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Optimum Conditions for Convergence of Steepest Descents as Applied to Structure Determination

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The successive approximations to a structure, given by the method of steepest descents, converge to the true values of the parameters at a rate which depends very markedly on the scales of representation chosen for these parameters. The importance of this is discussed in detail and transformations are derived which secure the optimum rate of convergence and at the same time make all the parameters mathematically equivalent. The application of these transformations leads to a simple formula for the corrections ϵ_i, which has considerable advantages over existing formulae for steepest descents. An illustration of the use of this formula is given from the derivation of the structure of the hexagonal ζ-phase in the Ag–Zn alloy system.

Introduction

It has been suggested (Booth, 1947) that the method of steepest descents when applied to the analysis of crystal structures by X-rays has several advantages over the standard methods, notably a considerable saving of time and labour and the ability to obtain the structure from only a limited number of reflexions. However, a consideration of the rate of convergence of successive approximations to the actual values of the parameters is essential for the complete development of the potentialities of the method.

Briefly, the method of steepest descents consists in first forming the residual

$$R=\sum_{hkl} W^2(\phi_o-\phi_c)^2,$$

where the ϕ's represent any single-valued, differentiable function of the atomic parameters $x_1, x_2, \ldots, x_i, \ldots, x_n$. (The parameters are not necessarily restricted to position co-ordinates.) ϕ_o is the observed value of ϕ, and ϕ_c the corresponding calculated value, while W^2 is the weight allotted to any one value of $(\phi_o-\phi_c)^2$. The best values of the parameters are to be obtained by minimizing R. R, being a function of the n variables x_i, can be represented by constant-R surfaces in n-dimensional space. The essence of the method is that successive approximations are obtained by moving along grad R (i.e. the normal to the R contours) towards lower values of R. This process is indicated in Fig. 1 (*a*) for two variables; P_0 represents the initial values of x_1 and x_2, while P_1, P_2 represent the values obtained after one and two descents respectively. (It should be noted that a steepest descent in the strict mathematical sense implies descent along the geodesic shown by the broken line in Fig. 1 (*a*). In a numerical problem, however, the nearest approach to this is by means of the successive descents to $P_1, P_2, \ldots$.)

A little consideration will show that the distances of the successive approximations $P_1, P_2, \ldots$, from O will depend on the axial ratio of the contours, which are approximately elliptic in the neighbourhood of O. It is obvious that the slope of the normal to the R contour at P_2 is the same as the slope of the corresponding normal at P_0. Thus successive pairs of descents to P_3, P_4, ... will behave in the same way as the first pair (to P_1 and P_2) and we may, therefore, take some function of OP_2/OP_0 as a measure of the residual fractional error in the parameters after one descent. The correct function to use is given by the following considerations:

It can be shown (cf. equation (1) below) that

$$\frac{\epsilon_1^2}{a^2}+\frac{\epsilon_2^2}{b^2}=\frac{1}{k^2}(R-R_m),$$

where the ϵ's are the errors in the respective parameters, R_m is the absolute minimum value of R, and k is a constant. For $a=b$ this reduces to

$$(\epsilon_1^2+\epsilon_2^2)=\frac{a^2}{k^2}(R-R_m).$$

Thus $\sqrt{(R-R_m)}$ gives a measure of the root-mean-square error in the parameters, which is certainly valid for small deviations of ρ $(=a/b)$ from unity, and may, for simplicity in calculation, be extended to hold for larger deviations of ρ. It should be noted here that values of ρ between 1·0 and 1·5 are sufficient to indicate the slow convergence for $\rho \neq 1$ (cf. Table 1 below). The residual fractional error after one descent is thus given by

$$r=\frac{\sqrt{(R-R_m)_{P_1}}}{\sqrt{(R-R_m)_{P_0}}}.$$

Since a detailed analysis shows that

$$\frac{(R-R_m)_{P_1}}{(R-R_m)_{P_0}}=\frac{(R-R_m)_{P_2}}{(R-R_m)_{P_1}},$$

this expression for r can also be put as

$$r=\left\{\frac{(R-R_m)_{P_2}}{(R-R_m)_{P_0}}\right\}^{\frac{1}{2}}=\left\{\frac{OP_2}{OP_0}\right\}^{\frac{1}{2}}.$$

