Acta Cryst. (1955). 8, 445

An Analysis of the Efficiency of Convergence of Different Methods of Structure Determination. II. The Method of Fourier Synthesis: Centrosymmetric Case

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(*Received* 15 *October* 1954)

A discussion of the rate and 'efficiency' of convergence of the method of Fourier synthesis is presented for the case of *large departures* of the assumed approximation from the correct structure. The Fourier synthesis is first reduced to its *exactly* equivalent minimum-residual solution, with inclusion of the effect of incorrect signs of the structure factors. A mathematical expression is then obtained for the efficiency of convergence, $\eta_{F.S.}$ (= calculated correction/actual correction required), for an n-dimensional summation. $\eta_{F.S.}$ is finally expressed as a function of $U = 2\pi\Delta/d_{\min.}$, where Δ is the r.m.s. error per atomic coordinate. (In the process, graphs are obtained for the integral reliability index, $R_I = \Sigma W^2||F_o|-|F_c|| \div \Sigma W^2|F_c|$, as a function of U for both weighted and unweighted Fourier syntheses; these graphs are practically identical for 1-, 2- and 3-dimensional summations, and should be useful for estimating Δ directly from R_I.) The behaviour of $\eta_{F.S.}$ under various conditions is discussed, and is found to be similar to $\eta_{S.D.}$ for the methods of steepest descents and least squares. Curves are given for $\eta_{F.S.}$ against U, against $U_c = \eta_{F.S.} \times U$, and against R_I, all of which are useful under different conditions for (*a*) estimating $\eta_{F.S.}$ and (*b*) speeding up the convergence by dividing the calculated corrections by $\eta_{F.S.}$. The influence of neighbouring atoms and of statistical fluctuations on the reliability of the calculated value of $\eta_{F.S.}$ is discussed analytically.

1. Introduction

In Part I of this series (Qurashi, 1953), the desirability of evaluating the rates of convergence of various methods of structure determination was considered, and 'efficiency of convergence' (for one application) of any given method for a parameter, u_j, was defined as

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

where δu_{jo} is the actual correction required and δu_{jc} is the correction obtained from one refinement.

An expression was then obtained for the efficiency, $\eta_{S.D.}$, applicable to the methods of modified steepest-descents and to the linear approximation to the method of least squares. It was shown (cf. Part I, equations (6) and Fig. 5) that

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

where

$$\eta_F(x_i) = \left(\sum_{hkl}(1-2\beta_{hkl})W^2 f_i^2 h^2\right) / \left(\sum_{hkl} W^2 f_i^2 h^2\right),$$

and $\eta_{T,\beta}(x_i)$ is a slowly varying function of h, k, l, of value between 1 and $\frac{3}{4}$ in the practical case. W^2 is the weighting function and β_{hkl} is the fraction of the F's that are given wrong signs by the assumed approximation to the structure. Both η_F and $\eta_{T,\beta}$ were ultimately expressed in terms of $U = 2\pi\Delta/d_{\min.}$, where Δ is the r.m.s. error per coordinate, and $d_{\min.}$ is the minimum interplanar spacing for the reflecting planes used in the summation. Since the variation of the atomic scattering-factor, f, with $\sin\theta/\lambda$ (i.e. with h, k, l) is very similar for all the effective atoms in a structure, η_F becomes practically identical for all the parameters. It was also remarked (Part I, § 3, discussion of equation (6); and § 8, result (6)) that, although, for small values of U, η_F approximates to the efficiency of convergence, $\eta_{F.S.}$, of the method of Fourier synthesis, the value of $\eta_{F.S.}$ for large U is not directly deducible from that of η_F. The reason is that both processes of refinement are essentially discontinuous, with the discontinuities occurring at different values of Δ (because of the factor $\eta_{T,\beta}$) so that the two methods correct the phases of the F's at different stages.

We shall now establish the precise relationship between the two methods, and convert the Fourier synthesis into a minimum residual problem whence an expression for $\eta_{F.S.}$ will be derived. The contractions used in Part I of this paper are used here also.

