Acta Cryst. (1953). **6**, 577

An Analysis of the Efficiency of Convergence of Different Methods of Structure Determination. I. The Methods of Least Squares and Steepest Descents: Centrosymmetric Case.

BY M. M. QURASHI*

Physics Department, College of Technology, Manchester 1, *England*

(*Received* 25 *March* 1952)

A theoretical derivation of the 'efficiency of convergence' of the methods of least squares and steepest descents is given for large departures of the assumed approximation from the correct structure. The effect of incorrect signs is considered in detail and a mathematical expression is obtained for the efficiency of convergence, η, for an n-dimensional summation. (The effect of overlapping atoms and of unobservably weak reflexions is also discussed.) It is shown that η can be expressed as a function of $u = 2\pi\Delta/d_{hkl}$, where Δ is the root-mean-square error per atomic coordinate. The characteristic behaviour of η under various conditions is discussed, and approximate expressions are obtained for the radius of rapid convergence, within which it is possible to speed up the convergence by using the theoretical value of η. Curves to facilitate this are drawn, and a numerical example of their application is given.

1. Introduction

The methods of Fourier synthesis, least squares, steepest descents, and other allied techniques, as used in crystal-structure analysis, all depend essentially on the principle of successive approximations. Thus the corrections (to the assumed atomic parameters) furnished by one application of any one of these methods are in general less than the actual corrections required, and we may define the efficiency, η, (of a particular method) for a parameter, u_j, as

$$\eta(u_j) = \delta u_{jc}/\delta u_{jo}\,, \qquad (1a)$$

where

δu_{jo} = actual correction required,

and

δu_{jc} = correction obtained from one refinement.

An expression for η for the modified method of steepest descents has been derived elsewhere (Qurashi & Vand, 1953) on the assumption that the observed structure-factors, F_o, are known completely, i.e. both in magnitude and relative phase. A little consideration shows that, under these conditions, the efficiency of the Fourier-synthesis method is unity (provided there is no overlap), while for other methods it is less than unity. In actual practice, only $|F_o|$ is known experimentally, while the phases have to be obtained from the assumed approximation, and may be in error to a considerable extent. The efficiency, $\eta_{F.S.}$, for the Fourier-synthesis method now also falls below unity, as is shown by the necessity of using successive approximations to obtain the correct structure.

If the value of η appropriate to a particular parameter can be calculated for the method being used, it should be possible to obtain the actual correction from equation (1*a*) as

$$\delta u_{jo} = \delta u_{jc}/\eta(u_j)\,. \qquad (1b)$$

One application of the method of refinement used gives δu_{jc}, and division of this by η should give us the final correction, which would otherwise be obtained after a series of successive refinements. Thus, in addition to throwing light on the mechanism of the refinement and its convergence, the evaluation of η for different methods of structure refinement is of considerable practical importance.

The purpose of the following analysis is to derive and evaluate expressions for η for the methods of Fourier synthesis and modified steepest-descents, the expression obtained for the latter being valid also for refinement by least squares. It is convenient to consider first the method of steepest descents; the analysis for the Fourier-synthesis method is a considerable elaboration of that used here, and will be discussed separately. So far the results for centrosymmetrical structures only have been obtained in a complete form; it is hoped to publish those for the acentric case soon.

2. List of contractions

In order to simplify the writing of the equations involved, we use the following contractions, some of which are standard:

F_o = observed value of F.

F_c = calculated value of F.
(F is in general a complex quantity to include phase and magnitude.)

* Now at Pennsylvania State College, State College, Pa., U. S. A.

$\sum_{hkl} = \sum_h \sum_k \sum_l$.

$v = 2\pi\{(h/a)x+(k/b)y+(l/c)z\}$.

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

$x_{jc} = (x_j)_{\text{calculated}}$ or $(x_j)_{\text{assumed}}$.

$x_{jo} = (x_j)_{\text{observed}}$ or $(x_j)_{\text{actual}}$.

x_{joc} = value of x_j given by one application of the method of refinement under discussion.

$\delta x_{jo} = (\delta x_j)_o = x_{jo}-x_{jc}$.

$\delta x_{jc} = (\delta x_j)_c = x_{joc}-x_{jc}$.

$\delta v_{jo} = 2\pi\{(h/a)\delta x_{jo}+(k/b)\delta y_{jo}+(l/c)\delta z_{jo}\}$.

$\delta v_{jc} = 2\pi\{(h/a)\delta x_{jc}+(k/b)\delta y_{jc}+(l/c)\delta z_{jc}\}$.

3. Derivation of expression for η

Define a quantity, F_{oc}, as follows:

$$|F_{oc}| = |F_o|, \quad \arg F_{oc} = \arg F_c\,, \tag{2a}$$

i.e. F_{oc} has the phase of F_c and the magnitude of F_o. Thus F_{oc} is the quantity that replaces F_o in a practical Fourier synthesis

$$\varrho_{xyz} = \frac{1}{V}\sum_{hkl} F_o \exp\left[2\pi i\{(h/a)x+(k/b)y+(l/c)z\}\right].$$

Also, in the practical application of the methods of steepest descents and least squares, we must minimize the residual

$$R = \sum_{hkl} W^2(|F_o|-|F_c|)^2$$

instead of

$$R' = \sum_{hkl} W^2(F_o-F_c)^2\,,$$

where W represents the weight given to $(|F_o|-|F_c|)$ for any particular reflexion. This form of the residual will lead to the modified steepest-descents formula with optimum convergence (cf. Qurashi, 1949)

$$\delta u_{jc} = \varepsilon_j = \left(\sum_{hkl} W^2(|F_o|-|F_c|)\frac{\partial|F_c|}{\partial u_j}\right)\Big/\left(\sum_{hkl} W^2\left(\frac{\partial|F_c|}{\partial u_j}\right)^2\right). \tag{3a}$$

We have from equations (2a)

$$|F_{oc}|/F_{oc} = |F_c|/F_c\,, \tag{2b}$$

and, considering only the centro-symmetrical case, for which F is always real, formula (3a) transforms into

$$\delta u_{jc} = \varepsilon_j =$$

$$\left(\sum_{hkl} W^2\left(F_{oc}\frac{|F_{oc}|}{F_{oc}}\frac{\partial|F_c|}{\partial u_j}-|F_c|\frac{\partial|F_c|}{\partial u_j}\right)\right)\Big/\left(\sum_{hkl} W^2\left(\frac{\partial|F_c|}{\partial u_j}\right)^2\right)$$

$$=\left(\sum_{hkl} W^2(F_{oc}-F_c)\frac{\partial F_c}{\partial u_j}\right)\Big/\left(\sum_{hkl} W^2\left(\frac{\partial F_c}{\partial u_j}\right)^2\right). \tag{3b}$$

Thus the effect of introducing $|F|$ in place of F in the residual is equivalent to replacing F_o by F_{oc} in the final expression for δu_{jc}. Now,

$$F_{oc}-F_c = (F_o-F_c)+(F_{oc}-F_o)\,, \tag{4a}$$

and

$$F_{oc}-F_o = 0, \quad \text{if } \arg F_o = \arg F_c\,,$$

or

$$= -2F_o, \quad \text{if } \arg F_o \neq \arg F_c\,,$$

since the condition $\arg F_o \neq \arg F_c$ within F real implies that the sign of F_c (and therefore of F_{oc}) is opposite to that of F_o, i.e. the assumed approximation gives the wrong sign for F. Only for such reflexions is there a contribution from the term $(F_{oc}-F_o)$, which is then equal to

$$-2F_o = -2\times 2\sum_{j=1}^{n} f_j \cos v_{jo}\,, \tag{4b}$$

where f_j is a fraction of the scattering factor of the corresponding atom determined by the degeneracy in multiplicity of the atomic position.

Putting

$$f = \sum_{j=1}^{n} f_j/n, \quad N_j = f_j/f\,, \quad (N_j \sim 1)$$

we have

$$F = 2f\sum_j N_j \cos v_j \tag{4c}$$

and, on putting $v_{jo} = v_{jc}+\delta v_{jo}$, (4b) becomes

$$-2F_o = -4f\sum_j N_j(\cos v_{jc}\cos\delta v_{jo}-\sin v_{jc}\sin\delta v_{jo}). \tag{4d}$$

Also

$$F_o-F_c = 2f\sum_j N_j(\cos v_{jo}-\cos v_{jc})$$

$$= -2f\sum_j N_j(2\sin^2\tfrac{1}{2}\delta v_{jo}\cos v_{jc}+\sin v_{jc}\sin\delta v_{jo}). \tag{4e}$$