It follows from the geometry of the similar elliptical contours that

$$r^2=\frac{(1-1/\rho^2)^2}{(1+m^2/\rho^2)(1+1/m^2\rho^2)},$$

where ρ ($=a/b$ or b/a) is the axial ratio of the elliptical R contours, and m is the slope of the normal to the contour at P_0. It is to be noted that the above expression has the same value if $1/\rho$ is substituted for ρ, or $1/m$ for m, or both. Also

$$r=0 \quad \text{for} \quad m=0 \quad \text{and for} \quad 1/m=0,$$

and r has a maximum for $m=1$, when the above expression becomes

$$r_m=\left|\frac{1-1/\rho^2}{1+1/\rho^2}\right|=\left|\frac{\rho-1/\rho}{\rho+1/\rho}\right|.$$

The average value of r^2 (averaged over θ, where $\epsilon_1=a\cos\theta$ and $\epsilon_2=b\sin\theta$ give the equation of the R contours) can be easily obtained, and it is found that

$$\sqrt{(\overline{r^2})}=\frac{1}{\sqrt{2}}\left|\frac{\rho-1/\rho}{\rho+1/\rho}\right|=\frac{1}{\sqrt{2}}r_m.$$

Values of r_m and $\sqrt{(\overline{r^2})}$ are tabulated in Table 1 for various values of ρ.

Table 1. *The maximum residual fractional error r_m after one descent, and the corresponding root-mean-square error $\sqrt{(\overline{r^2})}$, as a function of the axial ratio ρ of the R contours*

ρ	1·0	1·25	1·5	2·0	2·5	3·0
r_m	0	0·22	0·38	0·60	0·72	0·80
$\sqrt{(\overline{r^2})}$	0	0·16	0·27	0·42	0·51	0·57

Table 1, together with Fig. 1 (*a*) and (*b*), clearly indicates the desirability of keeping ρ very nearly unity. Also, it is clear that when $\rho=0$ the geodesic becomes a radial line and coincides with the path of the first descent P_0P_1, which now brings P_1 into coincidence with O.

Similar considerations apply to n-dimensional R contours, except that the mathematical formulation is more complicated. By setting up the equation of the normal at P_0 and finding the condition for its being a tangent to another contour (the point of contact being P_1), one obtains

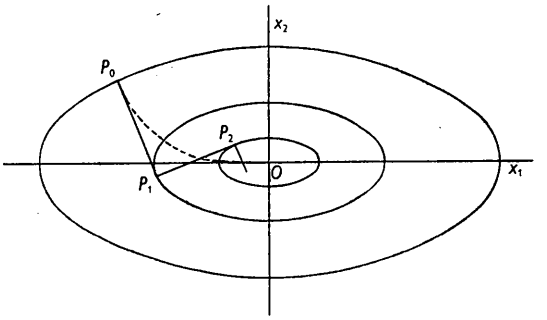
$$(r^2)_n=\frac{(R-R_m)_{P_1}}{(R-R_m)_{P_0}}=\frac{\left(\sum_{i=0}^{n}\frac{\epsilon_i^2}{a_i^2}\right)\left(\sum_{i=0}^{n}\frac{\epsilon_i^2}{a_i^6}\right)-\left(\sum_{i=0}^{n}\frac{\epsilon_i^2}{a_i^4}\right)^2}{\left(\sum_{i=0}^{n}\frac{\epsilon_i^2}{a_i^2}\right)\left(\sum_{i=0}^{n}\frac{\epsilon_i^2}{a_i^6}\right)},$$

where the ϵ_i's are the errors in the parameters and the a_i's the corresponding axes of the R contours. (The subscript for $(r^2)_n$ is used to avoid confusion with r^2 for the two-dimensional case.) On simplifying and putting $\epsilon_i/a_i=t_i$ and $a_i=\bar{a}\times\rho_i$, this becomes

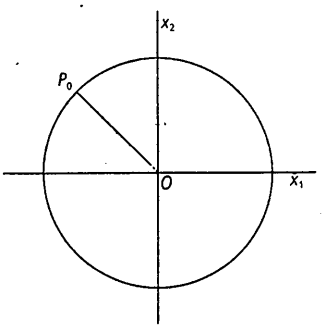
$$(r^2)_n=\frac{\frac{1}{2}\sum_{i\neq i'}\frac{t_i^2t_{i'}^2}{a_i^2a_{i'}^2}\left(\frac{\rho_i}{\rho_{i'}}-\frac{\rho_{i'}}{\rho_i}\right)^2}{\left(\sum_i t_i^2\right)\left(\sum_i\frac{t_i^2}{a_i^4}\right)}.$$