2. The Fourier synthesis as a particular case of the minimum residual solution

For the special case when the F_o's are *completely known* (i.e. both in magnitude and phase), Cochran (1948) has shown that the Fourier synthesis,

$$\varrho_o(x, y, z) = \frac{1}{V}\sum_{hkl} F_{hkl} \exp\left[-2\pi i\left(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c}\right)\right], \quad (1a)$$

(corrected for series termination, etc.) yields exactly the same coordinates for the jth atom as are got by minimizing

$$R_j = \sum_{hkl}\frac{1}{f_j}(F_o-F_c)^2. \quad (1b)$$

Since the phases of the F_o's are assumed to be known, this equivalence can apply only to the *ultimate* results of the refining process. What happens in practice is that a certain approximation to the structure is assumed or is otherwise known, the structure factors, F_c, are calculated for this approximation, and a Fourier synthesis is performed using coefficients whose magnitudes are those of F_o and whose phases are those of F_c. Thus F_o in the synthesis (1a) is to be replaced by F_{oc}, where

$$|F_{oc}| = |F_o|, \quad \text{and} \quad \arg F_{oc} = \arg F_c, \quad (2a)$$

and the first application of the Fourier method gives the following (real) electron-density distribution:

$$\varrho_{oc}(x, y, z) = \frac{1}{V}\sum_{hkl} F_{oc} \exp\left[-2\pi i\left(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c}\right)\right] = \frac{1}{V}\sum_{hkl} F_{oc}\exp[-iv]. \quad (2b)$$

The refined coordinates of the jth atom will be given by the corresponding peak in this ϱ_{oc} synthesis, i.e. by those values of $x_{joc}, y_{joc}, z_{joc}$, which satisfy

$$0 = \left(\frac{\partial\varrho}{\partial x}\right)_{x_{joc}, y_{joc}, z_{joc}} = -\frac{1}{V}\sum_{hkl} F_{oc}\,2\pi\frac{h}{a}i\exp[-iv_{joc}], \quad (3)$$

with similar equations for $\partial\varrho_{oc}/\partial y$ and $\partial\varrho_{oc}/\partial z$.

Now, consider a set of atomic coordinates, $(x_{jct}, y_{jct}, z_{jct})$, where the subscript '$t$' is added to distinguish these *variable* coordinates from the other sets. If we calculate F_{ct} from the formula

$$F_{ct} = \sum_{j=1}^{n} f_j \exp[iv_{jct}],$$

and then perform a Fourier synthesis with these F's, namely

$$\varrho_{ct}(x, y, z) = \frac{1}{V}\sum_{hkl} F_{ct}\exp[-iv],$$

it is clear that the electron-density peaks will occur at the points $(x_{jct}, y_{jct}, z_{jct})$, etc.,* i.e. we have

$$0 = \left(\frac{\partial\varrho_{ct}}{\partial x}\right)_{x_{jct}, y_{jct}, z_{jct}} = -\frac{1}{V}\sum_{hkl} F_{ct}\,2\pi\frac{h}{a}i\exp[-iv_{ct}], \quad (4)$$

* Provided that the series are suitably corrected for series-termination effects by one of the usual methods. If difference syntheses are used, this error is of course largely corrected for.

etc. From equations (3) and (4), after putting $x_{jct}=x_{joc}$, etc., we get for the x coordinate of the jth atom in the *first* Fourier refinement,

$$0 = \left[\sum_{hkl}(F_{oc}-F_{ct})2\pi\frac{h}{a}i\exp[-iv_{jct}]\right]_{x_{jct}=x_{joc}, \text{etc.}} = \left[\sum_{hkl}(F_{oc}-F_{ct})\times\frac{-1}{f_j}\frac{\partial F^*_{ct}}{\partial x_{jct}}\right]_{x_{jct}=x_{joc}, \text{etc.}} = \tfrac{1}{2}\left[\frac{\partial}{\partial x_{jct}}\sum_{hkl}\frac{1}{f_j}|F_{oc}-F_{ct}|^2\right]_{x_{jct}=x_{joc}, \text{etc.}}, \quad (5)$$

