\,. \qquad (11)\end{aligned}$$

With $w^2 = h^{-n}$, we have for $n = 2$ and 3, respectively,

$$\alpha(2) \simeq \sin U(\delta)/U(\delta)\,, \qquad (u_0(\delta)\text{ being small})$$

$$\begin{aligned}\alpha(3) &= \int_{u_0(\delta)}^{U(\delta)}\frac{\cos u}{u}\,du\Big/\int_{u_0(\delta)}^{U(\delta)}\frac{du}{u}\\ &= 1+\frac{1}{\log\Phi}\int_{u_0(\delta)}^{U(\delta)}\frac{\sin^2 u/2}{u/2}\,du \quad \left(\Phi = \frac{u_0}{U}\simeq\frac{h_0-\frac{1}{2}}{H}\right),\end{aligned}$$

The curves for α against $U(\delta)$ shown in Fig. 4 are somewhat similar to those of Fig. 2. It is seen from the curves that formula (9) is useful for $\delta > \frac{1}{4}d$, since for smaller values of δ the denominator in (9) becomes small and the probable error in determining δx_i and δx_j separately becomes large, increasing roughly as $(d/\delta)^2$. (This conclusion is generally true for solution by least squares and allied methods.) For smaller values of δ, only the quantities $(f_i\delta x_i+f_j\delta x_j)$, etc., can be determined accurately.

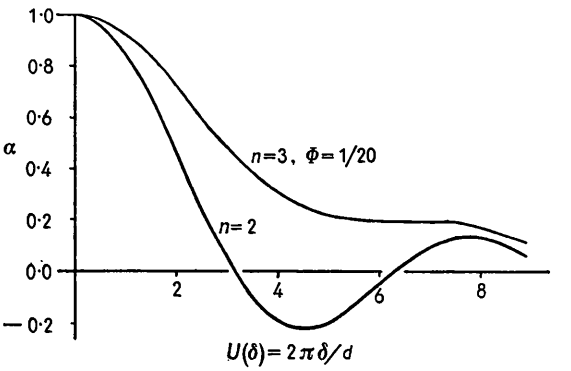

Fig. 4. Curves for the overlap coefficient, α, as a function of $U(\delta) = 2\pi(H/a)\delta$.

Further, it is significant that $w^2 = d^3$ is again a limiting case, since α oscillates for $n < 3$, being alternately positive and negative, while, for $n > 3$, α is positive and decreasing, and tends to a positive limit that increases rapidly with n; so that with $n > 3$ all atomic peaks will effectively overlap to a considerable extent. For $n = 3$, α is positive and drops rather rapidly for large $U(\delta)$; moreover the value of $\alpha(3)$ for $U(\delta) > 4$ is of the same order as the corresponding absolute value of $\alpha(2)$, the curve for which is identical with that for diffraction effects in a one-dimensional Fourier synthesis (cf. James, 1948). *These considerations indicate the desirability of making* $n \leqq 3$; *combining this with the previously obtained condition for a unique solution, namely* $n \geqq 3$, *we obtain* $n = 3$. *This then is the optimum value of* n.

4. Exponential form of weighting function

We can now consider the exponential forms $\psi = \exp[-2\sigma/d]$ and $\psi = \exp[-\sigma^2/d^2]$, where σ is a constant. These are particularly interesting because (1) the first form approximates closely to the variation of f over a large range of $\sin\theta/\lambda$ and atomic number, while the second is often used as a converging factor, and (2) these forms do not involve any trouble with divergent integrals. In one dimension and with $\psi = \exp[-2\sigma/d] = \exp[-2(h/a)\sigma]$, we have

$$\eta \simeq \left(\int_0^U u^2\exp\left[-\frac{\sigma}{\pi\delta x_i}u\right]\frac{\sin u}{u}\,du\right)\Big/\left(\int_0^U u^2\exp\left[-\frac{\sigma}{\pi\delta x_i}u\right]du\right)\,, \qquad (12)$$

which is evaluated numerically for the present purpose. The expression with $\psi = \exp[-\sigma^2/d^2]$ is very similar. Curves for η against U and against $2\pi\,(H/a)\varepsilon(x)$ have been drawn for these functions with two representative

* In the other limiting case, when $\delta^2 < ((\delta x_i)^2+(\delta y_i)^2)$, etc., α_i and $\alpha_j \to 1$, so that only $(\delta x_i+(f_j/f_i)\delta x_j)$ can be determined with any accuracy.