A considerable simplification can be effected if we consider only small deviations of the a_i's from their mean value $\bar{a}$. In this case we can write $\rho_i=1+\delta_i$ and therefore $(\rho_i/\rho_{i'}-\rho_{i'}/\rho_i)\cong 2(\delta_i-\delta_{i'})$. We can also put a_i and $a_{i'}$ equal to $\bar{a}$ in the remaining factors, and obtain

$$(r^2)_n\cong\frac{\frac{1}{2}\sum_{i\neq i'}t_i^2t_{i'}^2.4(\delta_i-\delta_{i'})^2}{\left(\sum_i t_i^2\right)\left(\sum_i t_i^2\right)}.$$



(*a*)



(*b*)

Fig. 1. (*a*) Elliptical R contours for two parameters x_1 and x_2. The lines of two successive 'descents' are indicated by P_0P_1 and P_1P_2. (*b*) Equi-axial R contours for two parameters x_1 and x_2. The first descent brings P to O, the position for the absolute minimum of R.

As, for large n, the t_i's are not correlated to any appreciable extent we can put $\overline{t_i^2t_{i'}^2}=(\overline{t_i^2})\,(\overline{t_{i'}^2})$. Using $\frac{\overline{t_i^2}}{\sum_i\overline{t_i^2}}=\frac{1}{n}$, this gives

$$(r^2)_n\cong\frac{2}{n^2}\sum_{i\neq i'}(\delta_i-\delta_{i'})^2=\frac{2}{n^2}n(n-1)\,\overline{(\delta_i-\delta_{i'})^2}$$

$$=4\frac{n-1}{n}\overline{\delta_i^2}.$$

Thus

$$\sqrt{\{(\overline{r^2})\}_n}\cong 2\sqrt{\left(\frac{n-1}{n}\right)}\sqrt{(\overline{\delta_i^2})}$$

$$\cong 2\sqrt{(\overline{\delta_i^2})} \text{ for large } n.$$

It is interesting to note that in the two-dimensional case $\rho\cong 1+2\delta_j$ for small δ_j ($\delta_1=\delta_2$ for $n=2$) and therefore

$$r_m\cong 2\delta_j=2\sqrt{(\overline{\delta_j^2})} \quad \text{and} \quad \sqrt{(\overline{r^2})}=r_m/\sqrt{2}\cong\sqrt{2}\sqrt{(\overline{\delta_j^2})}.$$

Since $\sqrt{\left\{\left(\frac{\rho_i}{\rho_{i'}}-\frac{\rho_{i'}}{\rho_i}\right)^2\right\}}\cong 2\sqrt{\{(\delta_i-\delta_{i'})^2\}}=2\sqrt{2}\sqrt{(\overline{\delta_i^2})}$,

it follows that, for small $(\rho-1)$, the values of r_m in Table 1 may be taken as representative of $\{\sqrt{(\overline{r^2})}\}_n$ if we put

$$\sqrt{2}\times\sqrt{\left\{\overline{\left(\frac{\rho_i}{\rho_{i'}}-\frac{\rho_{i'}}{\rho_i}\right)^2}\right\}}=\left(\rho-\frac{1}{\rho}\right)$$

and

$$\sqrt{\left\{\overline{\left(\frac{\rho_i}{\rho_{i'}}+\frac{\rho_{i'}}{\rho_i}\right)^2}\right\}}\cong\left(\rho+\frac{1}{\rho}\right)\cong 2.$$

For large deviations of the ρ_i's from unity it can be shown that $\{\sqrt{(\overline{r^2})}\}_n$ behaves like $\sqrt{(\overline{r^2})}$ in the two-dimensional case and tends to a limit in the neighbourhood of $1/\sqrt{2}$, the exact value being a function of the distribution of the ρ_i's about their geometric mean.

It thus appears that for rapid convergence of all the parameters to their final values the R contours should be as nearly equiaxial as possible. The transformations necessary to effect this will now be investigated.

Derivation of transformations

Let ϕ_{cm} be the value of ϕ_c at the absolute minimum of R. Then

$$\begin{aligned}R&=\sum_{hkl}W^2(\phi_o-\phi_c)^2=\sum_{hkl}W^2\{(\phi_o-\phi_{cm})+(\phi_{cm}-\phi_c)\}^2\\&=\sum_{hkl}W^2(\phi_c-\phi_{cm})^2+\sum_{hkl}W^2(\phi_o-\phi_{cm})^2\\&\qquad-2\sum_{hkl}W^2(\phi_c-\phi_{cm})(\phi_o-\phi_{cm}).\end{aligned}$$