and similar equations for y_{joc} and z_{joc}. Thus, the coordinates of the jth atom obtained from the *first Fourier synthesis* can be got by minimizing

$$R_j = \sum_{hkl}\frac{1}{f_j}|F_{oc}-F_{ct}|^2, \quad (6)$$

where the F_{oc}'s are fixed at the start and the F_{ct}'s will be varied during the minimizing procedure. The values of $x_{jct}, y_{jct}, z_{jct}$ that make R_j a minimum have now to be found; when this has been done, the efficiency $\eta_{F.S.}(x_j)$ will be given by

$$\eta_{F.S.}(x_j) = \frac{\delta x_{jc}}{\delta x_{jo}} = \frac{x_{jc}-[x_{jct}]_{\text{for minimum } R}}{x_{jc}-x_{jo}}.$$

It must be stressed here that the *general* minimum-residual (or least-squares) solution as in (6) is to be distinguished from the *linear approximation* to the least-squares, in which it is assumed that the derivatives, $\partial F/\partial x_{jct}$, etc., are linear functions of the parameters, and which is therefore suited to actual calculation. In numerical work, it is usual to designate this approximation as 'the method of least squares'; as such this method has been discussed in detail in Part I of this paper. It is also pertinent to remark that the *approximate* gradient formula,

$$\Delta x_{ji} = -(\partial D/\partial x_i)_j/C(\varrho_c)_j, \text{ (Cochran, 1951, equation (2·7))}$$

used to calculate the shifts from a difference electron-density map is *exactly* equivalent to this linear approximation (Cochran, 1951, remark after equation (2·7)); therefore, the efficiency of convergence for this formula is also exactly as in Part I.

3. The simplified minimizing procedure

We shall here deal with the case of a centrosymmetric structure or projection, and, for comparison with the results of Part I, we shall treat the general case of the weighted Fourier synthesis (cf. Cochran, 1948) in which each F is multiplied by a positive factor, W^2, which is a function* of h, k, l. In this case, equation (6) becomes

* When W^2 is a smooth monotonic function of d_{hkl}, its introduction is similar to that of an artificial temperature factor, and does not require Cochran's iterative process.

$$R_j = \sum_{hkl} \frac{W^2}{f_j}(F_{oc}-F_{ct})^2 = \sum_{hkl} \frac{W^2}{f_j}((F_o-F_{ct})+(F_{oc}-F_o))^2$$
$$= \sum_{hkl} \frac{W^2}{f_j}(F_o-F_{ct})^2 + \sum_{hkl} \frac{W^2}{f_j}(F_{oc}^2-F_o^2+2F_{ct}(F_o-F_{oc}))$$
$$= \sum_{hkl} \frac{W^2}{f_j}(F_o-F_{ct})^2 + \sum_{hkl} \frac{W^2}{f_j} 2F_{ct}(F_o-F_{oc}) , \qquad (6a)$$

since, in the centric case, $F_{oc} = \pm F_o$. Clearly the second term is identically zero for all reflexions that have arg F_o = arg F_c; however, for the reflexions that have the signs of F_o and F_c opposite,

$$(F_o-F_{oc}) = F_o-(-F_o) = 2F_o ,$$

so that if $\acute{\sum}_{hkl}$ denotes a summation over all *such reflexions only*, we can write

$$R_j = \sum_{hkl} \frac{W^2}{f_j}(F_o-F_{ct})^2 + \acute{\sum}_{hkl} 4\frac{W^2}{f_j} F_o F_{ct} . \qquad (6b)$$

The important point to be noted about the summation $\acute{\sum}_{hkl}$ is that the indices of the reflexions included in it are fixed at the outset, and are *not to be varied* during the minimization of R_j. The general procedure for the minimization is to evaluate R_j as a function of all the atomic coordinates, x_i, y_i, z_i, etc., describing the approach of the structure to its correct configuration, then to put

$$\partial R_j/\partial x_j = \partial R_j/\partial y_j = \partial R_j/\partial z_j = 0 ,$$

and to solve for x_j, y_j, z_j, accepting only such solutions as make the second derivatives positive; these will be the coordinates of the jth atom for minimum R_j. The procedure is then to be repeated for all j.