Multiplying $(F_{oc}-F_c)$ by

$$\frac{W^2}{2\pi}\frac{\partial F_c}{\partial x_i} = -2W^2 f N_i\frac{h}{a}\sin v_{ic}\,,$$

using equations (4a), (4d) and (4e), and summing over h, k, l, we obtain

$$\frac{1}{2\pi}\sum_{hkl} W^2(F_{oc}-F_c)\frac{\partial F_c}{\partial x_i}$$

$$= 4\sum_{hkl} W^2f^2\sum_j N_iN_j(h/a)\sin v_{ic}(2\sin^2\tfrac{1}{2}\delta v_{jo}\cos v_{jc}+\sin\delta v_{jo}\sin v_{jc})$$

$$+ 8\sum_{hkl}{}' W^2f^2\sum_j N_iN_j(h/a)\sin v_{ic}(\cos\delta v_{jo}\cos v_{jc}-\sin\delta v_{jo}\sin v_{jc}),$$

where $\sum'$ denotes a summation over those reflexions for which F_o and F_c have opposite signs. We have, with a fairly large number of terms in the summation (symmetrical over positive and negative hkl), and, for orthogonal axes,

$$\overline{\sin v_{jc}\sin v_{ic}} = 0 \quad \text{for} \quad i \neq j\,,$$

$$\overline{\cos v_{jc}\sin v_{ic}} = 0 \quad \text{for all } i, j\,,$$

whence it follows that

$$\frac{1}{2\pi}\sum_{hkl} W^2(F_{oc}-F_c)\frac{\partial F_c}{\partial x_i} = 4\overline{\sin^2 v_{ic}}\sum_{hkl} W^2 f^2 N_i^2 (h/a)\sin\delta v_{io} - 8\overline{\sin^2 v_{ic}}\sum_{hkl}' W^2 f^2 N_i^2 (h/a)\sin\delta v_{io}\,.$$

(Oblique axes can be treated as in § 7, Qurashi & Vand, 1953.) A little thought shows that no correlation exists between the value of $\sin^2 v_{ic}$ and the agreement or otherwise of the signs of F_o and F_c for the corresponding reflexions. (This is discussed in detail later in Appendix 2.) It follows that the two averages for $\sin^2 v_{ic}$ have the same value, and therefore, using $f_i = fN_i$,

$$\frac{1}{2\pi}\sum_{hkl} W^2(F_{oc}-F_c)\frac{\partial F_c}{\partial x_i} = 4\overline{\sin^2 v_{ic}}\Big(\sum_{hkl} W^2 f_i^2 (h/a)\sin\delta v_{io} - 2\sum_{hkl}' W^2 f_i^2 (h/a)\sin\delta v_{io}\Big)\,. \qquad (5a)$$

Suppose that in a small range of h, k, l, a fraction β_{hkl} of the total number of reflexions (in that range) has F_o and F_c of opposite signs. Then (5a) gives

$$\sum_{hkl} W^2(F_{oc}-F_c)\frac{\partial F_c}{\partial x_i} = 4\overline{\sin^2 v_{ic}}\sum_{hkl} W^2 f_i^2 (1-2(\beta_{hkl}\pm\Delta\beta))\times 2\pi(h/a)\sin\delta v_{io}\,, \qquad (5b)$$

where $\Delta\beta$ takes account of statistical fluctuations. Its effect is further discussed in Appendix 2.

Using the fact that

$$\sum_{hkl} W^2\left(\frac{\partial F_c}{\partial x_i}\right)^2 = 4\sum_{hkl} W^2 f_i^2 \times 4\pi^2(h^2/a^2)\sin^2 v_{ic}\,,$$

we obtain from equations (3b) and (5b)

$$\delta x_{ic} = \Big(\sum_{hkl} W^2 f_i^2 (1-2\beta_{hkl}) 2\pi(h/a)\sin\delta v_{io}\Big)\Big/\Big(\sum_{hkl} W^2 f_i^2 . 4\pi^2(h^2/a^2)\Big)\,.$$

The efficiency of the steepest-descents formula for the coordinate x_i can now be written as

$$\eta_{S.D.}(x_i) = \frac{\delta x_{ic}}{\delta x_{io}} = \Big(\sum_{hkl} W^2 f_i^2 (1-2\beta_{hkl}) h\sin\delta v_{io}\Big)\Big/\Big(\sum_{hkl} W^2 f_i^2 h(2\pi(h/a)\delta x_{io})\Big)\,, \qquad (6a)$$

$$= \frac{\sum_{hkl} W^2 f_i^2 (1-2\beta_{hkl}) h\sin\delta v_{io}}{\sum_{hkl} W^2 f_i^2 (1-2\beta_{hkl}) h(2\pi(h/a)\delta x_{io})} \times \frac{\sum_{hkl}(1-2\beta_{hkl}) W^2 f_i^2 h^2}{\sum_{hkl} W^2 f_i^2 h^2}\,,$$

$$= \eta_{T,\beta}(x_i)\times\eta_F(x_i)\,,$$

where

$$\eta_{T,\beta}(x_i) = \Big(\sum_{hkl} W^2 f_i^2 (1-2\beta_{hkl}) h\sin\delta v_{io}\Big)\Big/\Big(\sum_{hkl} W^2 f_i^2 (1-2\beta_{hkl}) h\,\delta v_{io}\Big)\,, \qquad (6b)$$

since replacement of $2\pi(h/a)\delta x_{io}$ by δv_{io} does not affect the result, and

$$\eta_F(x_i) = \Big(\sum_{hkl}(1-2\beta_{hkl}) W^2 f_i^2 h^2\Big)\Big/\Big(\sum_{hkl} W^2 f_i^2 h^2\Big)\,. \qquad (6c)$$

Let us suppose for a moment that the signs of all the F_o's are correctly known; then $\beta_{hkl}\equiv 0$, and therefore $\eta_F \equiv 1$; also in this case $\eta_{T,o}(=\eta_{S.D.})$ becomes the efficiency of the modified steepest-descents formula discussed elsewhere (Qurashi & Vand, 1953), where the subscript 'T' is used because $\eta_{T,o}$ is analogous to the efficiency of the first term of a Taylor series as an approximation to the series (curves for $\eta_{T,o}$ in Fig. 2). It can be shown (after Cochran, 1948) that the structure obtained by *one* Fourier synthesis in the centro-symmetric case is the same as that to which the steepest-descents method converges, if, instead of F_o, we use F_{oc} *as defined by the initially assumed structure*. This suggests that the quantity $\eta_F(x_i)$ gives at least approximately the efficiency ($\eta_{F.S.}$) of the Fourier synthesis method; this will be discussed further in Part II of this paper, and the subscript 'F' has been used here for η_F because of this relationship. It is interesting to note that η_F is independent of δx_j, etc., individually, and that (when $\beta_{hkl}\neq 0$) $\eta_{T,\beta}$ differs from the $\eta_{T,o}$ previously discussed in that the weight, W, is now replaced by

$$W' = W(1-2\beta_{hkl})^{1/2}\,.$$

Also we see from (6c) that η_F is in fact a specially-weighted mean value of $(1-2\beta_{hkl})$, averaged over the reflexions used. In order to evaluate η_F it is necessary to obtain an expression for β_{hkl}.

Before doing this, it is pertinent to remark that the modified steepest-descents formulae (3) are identical with the results obtained by the (linear) method of least squares, when the small cross-product terms are ignored (cf. Qurashi, 1949); also, the effect of the cross-product terms can be taken into account by means of an overlap coefficient, α_{ij}, (cf. § 3, Qurashi & Vand, 1953), so that

$$\delta x_{ic} = \eta_F\times(\eta_T(x_i)\delta x_{io} + \sum_{j\neq i}\alpha_{ij} f_j/f_i\,\eta_T(x_j)\delta x_{jo})\,,\ \text{etc.,} \qquad (6d)$$

where η_F is the same for all the atoms and η_T varies only slightly from atom to atom (§ 5 below) and is identical with the corresponding coefficient in the appropriately weighted least-squares solution. It follows that the least-squares solution will give the values of

$$\eta_F\eta_T(x_i)\delta x_{io} = \eta_{S.D.}\delta x_{io}\,,$$

so that

$$\eta_{L.S.} = \eta_{S.D.}\,, \qquad (6e)$$

and the formulae (6) and other formulae derived from them later will also be valid for the method of least squares (cf. also the discussion on page 581).

4. Evaluation of β_{hkl}

We now derive an expression for β_{hkl}.

Equation (4c) gives

$$\overline{|F_o|^2} = 4f^2\overline{(\sum_j N_j \cos v_{jo})^2}$$
$$= 4\,\overline{\cos^2 v_{jo}} f^2 \sum_j N_j^2 = 2f^2 \sum_j N_j^2 ,$$

and

$$\overline{|\delta F|^2} = \overline{(F_o - F_c)^2} = 4f^2\overline{(\sum_j N_j (\cos v_{jo} - \cos v_{jc}))^2}$$
$$= 4f^2\overline{(\sum_j -N_j \times 2 \sin v_{jm} \sin \tfrac{1}{2}\delta v_{jo})^2}$$
$$= \sum_j 4\,\overline{\sin^2 \tfrac{1}{2}\delta v_{jo}} . 4f^2 N_j^2 \overline{\sin^2 v_{jm}}$$
$$= 4\,\overline{\sin^2 \tfrac{1}{2}\delta v_o} . 2f^2 \sum_j N_j^2 .$$

($v_{jm} \equiv \frac{1}{2}(v_{jo}+v_{jc})$; $\overline{\sin^2 \frac{1}{2}\delta v_o} \equiv \sin^2 \frac{1}{2}\delta v_{jo}$ averaged over all j and some hkl.)

Thus

$$\sqrt{(\overline{|\delta F|^2})} \,/\, \sqrt{(\overline{|F_o|^2})} = 2\sqrt{(\overline{\sin^2 \tfrac{1}{2}\delta v_o})} = \gamma' ,$$

and is somewhat analogous to the customary 'figure of merit' for a structure.