The last term becomes small in comparison with the others for a large summation, while the second term can be put equal to R_m, the absolute minimum value of the residual. (Obviously R_m is a function of the experimental errors in the ϕ_o's and will be zero only for ideally accurate intensity values and for a structure containing ideally perfect atoms.) Thus we have

$$R-R_m=\sum_{hkl}W^2(\phi_c-\phi_{cm})^2.$$

If our initial values of the parameters are not very far from the correct ones, we can write

$$\phi_c=\phi_{cm}+\sum_i\left(\frac{\partial\phi_c}{\partial x_i}\right)\delta x_i,$$

where the δx_i's denote the departures from the values of the x_i's at the absolute minimum of R, and the higher terms of the Taylor expansion are neglected. It follows that

$$\begin{aligned}R-R_m&=\sum_{hkl}W^2\left(\sum_i\frac{\partial\phi_c}{\partial x_i}\delta x_i\right)^2\\&=\sum_{hkl}W^2\sum_i\left(\frac{\partial\phi_c}{\delta x_i}\right)^2(\delta x_i)^2+\sum_{hkl}W^2\sum_{i\neq i'}\frac{\partial\phi_c}{\partial x_i}\frac{\partial\phi_c}{\partial x_{i'}}\delta x_i\delta x_{i'}\\&=\sum_i(\delta x_i)^2\left\{\sum_{hkl}W^2\left(\frac{\partial\phi_c}{\partial x_i}\right)^2\right\}\\&\qquad+\sum_{i\neq i'}\delta x_i\delta x_{i'}\left\{\sum_{hkl}W^2\frac{\partial\phi_c}{\partial x_i}\frac{\partial\phi_c}{\partial x_{i'}}\right\}.\end{aligned}$$

The second term becomes small in comparison with the first for a reasonably large number of reflexions, the summation $\sum_{hkl}$ being carried out over a region symmetrical about the origin in the reciprocal lattice. Subject to this condition, we have

$$\begin{aligned}R-R_m&=\sum_i(\delta x_i)^2\left\{\sum_{hkl}W^2\left(\frac{\partial\phi_c}{\partial x_i}\right)^2\right\}\\&=\sum_i a_i^2(\delta x_i)^2,\end{aligned}\qquad(1)$$

where

$$a_i^2=\sum_{hkl}W^2\left(\frac{\partial\phi_c}{\partial x_i}\right)^2.\qquad(2)$$

Equation (1) obviously represents an n-dimensional ellipsoid, which can be reduced to an n-dimensional sphere by means of the transformations

$$x_i'=a_ix_i.\qquad(3)$$

Equation (1) then becomes

$$R-R_m=\sum_i(\delta x_i')^2.\qquad(4)$$

(It is to be noted that any transformation of the form $x_i'=\alpha a_ix_i$, with α a constant, will effect the reduction of (1) to an n-dimensional sphere. Also, for a fairly large number N of reflexions, we have (Brunt, 1917, pp. 38, 58)

$$a_i^2=\sum_{hkl}W^2\left(\frac{\partial\phi_c}{\partial x_i}\right)^2=\frac{\beta}{N}\left\{\sum_{hkl}W\left|\frac{\partial\phi_c}{\partial x_i}\right|\right\}^2,\qquad(2a)$$

where β is a constant of the order of 2·0, whose value depends on the form of the statistical distribution of $W(\partial\phi_c/\partial x_i)$. The use of $(2a)$ eliminates a very considerable amount of labour.)

Consideration of steepest-descents formulae

In order to obtain from (4) the values of the corrections required for the x_i's, we shall make use of the elegant variation of the first-derivative formula for steepest descents suggested by Vand (1948a). The first derivative formula for the corrections ϵ_i given by Booth (1947), viz.

$$-\epsilon_i=2R\frac{\partial R}{\partial x_i}\Big/\sum_i\left(\frac{\partial R}{\partial x_i}\right)^2,\qquad(5)$$

is valid only if the minimum of R along the direction of descent is zero or, at any rate, small in comparison with the initial value of R. When this is not true, we can still use (5) provided we replace R by $R-R_0$, where R_0 is the minimum value of R along the direction of descent given by the components $\partial R/\partial x_i$ of grad R. Equation (5) then becomes

$$-\epsilon_i=2(R-R_0)\frac{\partial R}{\partial x_i}\Big/\sum_i\left(\frac{\partial R}{\partial x_i}\right)^2.\qquad(6)$$