We can, however, effect a great simplification by noting certain features common to $\eta_{F.S.}$ and η_F (the latter corresponding to the *linear* least-squares method). First, if $f = \left(\sum_{i=1}^{n} f_i\right) \Big/ \left(\sum_{i=1}^{n} 1\right)$, then f_i/f does not vary rapidly over the useful range of $\sin\theta/\lambda$ and we can therefore replace f_j by f in equation (6b), which makes it possible to put down a single set of equations $\partial R/\partial x_i = 0$, etc., for simultaneous solution. Further, as pointed out in the introduction, when f_j has been replaced by f, η_F is identical for all the parameters, so that we can expect the same behaviour for $\eta_{F.S.}$ In any case, if we take $\eta_{F.S.}$ as being identical for all the parameters, and then minimize R, we shall finally obtain the value of $\bar{\eta}_{F.S.}$ representing $\eta_{F.S.}$ averaged over all the variable coordinates, and this value will represent the individual values of $\eta_{F.S.}$ to a high accuracy.* This assumption implies that, in our analysis, we only need to consider the case when all the errors, δx_i, δy_i, δz_i, etc., decrease in the same ratio, so that, for the purpose of minimizing R in equations (6), the $3n$ variables, x_i, y_i, z_i, can be replaced by *one* independent variable, which may be a suitable function of these x_i's, etc. For, considering the reflexions in a small range of Bragg angles, we know from Part I, equation (11), that a good parameter is

$$u = \sqrt{(\overline{\delta v})^2} = 2\pi \sqrt{\left(\frac{h^2}{a^2}(\delta x)^2 + \frac{k^2}{b^2}(\delta y)^2 + \frac{l^2}{c^2}(\delta z)^2\right)}$$
$$= 2\pi\Delta/d_{hkl} ,$$

where Δ is the r.m.s. error (in Å) *per coordinate*. For our present analysis it is more convenient to use the parameter

$$t = \Delta/\Delta_o , \qquad (6c)$$

where Δ_o is the initial value of Δ. Clearly 't' is a linear function of Δ, and ranges from $t = 1$ for the assumed approximation (i.e. $F_{ct} \equiv F_c$) to $t = 0$ for the correct structure (i.e. $F_{ct} \equiv F_o$). Also, by comparison with the definition of $\eta_{F.S.}$, if t_m is the value of 't' for the minimum of R, then

$$\bar{\eta}_{F.S.} = 1-t_m . \qquad (6d)$$

4. Location of minimum of R

Rewriting equation (6b) with f in place of f_j, and writing $R = R(t)$ to show its dependence on 't', we get

$$R(t) = \sum_{hkl} \frac{W^2}{f}(F_o-F_{ct})^2 + \acute{\sum}_{hkl} 4\frac{W^2}{f} F_o F_{ct}$$
$$= \sum_{hkl} W^2 f(\varphi_o-\varphi_{ct})^2 + \acute{\sum}_{hkl} 4W^2 f \varphi_o \varphi_{ct} \quad (\varphi = F/f)$$
$$= \sum_{hkl} W^2 f[\overline{(\varphi_o-\varphi_{ct})^2_\theta} + 4(\acute{\sum}_{hkl} \varphi_o\varphi_{ct}/\sum_{hkl} 1)_\theta] , \qquad (7)$$

where the summations within the square brackets are carried out in a small range of h, k, l, (or of Bragg angles, $\theta \pm d\theta/2$, since the averages are ultimately functions of d_{hkl} only). To evaluate the quantities in the square brackets, we need to know three different distributions:

(1) for φ ,
(2) for φ when φ_o is known, and
(3) for φ_{ct} when φ_o and $\varphi_c\,(\equiv(\varphi_{ct})_{t=1})$ are both known.