It can be seen in a general way that approximately

$$\beta_{hkl} \propto \sqrt{(\overline{|\delta F|^2})} \,/\, \sqrt{(\overline{|F_o|^2})} = \gamma' , \qquad (7a)$$

and therefore, for small $u = \sqrt{((\delta v_o)^2)}$,

$$\beta_{hkl} \propto u . \qquad (7b)$$

The constant of proportionality and the exact expression for β_{hkl} have to be derived from a consideration of the statistical distribution of the F's and the errors $(F_o - F_c)$. This is done in Appendix 1, and the validity of the assumptions and approximations made in the analysis is discussed in Appendix 2. In Fig. 8, $\beta_\theta \equiv \beta_{hkl}$ is graphed as a function of u. Also, u is shown (in Appendix 2) to be equal to

$$2\pi\Delta/d_{hkl} = (4\pi/\lambda . \Delta) \sin\theta ,$$

where

$$\Delta^2 = \overline{(\delta x)^2} = \overline{(\delta y)^2} = \overline{(\delta z)^2} .$$

5. Evaluation of $\eta_{S.D.}$

We can now calculate $\eta_{S.D.}$ numerically as a function of u_0 and U, the minimum and maximum values of u, assuming that all reflexions between the corresponding Bragg angles, θ_0 and Θ, are used. Using the results of the analysis for η_T (Qurashi & Vand, 1953), we take $W^2f^2 = d^\nu$, ($\nu \sim n+2$ for an n-dimensional summation). We shall consider in detail the cases $\nu - n = 2$ (optimum value), and $\nu - n = 1$. The smaller value is desirable for the later stages of refinement in order to make full use of the high-angle reflexions. Since $f_i/f = N_i$ does not in general vary greatly in the useful range of $\sin\theta/\lambda$ (Harker & Kasper, 1948), we replace f_i by f in formulae (6); any significant variation of N_i can be allowed for by varying the index, ν. (It will appear from the curves for η_F in Figs. 1(a) and 1(b) that the effect of this variation is usually unimportant.)

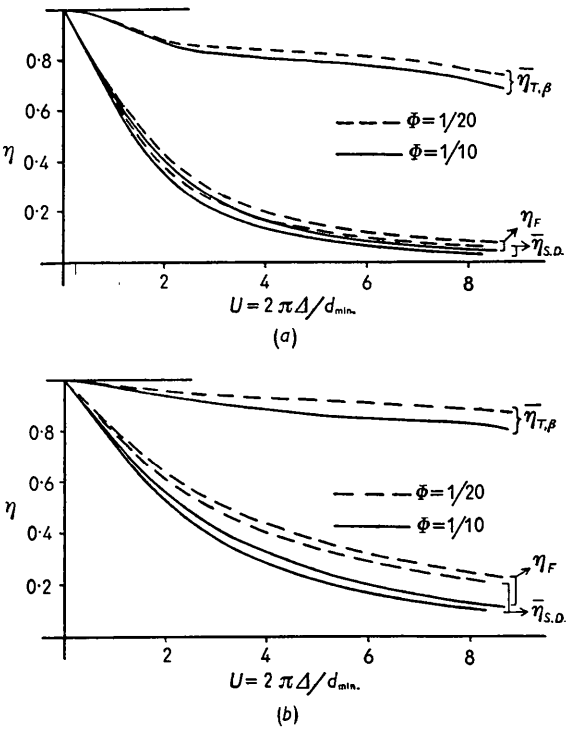

Fig. 1. Curves for $\bar{\eta}_{T,\beta}$, η_F and $\bar{\eta}_{S.D.}$, against $U = 2\pi\Delta/d_{\min.}$ for a one-dimensional summation with (a) $W^2f^2 = d^2$, (b) $W^2f^2 = d^3$.

(a) The one-dimensional case

Using the symbol $\eta^{n,\nu}$ to denote the value of η for an n-dimensional summation with $W^2f^2 = d^\nu$, we have, on replacing the summation by an integration (valid in most practical cases, e.g. the error in $\eta_{S.D.}$ is less than 0·02 when $\Delta/a = 0{\cdot}1$),

$$\eta_{T,\beta}^{1,\nu}(x_i) = \int_{u_0}^{U} (1-2\beta_\theta) u^{2-\nu} \frac{\sin u'}{u'} du \Big/ \int_{u_0}^{U} (1-2\beta_\theta) u^{2-\nu} du , \qquad (12a)$$

where

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

$$u_0/U \simeq (h_0 - \tfrac{1}{2})/H \simeq d_{\min.}/d_{\max.} ,*$$

and

$$\eta_F^{1,\nu}(x_i) = \int_{u_0}^{U} (1-2\beta_\theta) u^{2-\nu} du \Big/ \int_{u_0}^{U} u^{2-\nu} du . \qquad (12b)$$

Putting $u_0/U = \Phi$, we obtain, after simplification, the following series

* For exact equivalence of the summations and the integrals,

$$u_0 \simeq 2\pi \frac{\Delta}{a}\left(h_0 - \tfrac{1}{2} + \tfrac{1}{12}\frac{\nu-2}{2h_0-1}\right), \qquad U \simeq 2\pi \frac{H+\frac{1}{2}}{a}\Delta .$$

$$\left.\begin{aligned}\eta_F^{1,2} &= 1-\frac{U}{\pi}(1+\Phi)\left(1-\frac{U^2}{24}(1+\Phi^2)+\ldots\right),\\ \eta_F^{1,3} &= 1-\frac{U}{\pi}\frac{2(1-\Phi)}{\log 1/\Phi}\left(1-\frac{U^2}{36}(1+\Phi)+\ldots\right).\end{aligned}\right\} \quad (13)$$

Curves for η_F with $\Phi = 1/10$ and $1/20$ are drawn in Fig. 1. It should be noted that the portion $U < \pi$ is the most important, since with $U = \pi$, the reliability index, $R = \Sigma||F_o|-|F_c||\div\Sigma|F_c|$, is of the order of 70% as against the limiting value of 83% (Luzzati, 1952). Also, it is shown below that the η-curves can be used unambiguously only in the region $\eta_{S.D.} > 0{\cdot}5$ or $U < \frac{1}{2}\pi$ approximately. Comparison of the η_F-curves with those for $\eta_{T,O}(\beta_\theta \equiv 0$; shown in Fig. 2)

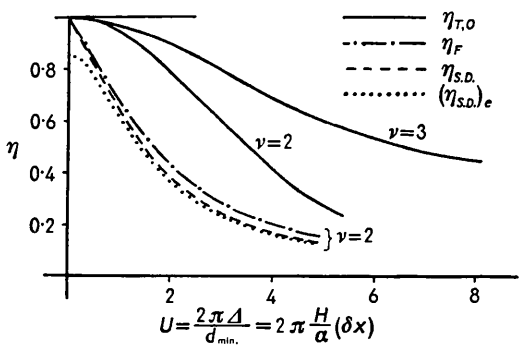

Fig. 2. Comparative curves for $\eta_{T,O}$, η_F, and $\eta_{S.D.}$ in a typical case with $\Phi = 1/20$. The curve labelled $(\eta_{S.D.})_e$ includes allowance for the effect of unobserved reflections (§ 6).

indicates that η_F is the dominant quantity in determining the curve for $\eta_{S.D.}$ $(= \eta_F \cdot \eta_{T,\beta})$ especially when $U < \pi$. This suggests that in calculating $\eta_{T,\beta}$, it is sufficient to put

$$|\delta x_i| = \sqrt{(\overline{(\delta x)^2})} = \Delta\,.$$

$(\sin u)/u$ now replaces $(\sin u')/u'$ in equation (12*a*), and we get

$$\overline{\eta_{T,\beta}^{1,\nu}} = \int_{u_0}^{U}(1-2\beta_\theta)u^{2-\nu}\frac{\sin u}{u}\,du \Big/ \int_{u_0}^{U}(1-2\beta_\theta)u^{2-\nu}du \simeq \eta_{T,O}^{1,\nu} \quad \text{for } U < \tfrac{1}{2}\pi\,. \quad (12c)$$

(Deviations of the actual $|\delta x_i|$'s from Δ can be taken account of sufficiently accurately by drawing the curve for $\eta_{T,\beta}$ from the following characteristics: (1) $\eta_{T,\beta}(U) \simeq \eta_{T,O}(U')$ for small U' where $U'/U = |\delta x_i|/\Delta$, (2) $\eta_{T,\beta}(U) \simeq \eta_{T,O}(\frac{1}{4}U)$ for large U', and (3) the transition from (1) to (2) occurs at about $U = 2{\cdot}5$.) The first two terms in the power series for $\eta_{S.D.}$ are identical with those in the corresponding series (13) for η_F.