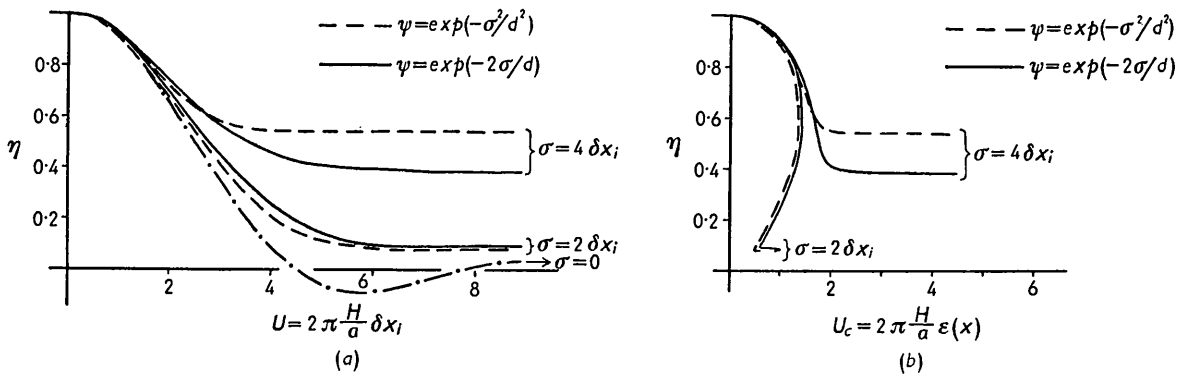

Fig. 5. Efficiency of convergence curves with exponential weighting-functions. The behaviour of the curves with σ greater and less than the critical value, $\sim 3\delta x_i$, is strikingly different.

values of σ, namely $2\delta x_i$, $4\delta x_i$ (Figs. 5(*a*) and 5(*b*)). The curves show the same general characteristics as those for the power law, the critical value of σ being approximately $3\delta x_i$; unique solutions are obtained when $\sigma > 3\delta x_i$ and multiple solutions occur when $\sigma < 3\delta x_i$. The unfortunate feature is that the critical value of σ is a multiple of the unknown δx_i; that this must be so follows immediately from equation (12). Thus if we use these exponential forms, we cannot weight the reflexions properly until we know δx_i, and therefore the actual atomic coordinates! Further, the exponential law has the disadvantage that unique η–U curves, independent of δx_i, etc., cannot be drawn.

We are therefore left with the power law as the most satisfactory form of weighting function so far considered.

5. The two-dimensional case

In the two-dimensional case,

$$\psi = \sum_k w^2 .$$

If the summation contains enough terms, we can to a sufficient degree of approximation again replace the sum by an integral and write

$$\psi = \int_{-K}^{+K} (w(hk))^2 dk .$$

It is reasonable to assume that the weight is a function of the distance of the reciprocal point (hk) from the origin in reciprocal space. Calling this distance r, we have

$$r^2 = (h/a)^2+(k/b)^2 = (1/d)^2 .$$

If a power law is valid for the weight, $w^2 = r^{-n}$, so that

$$\psi \propto \int_{-K}^{K} (h^2/a^2+k^2/b^2)^{-\frac{1}{2}n} dk .$$

The value of ψ depends on the particular shape of the region of integration. Let us assume that the region of a plane over which the integration is taking place is bounded by a circle round the origin and of a radius R, so that the limits of the integral are

$$K = \pm b\sqrt{\{R^2-(h/a)^2\}} .$$

The efficiency integral is now more difficult to solve, and no general method of solution for the power series could be found. However, from a solution of several special instances, it appears that the series has the following form

$$\eta_2(n) = 1-\frac{1}{3!}\frac{3}{4}\frac{4-n}{6-n}U^2 + \frac{1}{5!}\frac{3.5}{4.6}\frac{4-n}{8-n}U^4-\frac{1}{7!}\frac{3.5.7}{4.6.8}\frac{4-n}{10-n}U^6+\dots ,$$

valid for $n < 4$. In this series, $U = 2\pi H\delta x_i/a = 2\pi R\delta x_i$, R being the radius of the region over which the summation takes place. For $n \geqq 4$, in order to avoid singularity at $u = 0$, the integration should be split as in the one-dimensional case. The results are similar to those in three dimensions and therefore they will be discussed along with the three-dimensional case below.