The first is the simple Gaussian distribution given by Wilson (1949), the second has been given by Luzzati (1952) and also in Part I of this paper (Qurashi, 1953), and the third is derived in Appendix I. $\overline{(\varphi_o-\varphi_{ct})^2_\theta}$ is easily obtained as

$$\overline{(\varphi_o-\varphi_{ct})^2_\theta} = \overline{(2\sum_j N_j(\cos v_{jo}-\cos v_{jct}))^2} \qquad (N_j = f_j/f)$$
$$= 4\overline{\sum_j 4N_j^2 \cos^2\tfrac{1}{2}(v_{jo}+v_{jct}) \sin^2\tfrac{1}{2}\delta v_{jt}}$$
$$(\delta v_{jt} = (v_{jo}-v_{jct}) = t\delta v_{jo})$$
$$= 4\overline{\sin^2\tfrac{1}{2}\delta v_{jt}} \sum_j 2N_j^2 = \sigma^2 . 4\overline{\sin^2\tfrac{1}{2}t\delta v_{jo}} ,$$
$$(\sigma^2 = \overline{\varphi^2} = \sum_j 2N_j^2)$$

* The effect of departures of $\eta_{F.S.}$ from the average value, $\bar{\eta}_{F.S.}$, is analysed in Appendix 3.

whence, using a Gaussian distribution (Part I, Appendix 2) for δv_{jo}, we get

$$\overline{(\varphi_o-\varphi_{ct})^2_\theta} = 2\sigma^2(1-\exp[-\tfrac{1}{2}u^2t^2]), \qquad (8)$$

where $u = \gamma(\overline{(\delta v_{jo})^2}) = 2\pi\Delta/d$.

The second term in equation (7) requires some involved integrations for its evaluation, and the process is therefore outlined in Appendix 2. It turns out that

$$\overline{(\sum_{hkl}{}' \varphi_o\varphi_{ct}/\sum_{hkl} 1)_\theta} = \frac{\sigma^2}{2\pi}(a_t\Gamma_a+b_t\Gamma_b), \qquad (9)$$

where

$$\left.\begin{aligned}
\Gamma_a &= (1-\exp[-u^2/2]) \\
&\quad\times\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}+(1-\exp[-u^2])^{\frac{1}{2}}\}, \\
a_t &= \frac{\exp[-t^2u^2/2]-\exp[-(1-t)^2u^2/2]}{1-\exp[-u^2/2]}; \\
\Gamma_b &= (1+\exp[-u^2/2]) \\
&\quad\times\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}-(1-\exp[-u^2])^{\frac{1}{2}}\}, \\
b_t &= \frac{\exp[-t^2u^2/2]+\exp[-(1-t)^2u^2/2]}{1+\exp[-u^2/2]}.
\end{aligned}\right\} 9(a)$$

Substitution of (8) and (9) in (7) finally gives

$$R(t) = \sum_{hkl} 2W^2f\sigma^2((1-\exp[-\tfrac{1}{2}u^2t^2])+\frac{1}{\pi}(a_t\Gamma_a+b_t\Gamma_b)). \qquad (10)$$

If we put $t = 1$ and divide by

$$\sum_{hkl}\frac{W^2}{f}|F_c|^2 = \sum_{hkl} W^2f\sigma^2,$$

this expression can be used to give the reliability index,

$$(R')^2 = \sum_{hkl}\frac{W^2}{f}(|F_o|-|F_c|)^2\Big/\sum_{hkl}\frac{W^2}{f}|F_c|^2,$$

as a function of u. The dependence of R' on u, when the summation extends over an infinitesimal range of Bragg angles, is

$$R'_\theta = \gamma[1-\exp[-u^2/2]-\frac{2}{\pi}\{(1-\exp[-u^2])^{\frac{1}{2}} -\exp[-u^2/2]\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}\}].$$

This is shown by the broken line in Fig. 1 and is to be compared with Luzzati's (1952) curves* for