Curves for $\overline{\eta_{T,\beta}}$ and $\overline{\eta_{S.D.}}$ are also shown in Fig. 1. The rapid fall of $\eta_{S.D.}$ for large U is remarkable; although the primary radius of convergence R_1 (defined as the value of $u_0 = U \times \Phi$, for which $\overline{\eta_{S.D.}}$ first becomes zero (cf. Qurashi & Vand, 1953)) is not greatly affected, an important effect appears when $\eta_{S.D.}$ is plotted against $U_c = U \times \eta_{S.D.} = 2\pi\Delta_c/d_{\min.}$, Δ_c being $\sqrt{(\varepsilon_i^2)}$, where ε_i is what would be obtained from the steepest-descents formula (3*b*). The curves (cf. Fig. 3) now give a double solution for $\eta_{S.D.}$ throughout

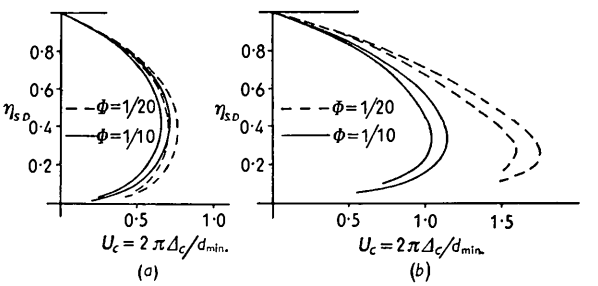

Fig. 3. Curves for $\eta_{S.D.}$ against $U_c = 2\pi\Delta_c/d_{\min.}$ for n-dimensional summations with (*a*) $W^2f^2 = d^{n+1}$, (*b*) $W^2f^2 = d^{n+2}$; the outer pair of curves is for $n = 1$ and the inner pair for $n = 3$.

the usable range $(u_0 < R_1)$. In order to use the η-curves to correct for low efficiency, it is necessary to know which solution to use. In some cases we may have other evidence, e.g. from an analysis of the reliability factor (Luzzati, 1952), which indicates the upper branch of the curve; a general criterion can be obtained as follows:

Suppose we begin with an approximate structure with known $\delta x_i = \delta$. The first refinement gives $\varepsilon_1 = \eta(\delta)\times\delta$; the second will give $\varepsilon_2 = \eta(\delta-\varepsilon_1)\times(\delta-\varepsilon_1)$. If we plot $\eta(\delta-\varepsilon_1)$ against the 'convergence ratio'

$$\varrho = \varepsilon_2/\varepsilon_1 = \eta(\delta-\varepsilon_1)\times(\delta/\varepsilon_1-1) = (1/\eta(\delta)-1)\eta(\delta-\varepsilon_1)\,,$$

it turns out that the curve will give the value of $\eta_{S.D.}$ uniquely, provided $\varrho < 1$; the region of multiple solutions lies at $\varrho > 1$. (For large U, ϱ tends to a limit greater than unity.) Such curves can be derived from those already drawn, and are shown in Fig. 4. When $\varrho \geqq 1$ or $\simeq 1$, it is safe to assume that $\eta_{S.D.} \leqq (\eta_{S.D.})_{\varrho=1}$, and it will always be useful to employ this value $(\sim 0{\cdot}5)$ of η to speed up the convergence in such cases, without any risk of overshooting the correct structure; this is equivalent to doubling the shifts obtained from formula (3*b*). As the

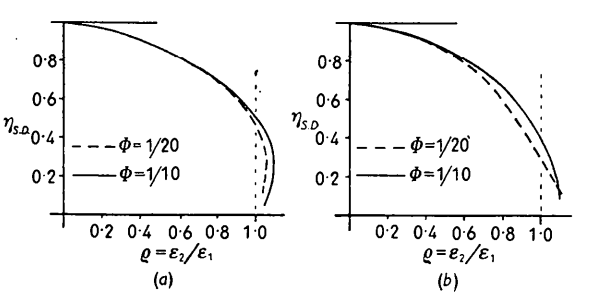

Fig. 4. Curves for $\eta_{S.D.}$ against the convergence ratio, $\varrho = \varepsilon_2/\varepsilon_1$ for n-dimensional summations with (*a*) $W^2f^2 = d^{n+1}$, (*b*) $W^2f^2 = d^{n+2}$.

correct structure is approached, the value of ϱ will drop significantly below unity, and we can then obtain the correct value of $\eta_{S.D.}$ from the curves of Figs. 3 or 4; use of this value should theoretically give the final structure in one step. However, when ε_i is obtained from formula (3*b*), in deriving which cross-product terms are ignored, the value of $\eta_{S.D.}$ is subject to a statistical error of the order of $\frac{1}{2}\sqrt{(n/N)}$, where n is the number of atoms involved and N is the number of reflexions used in the summation. This will leave us with a small residual error to be removed by further refinement. If, as in the least-squares method, the cross-product terms are included, this error is reduced to a negligibly small value. Finally, it should be mentioned that in practical applications it would be better to use an average value of ϱ, namely

$$\bar{\varrho} = \sqrt{(\overline{\varepsilon_2^2})}/\sqrt{(\overline{\varepsilon_1^2})} = (\Delta_c)_2/(\Delta_c)_1 .$$

Since we cannot correct for the small efficiency in the region of multiple solutions, it is important to study its extent and to minimize it. When $\bar{\varrho} = (\Delta_c)_2/(\Delta_c)_1 = 1$, the mean of the values of U for the two refinements used to determine $\bar{\varrho}$ corresponds to the maximum of U_c (cf. Fig. 3), and we use this to define a secondary radius of (rapid) convergence as

$$R_2 = (u_0)_{U_c=\max.} = \Phi \times (U)_{U_c=\max.} .$$

Calculation gives the following approximate values for R_2:

ν:	1	2	3	4	...	∞
R_2:	$\pi\Phi(1-\sqrt{2\Phi})$	$\pi\Phi(1-\sqrt{2\Phi})$	0·36	0·44	...	0·62

For $\nu \geqq 3$, R_2 is seen to be independent of $\Phi = u_0/U$, the variation with ν being

$$R_2 \simeq \frac{\pi}{5}\frac{\nu-2}{\nu-1}, \qquad (\nu \geqq 3) .$$

Thus $\nu = 3$ is important as being the smallest index that makes R_2 independent of Φ; further increase of ν will increase R_2 slowly, this increase being more than offset by the rapidly increasing overlapping (cf. Fig. 4, Qurashi & Vand, 1953) between distant atoms.

(b) n-Dimensional summations

For a three-dimensional summation, we consider integration over three variables, $u_1 = 2\pi(h/a)\Delta$, $u_2 = 2\pi(k/b)\Delta$, $u_3 = 2\pi(l/c)\Delta$, so that

$$u^2 = \overline{(\delta v)^2} = u_1^2+u_2^2+u_3^2 .$$

Then

$$\eta_F^{3,\nu}(x_i) = \iiint (1-2\beta_\theta)u^{-\nu}u_1^2 du_1 du_2 du_3 \Big/ \iiint u^{-\nu}u_1^2 du_1 du_2 du_3 .$$

In order to integrate over a spherical annulus from $u = u_0$ to $u = U$, we first consider a narrow annulus of radius u and thickness du; we perform the integration with respect to u_1 over this annulus and obtain, after putting $u_1/u = \sin\omega$,

$$\eta_F^{3,\nu}(x_i) = \int_{u_0}^{U}(1-2\beta_\theta)u^{-\nu}\left(\int_{-u}^{+u} u_1^2 . 2\pi u \cos\omega \frac{du_1}{\cos\omega}\right) du \Big/ \int_{u_0}^{U} u^{-\nu}\left(\int_{-u}^{+u} u_1^2 . 2\pi u \cos\omega \frac{du_1}{\cos\omega}\right) du$$

$$= \int_{u_0}^{U}(1-2\beta_\theta)u^{4-\nu}du \Big/ \int_{u_0}^{U} u^{4-\nu}du , \qquad (14)$$

which is precisely the expression (12*b*) for $\eta_F^{1,\nu}(x_i)$ with $\nu-2$ in place of ν.

Thus

$$\eta_F^{3,\nu} \equiv \eta_F^{1,\nu-2}, \text{ and similarly } \eta_F^{2,\nu} \equiv \eta_F^{1,\nu-1},$$

so that $\eta_F^{n,\nu}$ curves with a given value of $(\nu-n)$ are identical; since $\eta_{T,\beta}$ has only a small effect on $\eta_{S.D.}$, the discussion of the one-dimensional case will apply to n-dimensional summations on replacing $(\nu-1)$ by $(\nu-n)$.