R_0 is evaluated by calculating the value of R at the point A (Fig. 2) given by equation (5) and then using the formula

$$R_0=\frac{R_A}{1+R_A/R_P}.\qquad(7)$$

Formula (7) is derived on the assumption of a parabolic variation of R between P and A. Equations (6) and (7) together give the co-ordinates for the minimum somewhat more accurately and with considerably less labour

than Booth's formula involving second derivatives at P, viz.

$$-\epsilon_i = \frac{\left\{\sum_i \left(\frac{\partial R}{\partial x_i}\right)^2\right\}\frac{\partial R}{\partial x_i}}{\sum_i \sum_{i'} \frac{\partial^2 R}{\partial x_i \partial x_{i'}} \frac{\partial R}{\partial x_i}\frac{\partial R}{\partial x_{i'}}}. \qquad (5a)$$

The use of (7), however, involves the assumption that the minimum of R along the direction of descent definitely lies between P and A. This will invariably be true if P is near the minimum. In any case, the error introduced by this assumption, when P is far from the minimum, is of the same order as the other errors inherent in the formulation of the steepest-descents formulae (5) and (5a).

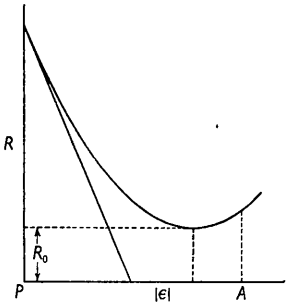


Fig. 2. Variation of R with $|\epsilon|$, the distance moved along grad R in the direction of descent. R_0 is the minimum value of R along this line, while A corresponds to the position given by formula (5).

Application of transformations to the steepest-descents formula

We can proceed to apply the formula (6) in the transformed co-ordinates x_i' given by (3) and obtain for the corrections in these co-ordinates

$$-\epsilon_i' = \frac{2(R-R_m)\frac{\partial R}{\partial x_i'}}{\sum_i \left(\frac{\partial R}{\partial x_i'}\right)^2} = \frac{2\left\{\sum_i (\delta x_i')^2\right\}\frac{\partial R}{\partial x_i'}}{\sum_i (2\delta x_i')^2} = \frac{1}{2}\frac{\partial R}{\partial x_i'} = \frac{1}{2a_i}\frac{\partial R}{\partial x_i},$$

whence the corrections in the original co-ordinates are

$$\epsilon_i = \frac{\epsilon_i'}{a_i} = -\frac{1}{2a_i^2}\frac{\partial R}{\partial x_i} = \frac{\sum_{hkl} W^2(\phi_o - \phi_c)\frac{\partial \phi_c}{\partial x_i}}{\sum_{hkl} W^2\left(\frac{\partial \phi_c}{\partial x_i}\right)^2} \qquad (8)$$

(on substituting for a_i^2 and $\partial R/\partial x_i$ in terms of $\partial\phi_c/\partial x_i$, etc.). The values of $\partial\phi_c/\partial x_i$ used in the derivation of the formula are those at the absolute minimum of R; more accurately, mean values over the path of the descent should have been used. We may, however, subject to the initial values of the parameters being near the minimum, use the values of $\partial\phi_c/\partial x_i$ calculated with our assumed values of the parameters. Further, (8) is strictly valid only if the summation $\sum_{hkl}$ satisfies the condition of symmetry noted before when obtaining equation (1). The necessity for this can be seen as follows:

If $\phi = \phi(u)$, where $u = 2\pi(hx+ky+lz)$,

$$\frac{\partial\phi}{\partial x} = 2\pi h\frac{\partial\phi}{\partial u}, \quad \frac{\partial\phi}{\partial y} = 2\pi k\frac{\partial\phi}{\partial u}, \quad \frac{\partial\phi}{\partial z} = 2\pi l\frac{\partial\phi}{\partial u},$$

whence $$\sum_{hkl}\frac{\partial\phi}{\partial y}\frac{\partial\phi}{\partial z} = \sum_{hkl} 4\pi^2 kl\left(\frac{\partial\phi}{\partial u}\right)^2,$$

which becomes small statistically when the summation extends from $-K$ to $+K$, or from $-L$ to $+L$, or both.

It will be seen that, in the majority of practical cases, this condition will be satisfied, at least approximately, and therefore formula (8) will be valid.

A further condition is that when x_i and $x_{i'}$ refer to different atoms, $\partial\phi_c/\partial x_i$ and $\partial\phi_c/\partial x_{i'}$ should not always be of the same sign. This implies good separation of the electron-density peaks in three-dimensional space. If the number of reflexions used is so small that an atom lies well within the first diffraction minimum (James, 1948) surrounding another, it is best to treat the two as one unit situated at their centroid. This, however, is mainly of theoretical interest.