6. The three-dimensional case

In three dimensions,

$$\psi = \sum_k \sum_l (w(hkl))^2 .$$

We introduce again the distance from the origin as

$$r^2 = (h/a)^2+(k/b)^2+(l/c)^2 = (1/d)^2 ,$$

and another variable ϱ, defined by

$$\varrho^2 = (k/b)^2+(l/c)^2 ,$$

and obtain

$$\psi \propto \int_\varrho \int_\theta w^2 d\varrho . \varrho d\theta .$$

With U as defined previously, the general solution is

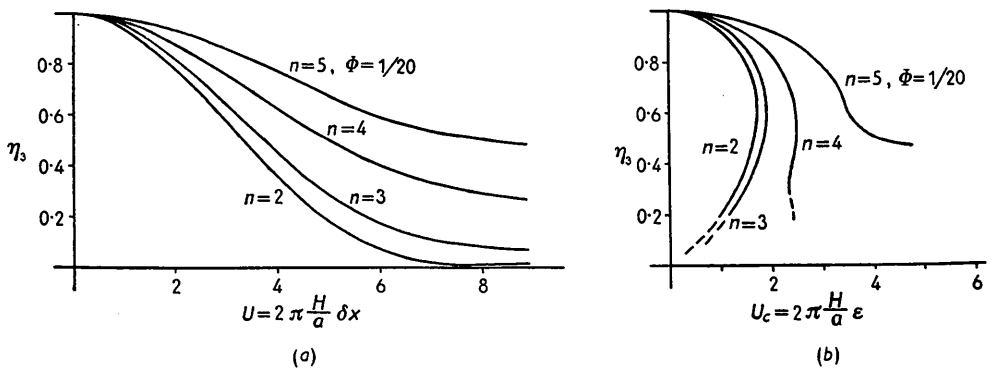

Fig. 6. Curves for η_3, the efficiency of convergence for a three-dimensional summation. The curve for the optimum value (5) of n is very close to the corresponding curve for η_1.

$$G_p = \frac{\int (U^{2-n} - u^{2-n}) u^{p+1} du}{\int (U^{2-n} - u^{2-n}) u^2 du} = \frac{3(5-n)U^{p-1}}{(p+2)(4+p-n)} \quad (n \neq 2),$$

and we have

$$\eta_3(n) = 1 - \frac{1}{3!}\frac{3}{5}\frac{(5-n)}{(7-n)}U^2 + \frac{1}{5!}\frac{3}{7}\frac{(5-n)}{(9-n)}U^4 - \ldots,$$

In three dimensions, it is again easy to evaluate $\eta_3(n)$ for integral values of n, and in the most important range we have

$$\eta_3(2) = \frac{9}{U^3}(\mathrm{Si}(U) - \sin U) \qquad n = 2,$$

$$\eta_3(3) = \frac{6}{U^3}(U - \sin U) \qquad n = 3,$$

$$\eta_3(4) = \frac{3}{2U^3}(U\cos U - \sin U + U^2\mathrm{Si}(U)) \qquad n = 4,$$

and $$\eta_3(5) = \eta_1(3) - \frac{1}{3\log\Phi + 1}$$

$$\times\left(\eta_1(3) - \frac{3}{U^2}\left(\frac{\sin U}{U} - \cos U\right)\right) + O\left(\frac{\Phi^3}{3\log\Phi}\right) \qquad n = 5.$$

For $n = 5$, the integrations are split as in the one-dimensional case. As n increases, the efficiency increasingly depends on the lower limit of the summation, and therefore on Φ. Since the formulae are very similar to the one-dimensional ones, they need not be discussed in detail. Certain important features of the two-, and three-dimensional cases, however, deserve notice (cf. Figs. 6(*a*) and (*b*), in which curves for $\eta_3(n)$ with $n = 2$ to $n = 5$ are shown).

When the results calculated for different number of dimensions are represented graphically, in all cases when n is small, the efficiency η is an oscillating function. As n increases, the oscillations decrease in amplitude until they are completely damped and the displacement δx_i becomes a single-valued function of $\varepsilon(x_i)$. If a single-valued solution is desired, we should choose $n \geqq 3$ in one dimension, $n \geqq 4$ in two dimensions and $n \geqq 5$ in three dimensions. (This increase of n with the number of dimensions can be readily understood; it compensates for the increased relative number of high-order reflexions entering into the summations.) Combining this result with considerations of overlapping peaks, as for the one-dimensional case, we obtain $n = 3$, 4 and 5, respectively, as the optimum values of the exponent.