Next consider $\eta_{T,\beta}^{3,\nu}$. Transforming the axes to make the x-axis parallel to the resultant displacement δ_i of the ith atom, and writing $u_1' = (\delta_i/\Delta)u_1$, we have

$$\eta_{T,\beta}^{3,\nu}(x_i) = \iiint u^{-\nu}(1-2\beta_\theta)u_1^2 \frac{\sin u_1'}{u_1'} du_1 du_2 du_3 \Big/ \iiint u^{-\nu}(1-2\beta_\theta)u_1^2 du_1 du_2 du_3$$

$$= \int_{u_0}^{U}(1-2\beta_\theta)u^{1-\nu}\left(\int_{-u}^{+u} u_1^2 \frac{\sin u_1'}{u_1'} du_1\right) du \Big/ \int_{u_0}^{U}(1-2\beta_\theta)u^{1-\nu}\left(\int_{-u}^{+u} u_1^2 du_1\right) du .$$

Ignoring the variation of δ_i as before, and taking its r.m.s. value $\sqrt{(\overline{\delta_i^2})} = \sqrt{3}.\Delta$, we get

$$\overline{\eta_{T,\beta}^{3,\nu}} = \int_{u_0}^{U}(1-2\beta_\theta)u^{4-\nu}\left(\frac{3}{2}\int_{-u}^{+u}\frac{u_1^2}{u^2}\frac{\sin \sqrt{3}.u_1}{\sqrt{3}.u_1}\frac{du_1}{u}\right) du \Big/ \int_{u_0}^{U}(1-2\beta_\theta)u^{4-\nu}du .$$

Curves for $\overline{\eta_T^{3,\nu}}$ are drawn in Fig. 5 as functions of U and of $U_3 = \sqrt{3}.U$; for $|\delta_i| \neq \sqrt{3}\Delta$, the dependence on U' (now $= (\delta_i/\Delta)U$) is much the same as in one dimension. Curves for $\overline{\eta_{S.D.}^{3,\nu}}$ are shown in Fig. 3 alongside the one-dimensional curves; the curves for $\overline{\eta_{S.D.}^{3,\nu}}$ against ϱ are too close to the corresponding one-dimensional curves to be shown separately, and therefore mean curves ($\overline{\eta_{S.D.}}$ correct to within $\pm 0{\cdot}010$ for $n = 1$ to 3) are drawn in Fig. 4.

6. Effect of unobservably weak reflexions

When some of the reflexions are unobservably weak and it is desired to include them (e.g. to obtain a more representative value of the coordinates), the effect on η can be estimated as follows:

From equation (4*a*), replacement of any F by zero has half the effect of reversing its sign. If, therefore,

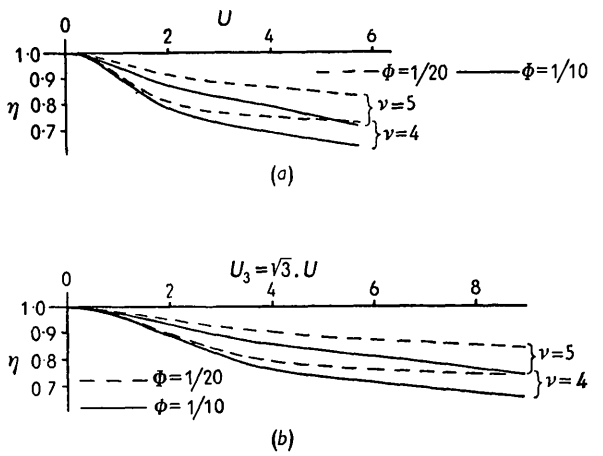

Fig. 5. Curves for $\bar{\eta}_{T,\beta}$ as a function of (*a*) U, (*b*) $\sqrt{3}U$, for a three-dimensional summation; the curves of Fig. 5(*b*) are to be compared with the corresponding $\eta_{T,O}$ curves (Fig. 6(*a*), Qurashi & Vand, 1953).

there is a fraction $\beta_{1\theta}$ of such reflexions in a small range of Bragg angles, the effective value of β_θ becomes

$$(\beta_\theta)_e = \tfrac{1}{2}\beta_{1\theta}+\beta'_\theta ,$$

where β'_θ is β_θ evaluated for the measured reflexions only. Knowing β_θ, β'_θ can be calculated and a corrected η-curve can be obtained; η at $U = 0$ for such a curve is given by

$$1-\overline{\beta_{1\theta}} = 1-\Big(\sum_{hkl}\beta_{1\theta}W^2f^2h^2\Big)\Big/\Big(\sum_{hkl}W^2f^2h^2\Big) .$$

A typical curve with $\overline{\beta_{1\theta}} = 0{\cdot}15$ is shown in Fig. 2; it is clear that the effect of $\beta_{1\theta}$ is appreciable only for small U.

7. Application of the results

We consider the convergence of successive refinements in a *somewhat extreme* three-dimensional case, and show how the above analysis can be utilized to shorten the work. We take $\Phi \simeq d_{\min.}/d_{\max.} = 1/10$, Initial $U = 2\pi\Delta/d_{\min.} = 8$, ($\Delta = \sqrt{(\overline{\Delta_j^2})}$, Δ_j = r.m.s. error per coordinate in jth atom), and $\Delta_j = \Delta$ for simplicity; so that $\Delta/d_{\min.} = 1{\cdot}273$, and, with $d_{\min.} = \frac{1}{2}\lambda_{\mathrm{Mo}\,K} = 0{\cdot}355$ Å, this gives $\Delta = 0{\cdot}45$ Å. The process of refinement is shown in Table 1; clearly we do not need to go beyond the tenth refinement. For smaller initial values of U, one can start from an intermediate column of Table 1. The diminution in Δ per refinement is seen to increase steadily from 0·04 Å to 0·06 Å and then to drop rapidly to zero—this is often observed in a series of Fourier syntheses.

Table 2 shows the convergence speeded up by multiplying the calculated corrections by the factor K (~ 2) when $\bar{\varrho} \sim 1$, and by $1/\overline{\eta_{S.D.}}$ when $\bar{\varrho} < 1$. (It is to be noted that when $K > 1$ we cannot obtain $\bar{\varrho}$ as defined; instead we use

$$\sqrt{(\bar{\varrho}_m\bar{\varrho}_{m-1})} \simeq ((\Delta_c)_m/(\Delta_c)_{m-1})^{1/K} = ((U_c)_m/(U_c)_{m-1})^{1/K} ,$$

from which all the $\bar{\varrho}_m$'s can be obtained since $\bar{\varrho}_2$ is known directly.) It is seen that the number of refinements required is approximately halved, allowing for a possible fluctuation of 0·10 in the value of $\overline{\eta_{S.D.}}$ used in the last refinement.

Another possible application is to terminate a Fourier series (or other refinement technique) at a suitable upper limit of indices so as to obtain a large value of η. From Luzzati's analysis (1952) of the dependence of the reliability index on $\sin\theta/\lambda$ and on Δ, it is easy to estimate the value of Δ. This can then be used to fix the minimum d_{hkl} so that

$$2\pi\Delta/d = U < \tfrac{1}{2}\pi ,$$

i.e.

Table 1. *Normal process of refinement of a typical structure*

m=no. of refinement	1	2	3	4	5	6	7	8	9	10	11
Initial $U=U_i$	8·00	7·36	6·66	5·88	5·03	4·09	3·08	2·04	1·06	0·314	0·028
$\eta_{S.D.}$	0·080	0·095	0·117	0·145	0·186	0·247	0·337	0·481	0·706	0·912	0·986
$U_c=U_i.\eta_{S.D.}$	0·64	0·70	0·78	0·85	0·94	1·01	1·04	0·98	0·75	$0{\cdot}28_6$	$0{\cdot}027_6$
Final $U=U_i-U_c$	7·36	6·66	5·88	5·03	4·09	3·08	2·04	1·06	0·314	0·028	0·0004
Final $\Delta/d_{\min.}$	1·17	1·06	0·933	0·800	0·650	0·490	0·324	0·168	0·050	0·004	—
Δ (Å)	0·415	0·375	0·332	0·284	0·231	0·174	0·115	0·060	0·018	0·002	—
$\bar{\varrho}_m=(U_c)_m/(U_c)_{m-1}$		1·10	1·11	1·09	1·10	1·08	1·03	0·96	0·77	0·38	—

Table 2. *The process of refinement of the same structure, speeded up with the aid of the theoretical η-curves*

	$K = 2{\cdot}5$					$K = 2{\cdot}0$					
m=no. of refinements	1	2	3	4	5	1	2	3	4	5	6
Calc. correction $=\Delta_c$	0·036	0·040	0·050	0·059	0·034	0·036	0·040	0·048	0·056	0·057	0·012
$\sqrt{(\bar{\varrho}_m\bar{\varrho}_{m-1})}$	—	—	1·10	1·07	0·80	—	—	1·09	1·08	1·01	0·50
$\bar{\varrho}_m$	—	1·11	1·08	1·05	0·60	—	1·11	1·08	1·08	0·96	0·26
$K\times\Delta_c$	—	0·100	0·125	0·148	(η=0·782)	—	0·080	0·096	0·112	0·114	(η=0·920)
Final Δ (Å)	0·415	0·315	0·190	0·042	0±0·005	0·415	0·335	0·239	0·127	0·013	0±0·002

$$d > 4\Delta .$$

This ensures that η is of the order of 0·5 or more. (Since $\Delta_{\max.} \sim 0{\cdot}5$ Å, it is always safe to take $d > 2$ Å.) A more rigorous discussion is given in Appendix 2(*d*).

8. Conclusion

The main results of the foregoing analysis are summarized below:

(1) When the effect of incorrect signs of the F's is included, the earlier results regarding the suitability of the power law as a weighting function and the optimum value of the index remain unchanged. For $W^2f^2 = (d_{hkl})^\nu$, the optimum value for a n-dimensional summation is $\nu = n+2$.

(2) It is found that $\eta_{L.S.} = \eta_{S.D.} = \eta_F \times \eta_{T,\beta}$, where the dominant term, η_F, (due to the incorrect signs) is the same for all n with optimum ν, and $(1-\eta_{T,\beta})$, which represents the loss of efficiency caused by the failure of the linear approximation necessary in the least-squares and steepest-descents methods, is less than about 0·25 even for large values of U.