Discussion and application of formula

A noteworthy feature of (8), apart from the fact that it secures the maximum rate of convergence to the correct values of the parameters, is that the value of R_m no longer appears in the formula; as, indeed, it should not, being a function of the experimental errors.

Furthermore, the expression for ϵ_i now involves derivatives with respect to x_i only, thus permitting the refining of each parameter individually. In addition, the exact equivalence of all the parameters (shown by the transformed equation (4)) permits the introduction of additional parameters of a different nature, for example the degree of order in alloys, for which the scale of measurement selected is in no way compatible with that used for the position co-ordinates. The use of (8) in such a case automatically adjusts the value of the transformation constant a_i so as to make the R contours equiaxial and to secure simultaneous convergence of all the parameters to their final values.

The behaviour of (8), when the errors in the assumed parameters are such that the higher order terms of the Taylor expansion of the ϕ_c's can no longer be neglected, is particularly interesting. It is easily seen that, in general, (8) is equivalent to applying the first-derivative formula (5) to the function $R' = R - R_m$ (after applying the transformation (3)). This makes (8) behave like (5) for $R \gg R_m$ and like the second-derivative formula (5a) for $R \sim R_m$. Thus, the use of (8) eliminates the necessity for changing over from Booth's formula (5) to his formula (5a) as the absolute minimum of R is approached in successive descents, while the transformations (3) (used in the derivation of (8)) greatly reduce the number of descents required.

Fig. 3 is typical of the two-dimensional behaviour of

the R contours at large distances from O. In the figure P_1p_1, P_2p_2 and P_3p_3 represent the refinements of the parameters effected by the application of (8) at P_1, P_2 and P_3 respectively. It is clear that within a circle centre O and radius of the order of $\frac{1}{2}OS$, (8) converges rapidly to O, while the convergence is very slow in the vicinity of S. (At points in the sector $A_1'SA_2'$, all formulae will converge not to O but towards another minimum of R at O'.) However, in common with other methods for structure analysis from X-ray data, the use of (8) assumes a knowledge of the relative phases (or signs) of the F's. It is probable that when the distance OP is at all large, our lack of knowledge of these phases would become the dominant factor governing the convergence of the formula. Another important factor influencing the convergence for large values of OP is the assignment of the weights W, which is connected with the choice of the function ϕ. In the neighbourhood of O, however, the exact values allotted to the weights have little effect on the convergence. It is hoped to discuss some of these aspects of the problem in a further paper.

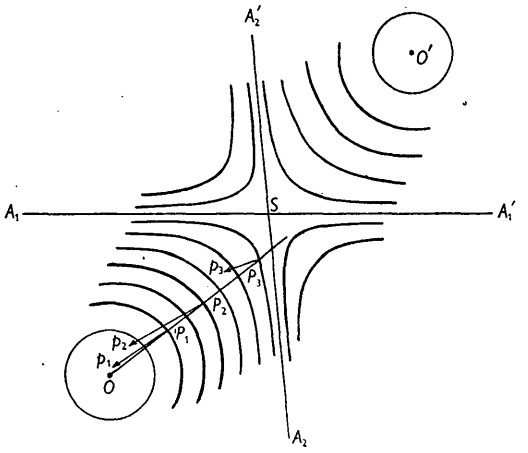


Fig. 3. Schematic representation in two dimensions of R contours for large distances from O.

If formula (8) is written as

$$\sum_{hkl} W^2(\phi_o-\phi_c)\frac{\partial\phi_c}{\partial x_i}=\epsilon_i\sum_{hkl} W^2\left(\frac{\partial\phi_c}{\partial x_i}\right)^2, \qquad (8a)$$

it is seen that this is very similar to the result obtained by the method of least squares when the ϕ_c's are linear functions of the variables x_i. The method of least squares was applied by Hughes (1941) to the refinement of the structure of melamine. He begins with an equation of the type

$$W_{hkl}(\phi_o-\phi_c)_{hkl}=W_{hkl}\sum_i\left(\frac{\partial\phi_c}{\partial x_i}\right)_{hkl}\epsilon_i$$
$$=W_{hkl}\left\{\frac{\partial\phi_c}{\partial x_1}\epsilon_1+\frac{\partial\phi_c}{\partial x_2}\epsilon_2+\ldots+\frac{\partial\phi_c}{\partial x_i}\epsilon_i+\ldots+\frac{\partial\phi_c}{\partial x_n}\epsilon_n\right\}_{hkl}.$$