7. Practical application to the modified steepest-descents calculation

The efficiency formulae derived in the preceding section can be used in practice either to find corrections to the values of ε when a weighting function of a given n is used, or to restrict the limits of summation when it is found that the inclusion of high-index terms is detrimental to the convergence.

To simplify previous discussion, the vector ε was taken parallel to the x axis. Now it is necessary to transform our results back to general co-ordinates and the efficiency is to be calculated on the basis of the absolute length

$$|\varepsilon| = +\sqrt{\{\varepsilon(x_i)^2 + \varepsilon(y_i)^2 + \varepsilon(z_i)^2\}}.$$

After rewriting the efficiency formulae, it is possible to prepare graphs or tables of $\eta(2\pi R|\varepsilon|)$, or preferably its reciprocal, as functions of $2\pi R|\varepsilon|$. The corrected atomic shifts can then be obtained from the equations

$$\delta x_i = \varepsilon(x_i)/\eta,$$
$$\delta y_i = \varepsilon(y_i)/\eta,$$
$$\delta z_i = \varepsilon(z_i)/\eta,$$

the same value of η being used for all coordinates of one atom.

It is to be noted that, although curves for η are given only for the one- and three-dimensional cases, corresponding curves are close enough in the practically useful range to enable the curves for the two-dimensional case to be got by interpolation.

Also, it can be shown that the above results for η hold substantially unaltered when the lattice is non-

orthogonal, provided that $\varepsilon(x)$, $\varepsilon(y)$, $\varepsilon(z)$, are now replaced by ε_1, ε_2, ε_3, obtained by solution of the following equations

$$\varepsilon(x) = \varepsilon_1+\varepsilon_2 \cos\gamma+\varepsilon_3 \cos\beta ,$$
$$\varepsilon(y) = \varepsilon_1 \cos\gamma+\varepsilon_2+\varepsilon_3 \cos\alpha ,$$
$$\varepsilon(z) = \varepsilon_1 \cos\beta+\varepsilon_2 \cos\alpha+\varepsilon_3 ,$$

α, β, γ, being the inter-axial angles (cf. Booth, 1946*a*, *b*), with corresponding equations for the two-dimensional case.

8. Conclusions

(*a*) It has been shown that the efficiency of convergence of the modified steepest-descents and the least-squares methods depends on the form of weighting function adopted. From three possible forms of weighting function discussed, only functions of a type

$$w^2 = d^n, \quad \text{i.e. } W^2 = (1/f^2)d^n ,$$

where d is the inter-planar spacing for the reflexion concerned, are found to be effective in giving single-valued solutions. The optimum value of n is found to be 3, 4 and 5, for one-, two- and three-dimensional summations, respectively. When n is smaller than the optimum value, the efficiency oscillates and there are multiple solutions in certain ranges of the shifts, ε. However, the solution is always unique when n is greater than or equal to the optimum value. This apparently corresponds to the spreading of the atomic peaks of the Cochran theory so that they extend over the whole unit cell, as is shown by considering in detail the overlap of atomic peaks. For n greater than the optimum value, the overlap between distant atoms becomes excessive.

(*b*) The value of η obtained from the appropriate curve can be used to correct the calculated ε's and thus speed up convergence. Before the results can be confidently applied in practice, other important effects such as uncertainty of signs, experimental errors, etc., need to be incorporated into the theory. It is hoped to do this in a later paper.

(*c*) Finally, it is pertinent to emphasize that the particular efficiency of convergence considered above is peculiar to the least-squares and steepest-descents methods, and does not have a counterpart in the Fourier-synthesis method; this is easily seen by noting that, under the conditions stipulated, namely, knowledge of the signs of the observed F's, $\eta \equiv 1$ for the Fourier synthesis, apart from diffraction effects due to series termination. Cochran (1948*b*) and Cruickshank (1950) show that the least-squares solution is identical with that given by a modified Fourier-synthesis, but this conclusion refers to the ultimate solution and *not* to the rate of convergence of successive approximations. Cruickshank, in fact, notes that in a typical case the rates are significantly different for $\varepsilon > 0{\cdot}10$ Å. The special significance of the present calculations for η is that, after this η has been corrected for, the least-squares and Fourier-synthesis methods become comparable (or approximately so) in so far as concerns the effect of incorrect signs, etc., on the over-all efficiency of convergence.

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