(3) The convergence ratio ϱ of two successive refinements enables the $\eta_{S.D.}$-curves to be used practically; for $\varrho \sim 1$, or $\varrho > 1$, it is useful to multiply all calculated corrections by a factor K (2–3); for $\varrho < 1$, the precise value of $1/\eta_{S.D.}$ can be obtained from a curve and the corrections can be multiplied by this to obtain rapid convergence. This process halves the number of refinements required.

(4) When the r.m.s. error in the coordinates can be estimated, as by Luzzati's analysis, the η-curves can be used to limit the indices of the reflexions utilized and thereby ensure a high value of η.

(5) It is clear from general physical considerations, and also from the analysis for overlap (Qurashi & Vand, 1953), that the foregoing analysis is valid if $\sqrt{3}\Delta < \frac{1}{2}$ (mean interatomic distance) $\simeq 0{\cdot}5$–$1{\cdot}0$ Å.

(6) It appears that for small U, $\eta_{F.S.}$ (for the Fourier-synthesis method) is approximately equal to η_F, but since the Fourier-synthesis and least-squares methods correct their signs progressively at different values of Δ or U, the $\eta_{F.S.}$-curves for large U cannot be deduced in any simple way from those for η_F. For large U, $\eta_{F.S.}$ must be obtained by a direct process of setting up the residual, R, as a function of β, x_j, y_j, z_j, and finding the values of the coordinates that make it a minimum.

I am indebted to Dr H. Lipson for his interest and to Dr I. G. Edmunds and Dr V. Vand for valuable criticism. A large part of this work was made possible by a grant from the Government of Pakistan.

APPENDIX 1

We have first to discuss Wilson's asymptotic form of statistical distribution of the F's. Wilson (1949) has shown that with n pairs of atoms in the centrosymmetric unit cell, the distribution tends to the normal Gaussian error-function as $n \to \infty$. However, because of the marked departure of the distribution for one atom-pair (cf. Fig. 6(*a*)) from the Gaussian curve, it is desirable to consider the shape of the distribution curve for finite and small n. It is convenient to use the quantity

$$\varphi = F/f = 2\sum_j N_j \cos v_j = \sum_j \varphi_j ,$$

where $\varphi_j = 2N_j \cos v_j$ is the corresponding function for the jth atom-pair. If the jth atom is in a general position, the values of v_j for a small group of reflexions will be randomly distributed, i.e.

$$P_j(v) \equiv P_j(v_j, v_j+dv_j) = K dv_j \quad \left(K = \frac{1}{\pi} \text{ for } \int_0^\pi K dv_j = 1\right),$$

where $P_j(v_j, v_j+dv_j)$ = probability of finding v_j between v_j and v_j+dv_j.

This gives

$$P_j(v) = K|dv_j/d\varphi_j|d\varphi_j ,$$

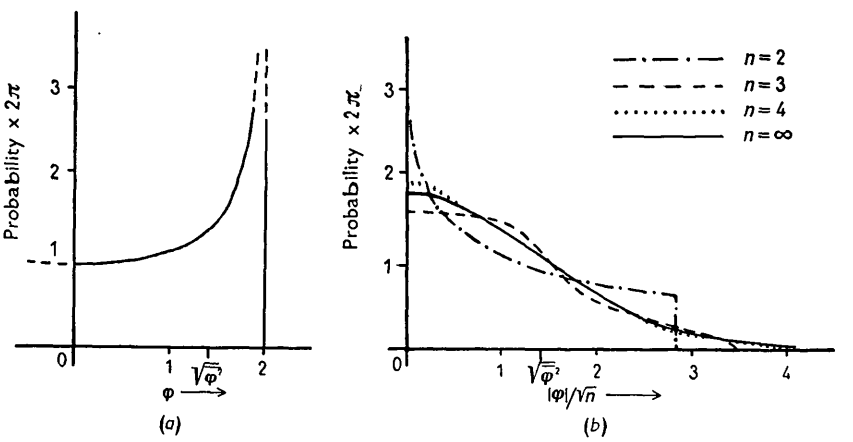

Fig. 6. Probability distribution of $\varphi = F/f$ for a centrosymmetric unit cell (or projection) with (*a*) one atom-pair, (*b*) n atom-pairs, $n = 2, 3, 4, \infty$, showing the gradual approximation to the Gaussian distribution.

whence the distribution function for φ_j is

$$\left.\begin{aligned} P_j(\varphi) &= \frac{1}{\pi}\Big/(4-\varphi_j^2/N_j^2)^{1/2}\,\frac{d\varphi_j}{N_j}\quad (2 \geqslant \varphi_j/N_j \geqslant -2)\,, \\ \text{and} \\ P_j(\varphi) &= 0\quad (-\infty < \varphi_j/N_j < -2;\ 2 < \varphi_j/N_j < \infty)\,. \end{aligned}\right\} \quad (8a)$$

A graph of the function is shown in Fig. 6(*a*); it has infinite discontinuities at $\varphi_j/N_j = \pm 2$, and is far from anything like the Gaussian distribution. The pth moment, however,

$$\mu_p = \int_{-\infty}^{+\infty} \varphi_j^p P_j(\varphi)\,,$$

is finite for all p. Application of the central-limit theorem shows that, with

$$\varphi = \sum_{j=1}^{n} \varphi_j\,,$$

we have, when $n \to \infty$,

$$P(\varphi) \equiv P(\varphi,\ \varphi+d\varphi) \propto \exp\,[-\varphi^2/2\sigma^2]d\varphi\,, \quad (8b)$$

where

$$\sigma^2 = \sum_{j=1}^{n}\int_{-\infty}^{+\infty}\varphi_j^2 P_j(\varphi) = \frac{1}{\pi}\sum_{j=1}^{n}\int_o^{\pi} 4N_j^2\cos^2 v_j dv_j = \sum_{j=1}^{n} 2N_j^2\,. \quad (8c)$$

The transition from (8*a*) to (8*b*) can be studied (assuming $N_j \simeq 1$) by (*a*) calculating $(\mu_p)_n$ for various values of n and p, and (*b*) integrating numerically and plotting the actual distribution for various values of n.

In collecting the results for (*a*) it is convenient to give the series for $r_p \equiv ((\mu_p)_n/(\mu_p)_\infty)^{1/p}$, both numerator and denominator having been reduced to a common value of $\overline{\varphi^2}$. The resulting series are given below, and the calculated distributions for $n = 2, 3, 4$ and ∞ are shown in Fig. 6(*b*); the series are derivable from the results for the random-walk problem given by Hauptman & Karle (1952), equations (10 and (71).

$$\begin{aligned} r_1 &= 1+\frac{1}{16n}+\frac{2/3}{16n^2}+\dots\,, \\ r_2 &= 1\,, \\ r_3 &= 1-\frac{1}{16n}-\frac{41/144}{16n^2}+\dots\,, \\ r_4 &= 1-\frac{2}{16n}-\frac{3/8}{16n^2}+\dots\,, \\ r_5 &= 1-\frac{3}{16n}+\frac{43/24}{16n^2}+\dots\,. \end{aligned}$$

The series and the curves clearly show that, for $n \geqq 3$, the distribution of φ is Gaussian to a high degree of accuracy; this is certainly true for $\varphi \leqq 2\sigma$, and it can be proved that the error produced in 2β (by the departure from the Gaussian curve for large φ) is $< 0{\cdot}01$. Consideration of special atomic positions shows that, except for positions with all coordinates (involved in the summation) equal to zero, there is no significant effect on the φ-distribution; an atom in the 0, 0, 0, position obviously causes the distribution to be centred about $+2N_j$ instead of zero. Special symmetry elements (cf. Wilson, 1949, 1950) affect only a limited number of reflexions; moreover, the effect on the $\delta\varphi$-distribution is similar and the net effect on β_{hkl} is again negligible.

The procedure for obtaining the $\delta\varphi$-distribution is similar to that for φ:

$$\begin{aligned} \varphi_c &= 2\sum_j N_j\cos\,(v_{jo}-\delta v_{jo}) \\ &= 2\sum_j N_j\cos v_{jo} - 2\sum_j N_j\cos v_{jo}.2\sin^2\tfrac{1}{2}\delta v_{jo} \\ &\qquad +2\sum_j N_j\sin v_{jo}\sin\delta v_{jo} \\ &= \varphi_o - 2\,\overline{\sin^2\tfrac{1}{2}\delta v_{jo}}\,\varphi_o + 2\sum_j N_j \\ &\quad \times(-\cos v_{jo}(2\sin^2\tfrac{1}{2}\delta v_{jo} - 2\,\overline{\sin^2\tfrac{1}{2}\delta v_{jo}}) + \sin v_{jo}\sin\delta v_{jo}) \\ &= \varphi_o - \gamma_1\varphi_o \pm \gamma_2\sqrt{(\overline{\varphi_o^2})}\,, \end{aligned}$$

where

$$\begin{aligned} \gamma_1 &= 2\,\overline{\sin^2\tfrac{1}{2}\delta v_{jo}}\,, \\ \gamma_2 &= \sqrt{\left((2\sin^2\tfrac{1}{2}\delta v_{jo} - 2\,\overline{\sin^2\tfrac{1}{2}\delta v_{jo}})^2 + \sin^2\delta v_{jo}\right)}\,. \end{aligned}$$

Thus

$$\delta\varphi \equiv \varphi_o - \varphi_c = \gamma_1\varphi_o \pm \gamma_2\sqrt{(\overline{\varphi_o^2})}\,. \quad (8d)$$

From this relation, Luzzati (1952) has derived the value of $R = \Sigma||F_o|-|F_c||\div\Sigma|F_c|$. The relationship between the φ_o-distribution and the $(\delta\varphi)$-distribution

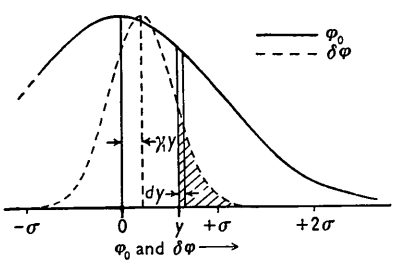

Fig. 7. Relationship between the probability distributions for φ_o and $\delta\varphi = \varphi_o - \varphi_c$; the vertical scale for $\delta\varphi$ is γ_2 times that for φ_o.

with φ_o between y and $y+dy$, is seen in Fig. 7. (The $\delta\varphi$-distribution is easily seen to be consistent with the overall distribution for $|\delta F|$ used in § 4.) The probability distribution of the second term in equation (8*d*) is Gaussian by the central-limit theorem.