The normal equation for ϵ_i in the solution by least squares of a number of such equations (for different reflexions) is

$$\sum_{hkl}\left\{W(\phi_o-\phi_c)\,W\frac{\partial\phi_c}{\partial x_i}\right\}=\sum_{i'}\epsilon_{i'}\sum_{hkl}\left\{W\frac{\partial\phi_c}{\partial x_i}W\frac{\partial\phi_c}{\partial x_{i'}}\right\},$$

i.e.
$$\sum_{hkl} W^2(\phi_o-\phi_c)\frac{\partial\phi_c}{\partial x_i}=\epsilon_i\sum_{hkl} W^2\left(\frac{\partial\phi_c}{\partial x_i}\right)^2$$
$$+\sum_{i'}{}'\epsilon_{i'}\sum_{hkl} W^2\frac{\partial\phi_c}{\partial x_i}\frac{\partial\phi_c}{\partial x_{i'}}, \qquad (9)$$

where $\sum_{i'}{}'$ implies that the term for $i'=i$ is to be omitted. It is at once apparent that (9) simplifies to (8a) when the cross-product terms $\sum_{hkl} W^2\frac{\partial\phi_c}{\partial x_i}.\frac{\partial\phi_c}{\partial x_{i'}}$ are negligibly small, i.e. when the normal equations are orthogonal. (It should be noted that statistical fluctuations in the values of these terms introduce a small error σ_i in the value of ϵ_i given by (8a). If N is the total number of reflexions used, the root-mean-square value of σ_i/ϵ_i is a function of n/N and is small for $N\gg n$.)

It thus appears that when the R contours have been made equi-axial by means of the transformations (3), the steepest descent along the now radial geodesic is identical with the application of the method of least squares. The use of equation (8a) retains the advantages claimed by Hughes for the method of least squares, namely:

(1) The method is not subject to errors caused by diffraction effects in Fourier syntheses.

(2) Somewhat better resolution is attainable than in Fourier syntheses. This is a consequence of the fact that the diffuse electron-density distribution of an atom is taken into account by being reduced to a point scatterer of strength f.

(3) A limited number of reflexions can be used to obtain the values of the parameters. Doubtful F values, such as those subject to extinction, can be ignored or given less weight. In this connexion it should be remembered that in order to obtain trustworthy estimates of the corrections, ϵ_i, the number of reflexions used should be considerably greater than the number of parameters involved.

This latter is particularly important when (8) is used, because of the statistical fluctuations previously referred to. When n/N is of the order of $\frac{1}{2}$, it may be advisable to apply the transformations (3) directly and then use the ordinary steepest-descents formulae; alternatively, refinement may be carried out by the method of least squares.

It is perhaps worth remarking that the methods of least squares and steepest descents as well as formula (8) are subject to errors due to neglect of derivatives of the second and higher orders. This, however, is not serious in the final stages of refinement of the parameters.

The above formulae have been successfully used in the determination of the structure of the ζ-phase of the

Ag–Zn alloy system (Edmunds & Qurashi, in preparation). The ζ-phase is hexagonal with 27 atoms to the unit cell and exhibits a certain amount of ordering. In order to take this into account, order parameters for the various atomic positions are introduced in the form $x=f/f_m$, where $f_m=\frac{1}{2}(f_{Ag}+f_{Zn})$ and f represents the effective scattering factor for the particular atomic position. As the structure is derived from powder photographs, it is convenient to use the function $\phi=\Sigma(F/f_m)^2$, where the summation extends over all the reflexions which have the same Bragg angle. As an illustration of the capabilities of the method, the calculations for four parameters and using only a few reflexions are set out in Table 2, where ϕ_{x_i} has been written for $\partial\phi/\partial x_i$.

The weight W for these reflexions varies from 0·11 to 0·09, and has been put equal to 0·10 throughout for simplicity. The quantities $\sum_{hkl} W^2\phi_{x_i}^2$ have been obtained by means of the formula (2a), viz.

$$\sum_{hkl} W^2\phi_{x_i}^2=\frac{\beta}{N}\left\{\sum_{hkl} W\,|\,\phi_{x_i}\,|\right\}^2,$$

where N is the number of reflexions and β is a constant which has the value 2·3 in the present case. This procedure effects a considerable saving in labour and, provided N is sufficiently large, gives the required corrections to the co-ordinates to within 5 or 10 %, i.e. better than 0·005 A. in the above example. (x_1, x_2 and x_3 are position co-ordinates, while x_4 is an order parameter defined as above.)