Since the values of δv (especially in a two- or three-dimensional summation) are distributed approximately in a Gaussian fashion (cf. Appendix 2), explicit expressions for the γ's are readily obtained.

We put $\overline{(\delta v)^2} = u^2$, and $\delta v = \mu$, the averaging being over the reflexions in a small range of h, k, l. Then

$$\gamma_1 = 2\overline{\sin^2 \tfrac{1}{2}\delta v} = \overline{1-\cos\mu} =$$

$$\int_o^\infty (1-\cos\mu)\exp[-\mu^2/2u^2]d\mu \Big/ \int_o^\infty \exp[-\mu^2/2u^2]d\mu$$

$$= \frac{u^2}{2.1!} - \frac{u^4}{2^2.2!} + \frac{u^6}{2^3.3!} - \ldots = 1-\exp[-\tfrac{1}{2}u^2]\,. \quad (9a)$$

Now,

$$\gamma_2^2 = \overline{(2\sin^2\tfrac{1}{2}\delta v-\gamma_1)^2+\sin^2\delta v}$$
$$= 4\overline{\sin^4\tfrac{1}{2}\mu}+\gamma_1^2-2\gamma_1.2\overline{\sin^2\tfrac{1}{2}\mu}+\overline{\sin^2\mu}$$
$$= 4\overline{\sin^4\tfrac{1}{2}\mu}+\overline{\sin^2\mu}-\gamma_1^2$$
$$= 2(\overline{1-\cos\mu})-\gamma_1^2 = 1-(1-\gamma_1)^2$$
$$= 1-\exp[-u^2]\,. \quad (9b)$$

The full curve of Fig. 7, representing the φ_o-distribution, has for its equation

$$P(\varphi_o, \varphi_o+d\varphi_o) = \exp[-\varphi_o^2/2\sigma^2]d\varphi_o \Big/ \int_{-\infty}^{+\infty}\exp[-\varphi_o^2/2\sigma^2]d\varphi_o\,.$$

The equation of the $\delta\varphi$-distribution (broken line) with φ_o between $+y$ and $+(y+dy)$ will then be

$$P(\delta\varphi, \delta\varphi+d(\delta\varphi)) = \exp[-(\delta\varphi-\gamma_1 y)^2/2\gamma_2^2\sigma^2]d(\delta\varphi) \Big/ \int_{-\infty}^{+\infty}\exp[-(\delta\varphi-\gamma_1 y)^2/2\gamma_2^2\sigma^2]d(\delta\varphi)\,.$$

It follows that the fraction of the $\delta\varphi$'s that are greater than y is (cf. shaded area in Fig. 7)

$$\psi = \int_y^\infty P(\delta\varphi, \delta\varphi+d(\delta\varphi))$$
$$= \int_{\frac{1-\gamma_1}{\sqrt{2}.\gamma_2\sigma}y}^\infty \exp[-x^2]dx \Big/ \int_{-\infty}^{+\infty}\exp[-x^2]dx$$
$$= \frac{1}{\sqrt{\pi}}\int_{\frac{y}{\sqrt{2}.\gamma\sigma}}^\infty \exp[-x^2]dx\,,$$

where

$$\gamma = \gamma_2/(1-\gamma_1) = (\exp[u^2]-1)^{\frac{1}{2}}\,. \quad (9c)$$

This fraction of the φ_o's between $+y$ and $+(y+dy)$ will have their signs changed; the φ_o's between $+y$ and $+(y+dy)$ form a fraction $d\psi_\varphi = 1/(2\pi)\exp[-y^2/2\sigma^2]dy$ of the total number of φ's under consideration; thus

$$\beta_{hkl} = \int \psi d\psi_\varphi$$
$$= \frac{2}{\sqrt{2}.\pi\sigma}\int_o^\infty \exp[-y^2/2\sigma^2]dy \int_{\frac{y}{\sqrt{2}.\gamma\sigma}}^\infty \exp[-x^2]dx$$
$$= \frac{2\gamma}{\pi}\int_o^\infty \exp[-\gamma^2t^2]\int_t^\infty \exp[-x^2]dx\,dt\,.$$
$$(t = y/\sqrt{2}.\gamma\sigma)$$

These integrals depend only on γ, and therefore on u; and u is a function of h, k, l, only through the Bragg angle, θ (cf. Appendix 2 below). β_{hkl} can therefore be written as β_θ, and integrating by parts, we obtain

$$\beta_\theta \equiv \beta_{hkl} = \frac{2\gamma}{\pi}\left|\left(\int_t^\infty \exp[-x^2]dx\right)\left(\int_0^t \exp[-\gamma^2t^2]dt\right)\right|_0^\infty + \frac{2\gamma}{\pi}\int_0^\infty \exp[-t^2]\left(\int_0^t \exp[-\gamma^2t^2]dt\right)dt$$
$$= 0+\frac{2\gamma}{\pi}\left(\frac{1}{2}-\frac{1}{2}\frac{\gamma^2}{3}+\frac{1}{2}\frac{\gamma^4.2}{5.2!}-\frac{1}{2}\frac{\gamma^6.2.3}{7.3!}+\ldots\right)$$
$$= \frac{1}{\pi}\tan^{-1}\gamma\,. \quad (10a)$$

The series is convergent in the domain $0 \leqq \gamma < 1$, but the result holds for all real γ by the principle of analytical continuation. Combining (10a) with (9c), we finally get

$$\beta_\theta = \frac{1}{\pi}\tan^{-1}\sqrt{(\exp[u^2]-1)}\,. \quad (10b)$$

Curves for u/γ against u, and $2\beta_\theta$ against u are plotted in Fig. 8. By expanding β_θ in powers of u, we get

$$\beta_\theta \simeq \frac{u}{\pi}\left(1-\frac{u^2}{12}+\frac{u^4}{320}\right), \quad (10c)$$

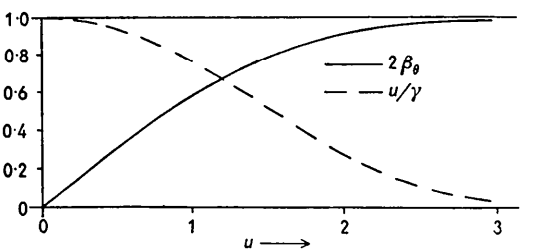

Fig. 8. u/γ and $2\beta_\theta$ as functions of u.

where the last term has been increased by a factor of 3/2; this approximation is correct to within 0·001 for $u \leqq 2$, and is useful in calculating the integrals for η_F, etc., the integral from 2 to U (> 2) being small and easily obtained numerically.

APPENDIX 2

Validity of the approximations

The simplifying assumptions and approximations made in the foregoing analysis are discussed briefly:

(*a*) It has been assumed that the δv_j's for the reflexions in a small range of h, k, l have a normal Gaussian distribution. For a one-dimensional summation, $\delta v_j = 2\pi(h/a)\delta x_j$. Now, there is a definite probability distribution of each δx_j, giving the probability that a particular δx_j lies within specified limits; a number of plausible distributions are shown in Fig. 9(*a*). The Gaussian curve is 'reasonable', ex-

cept that it is not truncated, and is in any case a close enough approximation to the others; this latter is strikingly brought out in Fig. 9(*b*) by the curves of $+2\beta_\theta$ against u for the distributions of Fig. 9(*a*).

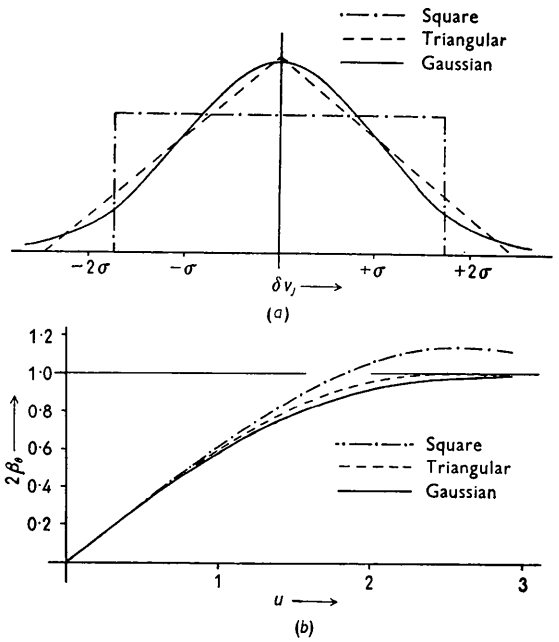

Fig. 9. (*a*) Some plausible probability distributions for δv_j. (*b*) The corresponding curves for $2\beta_\theta$ against u.