Table 2 (b) clearly brings out the fact that the original R contours are far from being equiaxial, e.g. $\left(\sum_{hkl} W^2\phi_{x_2}^2\right)\Big/\left(\sum_{hkl} W^2\phi_{x_3}^2\right)\cong 200$. Consequently, the ordinary steepest-descents formula (5a) would have yielded a value for ϵ_3 about 200 times smaller than the correct one. Similar considerations apply to the order parameter x_4. In deriving the actual structure of the ζ-phase, altogether about 60 reflexions were used. The corrections furnished by the last descent, from which the above illustration is taken, gave substantially good agreement between the observed and calculated structure factors, the mean factor of reliability $\frac{\Sigma\,|\,|F_{obs.}|-|F_{calc.}|\,|}{\Sigma\,|F_{calc.}|}$ being 0·12.

It may be mentioned that a formula somewhat similar to (8) has been derived by Vand (1948b) by a statistical method in the course of his development of a harmonic method for obtaining the corrections ϵ_i.

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Table 2. *Calculations for some ϵ_i's for the ζ-phase of* Ag–Zn, *using only a few reflexions*

(a)

The factor $1/4\pi$ in the quantities $\frac{W}{4\pi}\phi_{x_i}$ arises because ϕ_{x_i} is of the form $\frac{\partial}{\partial x_i}\{\cos 2\pi(hx_a+kx_b+lx_c)+\ldots\}^2$.

hkil	ϕ_o	ϕ_c	$\delta=\phi_o-\phi_c$	$\frac{W}{4\pi}\phi_{x_1}$	$\frac{W}{4\pi}\phi_{x_2}$	$\frac{W}{4\pi}\phi_{x_3}$	$\frac{W}{2}\phi_{x_4}$	$\frac{W^2}{4\pi}\delta\phi_{x_1}$	$\frac{W^2}{4\pi}\delta\phi_{x_2}$	$\frac{W^2}{4\pi}\delta\phi_{x_3}$	$\frac{W^2}{2}\delta\phi_{x_4}$
$20\bar{2}3$ $44\bar{8}1$	56·0	36·7	+19·3	+ 0·2	− 9·4	−0·23	−0·89	+ 0·5	−18·2	−0·44	−1·7
$53\bar{8}1$ $70\bar{7}1$	104·0	107·7	− 3·7	−10·2	+22·2	−0·42	+1·86	+ 3·8	− 8·2	+0·16	−0·7
$21\bar{3}3$	12·0	12·8	− 0·8	+ 2·9	− 0·3	−0·29	−1·10	− 0·2	0·0	+0·02	+0·1
$71\bar{8}0$	0·0	2·0	− 2·0	+ 0·2	+ 3·0	0·00	+0·26	0·0	− 0·6	0·00	0·0
$62\bar{8}1$	73·0	81·4	− 8·4	+ 9·2	+ 9·8	+0·13	+2·72	− 7·7	− 8·2	−0·11	−2·3
$60\bar{6}2$	80·4	50·4	+30·0	− 3·6	−16·6	0·00	+2·00	−10·8	−50·0	0·00	+6·0
$30\bar{3}3$	0·0	0·9	− 0·9	0·0	0·0	−2·50	0·00	0·0	0·0	+0·07	0·0
$43\bar{7}2$	8·2	35·2	−27·0	+10·2	+ 1·3	0·00	+1·08	−27·6	− 3·6	0·00	−2·9
$22\bar{4}3$	52·0	55·3	− 3·3	− 2·1	− 5·6	+1·22	0·00	+ 0·7	+ 1·8	−0·40	0·0

(b)

x_i	x_1	x_2	x_3	x_4
$\sum_{hkl}\frac{W}{4\pi}\,\lvert\phi_{x_i}\rvert$	38·6	68·2	4·79	9·91
$\sum_{hkl}\frac{W^2}{(4\pi)^2}\phi_{x_i}^2$	381	1186	5·86	25·0
$\sum_{hkl}\frac{W^2}{4\pi}\delta\phi_{x_i}$	−41·3	−87·0	−0·70	−1·5
ϵ_i	$-0{\cdot}008_6$	$-0{\cdot}005_8$	$-0{\cdot}009_5$	$-0{\cdot}03_0$
ϵ_i	$-0{\cdot}06_5$ A.	$-0{\cdot}04_4$ A.	$-0{\cdot}02_7$ A.	3·0 %