For a two-dimensional summation, $\delta v_j = 2\pi\{(h/a)\delta x_j+(k/b)\delta y_j\}$, so that, for a symmetrical summation over positive and negative h, k,

$$\overline{(\delta v_j)^2} = 4\pi^2\left(\overline{\left(\frac{h}{a}\delta x_j\right)^2}+\overline{\left(\frac{k}{b}\delta y_j\right)^2}\right).$$

For a large number of δx's and δy's, the r.m.s. errors in the x- and y-coordinates will be equal, i.e. $\overline{(\delta x)^2} = \overline{(\delta y)^2} = \Delta^2$. Thus

$$\overline{(\delta v)^2} = 4\pi^2\left(\overline{\left(\frac{h}{a}\Delta\right)^2}+\overline{\left(\frac{k}{b}\Delta\right)^2}\right) = 4\pi^2\Delta^2/d^2_{hk0},$$

whence

$$u = \sqrt{(\overline{(\delta v)^2})} = 2\pi\Delta/d_{hk0} = (4\pi/\lambda)\Delta\sin\theta, \quad (11)$$

and is a function of h, k, through the Bragg angle, θ. In this case the probability distribution of the δv_j's is smoothed out and approaches the Gaussian form more nearly because of the addition of the two symmetrical distributions of $(h/a)\delta x_j$ and $(k/b)\delta y_j$.

Similar considerations apply to the three-dimensional case.

(*b*) The validity of the tacit assumption made in deriving equations (5), that there is no correlation between the δv's and the v's, is fairly evident.

(*c*) When deriving equations (5) it was also assumed that there is no correlation between the value of $\sin^2 v_{ic}$ and the correctness or otherwise of the signs of F given by the assumed structure. Now,

$$F = 2f\sum_{j=1}^{n} N_j\cos v_j,$$

in which v_i enters in one of the n terms, and

$$\delta F = -4f\sum_{j=1}^{n} N_j\sin\tfrac{1}{2}(v_{jo}+v_{jc})\sin\tfrac{1}{2}\delta v_{jo},$$

which involves all the v_j's and δv_j's. Thus, for large n and small F's (which are the most likely to be given wrong signs), $\sin^2 v_{ic}$ is not appreciably correlated, either with F or with δF.

(*d*) In equation (5*b*), the quantity $\Delta\beta$ was inserted to cover the statistical fluctuations. These are: (1) fluctuations of $\overline{\sin^2 v_{ic}}$ about its mean value for the group of reflexions, and (2) fluctuations of β about its mean value as given by equations (10). It is easily seen that, if there are N_1 reflexions in the group, we can write

$$(N_1\Delta\beta)^2 \simeq (\tfrac{1}{2}\beta N_1+\beta N_1) = 1{\cdot}5N_1\beta.$$

Summing up over all the N reflexions, we have

$$\overline{(N\Delta\beta)^2} \simeq 1{\cdot}5N\overline{\beta},$$

whence

$$\Delta\eta = 2\sqrt{(\overline{(\Delta\beta)^2})} \simeq 2\sqrt{(1{\cdot}5\overline{\beta}/N)}$$
$$\simeq \sqrt{(3(1-\eta)/N)},$$

which is small for the useful values of η and $N(\sim 100)$. We can estimate the fraction (s) of the total number of corrections that are in the wrong direction. With $N = 300$, and a Gaussian distribution of $\Delta\eta$, we get

η:	1·0	0·5	0·2	0·15	0·10	0·05
$2s$:	0	0·00	0·04	0·12	0·30	0·61

It is also possible to find the limiting condition necessary to keep s small, say less than 0·15. This gives

$$\eta = \Delta\eta = \sqrt{\left(\frac{3(1-\eta)}{N}\right)} = \sqrt{\left(\frac{1-\eta}{0{\cdot}7}\right)}\times\frac{1{\cdot}45}{\sqrt{N}}\cdot\left(\frac{1-\eta}{0{\cdot}7}\sim 1\right).$$

For a two-dimensional summation with h_0 and $k_0\sim 1$, $u_0/U \simeq (h_0-\frac{1}{2})/H \simeq 1/\sqrt{N}$, (where u_0 and U are the minimum and maximum values of u in the summation) and therefore

$$\eta = \sqrt{\left(\frac{1-\eta}{0{\cdot}7}\right)}\times 1{\cdot}45\left(\frac{u_0}{U}\right).$$

From the two-dimensional curves corresponding to Fig. 1, the limiting values (with $U/u_0 > 1$) are:

$\nu = 3$: $u_0 \simeq 0{\cdot}35$, and $N \simeq (U/u_0)^2$ is not limited.
$\nu = 4$: $u_0 \simeq 0{\cdot}35(U/u_0)^{1/4}$, so that if $u_0 < 0{\cdot}35$, $N \simeq (U/u_0)^2$ is not limited.

For $U/u_0 \sim 10$, these limits are much the same as the corresponding radii of rapid convergence (cf. § 5) for two-dimensions. It is interesting that N is not

limited when $\nu = 3$ or 4. This occurs because the rate of decrease of η with increasing U is equal to or less than that of $\Delta\eta$, and it confirms the suitability of these indices.

References

COCHRAN, W. (1948). *Acta Cryst.* **1**, 138.
HARKER, D. & KASPER, J. S. (1948). *Acta Cryst.* **1**, 70.
HAUPTMAN, H. & KARLE, J. (1952). *Acta Cryst.* **5**, 48.
LUZZATI, V. (1952). *Acta Cryst.* **5**, 802.
QURASHI, M. M. (1949). *Acta Cryst.* **2**, 404.
QURASHI, M. M. & VAND, V. (1953). *Acta Cryst.* **6**, 341.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.
WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 258.

Acta Cryst. (1953). **6**, 588

Calculated Powder Patterns from Very Small Crystals: Body-Centered Cubic Cubes

BY CHANG MOROZUMI

Computing Service, Department of Mathematics, University of Wisconsin, Madison, Wisconsin, U.S.A.

AND H. L. RITTER*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

(*Received* 30 *September* 1952)

The X-ray scattering patterns of several cubic arrays of points arranged on a body-centered cubic lattice have been computed according to the Debye scattering formula, $I = \sum_i \sum_j (\sin r_{ij}s)/r_{ij}s$ and plotted as a function of $t = as$, where a is the unit translation of the lattice.

The dependence upon the scattering angle of X-ray intensity scattered from an assemblage of crystals in the Debye–Scherrer arrangement may be described in terms of Bragg's Law; or alternatively in terms of the Debye scattering formula

$$I(s) = \sum_i \sum_j f_i f_j \frac{\sin r_{ij}s}{r_{ij}s} ,$$

where $s = (4\pi/\lambda) \sin \frac{1}{2}\theta$. When the discrete crystallites making up the assemblage are large (of the order of tens of thousands of unit cells or more), these two relations give identical positions of maximum intensity. As the crystallites become smaller, the familiar line-broadening effect appears. In addition to the actual broadening of the powder lines, this effect includes also a loss of resolution between adjacent lines, coalescence of adjacent lines, and disappearance of both the weaker lines and the lines occurring at high θ. Numerous investigations into the relation between amount of peak-broadening and size of crystallite have been published. The companion questions: of minimum crystallite size for the appearance of a given (weak) line; of minimum crystallite size for the resolution of two or more adjacent lines; of the size below which the finer details of the pattern are absorbed into the background scattering; and of the preferential suppression of diffraction detail as the crystallites are asymmetrically reduced in size or the preferential appearance of characteristic lines as the crystallites are enlarged in preferred directions: have been more neglected.

Probably the conceptually most satisfactory answer to these questions is obtained by actual calculation of the scattering patterns characteristic of crystalline assemblages of appropriate dimensions. It is then possible to inspect plots of the Debye scattering function for a series of crystallite sizes and shapes, and to form a coherent and detailed mental picture of the gradual transition from the diffuse and characterless haloes of the patterns from very tiny crystallites to the family of discrete lines characteristic of indefinitely large crystallites. The availability of high-speed computing machines makes the task of numerical evaluation of the Debye scattering function rather less formidable than it once was, even for relatively large crystallites.

The present communication presents the results of such calculations for the case of body-centered cubic homoatomic crystallites, cubic in shape, and ranging from one unit cell (nine atoms) to a cube of 1000 unit cells (2331 atoms). Plots of this kind have already been published by Germer & White (1941) and by James (1948). The results of Germer & White cover the case of face-centered cubic assemblages. Their calculations were spaced at considerably larger intervals than in the present paper, however, with the result that the background is not well-delineated; and

* To whom inquiries concerning this article should be addressed at: Department of Chemistry, Miami University, Oxford, Ohio, U.S.A.