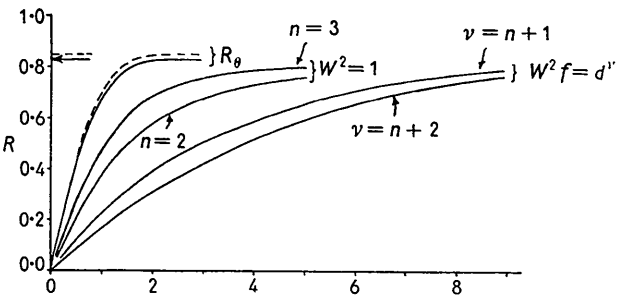

Fig. 1. Curves for the reliability index,
$R_\theta = (\overline{||F_o|-|F_c||}\div\overline{|F_c|})_\theta$,
against $u = 2\pi\Delta/d$, and for the integral reliability index, $R_I = \Sigma W^2||F_o|-|F_c||\div\Sigma W^2|F_c|$ against $U = 2\pi\Delta/d_{\min.}$. The broken line is for $R'_\theta = \gamma((|F_o|-|F_c|)^2\div|F_c|^2)_\theta$.

$$R_\theta = (\overline{||F_o|-|F_c||}\div\overline{|F_c|})_\theta,$$

cf. full line. It is noteworthy that $R'_\theta \simeq R_\theta$ for all u; an effect directly attributable to the reversal of signs of some F_o's, since $R'_\theta = (\frac{1}{2}\pi)^{\frac{1}{2}}R_\theta$ when all these signs are correct. For comparison with experimental values of the reliability index, it is desirable to calculate the 'integral value' of R over the full range of reflections, viz.

$$[R_I]_n = \Sigma W^2||F_o|-|F_c||\div\Sigma W^2|F_c| = \int_{u_o}^{U} W^2fR_\theta u^{n-1}du\Big/\int_{u_o}^{U} W^2fu^{n-1}du \qquad (U/u_0 \simeq d_{\max.}/d_{\min.})$$

for n dimensions. Curves for R_I for different values of W^2 are also drawn in Fig. 1. (R is used here in place of R' because it is more usual to calculate $\Sigma||F_o|-|F_c||$, etc., instead of the squares. Also, the values of R_I are not very sensitive to variation in u_0, and therefore U/u_0 has been fixed as 10.)

Differentiation of equation (10) with respect to 't' gives the equation for the value (t_m) of 't' at the minimum of $R(t)$, viz.

$$0 = \sum_{hkl} W^2f\sigma^2\left(2t_mu^2\exp[-t_m^2u^2/2] +\frac{2}{\pi}\left(\Gamma_a\left(\frac{da_t}{dt}\right)_{t_m}+\Gamma_b\left(\frac{db_t}{dt}\right)_{t_m}\right)\right),$$

whence

$$\frac{\pi}{2}t_m\sum_{hkl} W^2fu^2\exp[-t_m^2u^2/2] = \sum_{hkl} W^2f\left(-\tfrac{1}{2}\Gamma_a\left(\frac{da_t}{dt}\right)_{t_m}-\tfrac{1}{2}\Gamma_b\left(\frac{db_t}{dt}\right)_{t_m}\right) \qquad (11a)$$

$$= \sum_{hkl} W^2f\frac{u^2}{2}[\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}+(1-\exp[-u^2])^{\frac{1}{2}}\} \times\{t\exp[-t^2u^2/2]+(1-t)\exp[-(1-t)^2u^2/2]\}_{t_m} +\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}-(1-\exp[-u^2])^{\frac{1}{2}}\} \times\{t\exp[-t^2u^2/2]-(1-t)\exp[-(1-t)^2u^2/2]\}_{t_m}]$$

$$= \sum_{hkl} W^2fu^2\{t\exp[-t^2u^2/2]\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}} +(1-t)\exp[-(1-t)^2u^2/2](1-\exp[-u^2])^{\frac{1}{2}}\}_{t_m}, \qquad (11b)$$

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* Luzzati's calculations give different curves for 1, 2 and 3-dimensional summations. However, when we evaluate $\overline{|\Delta r|^2_n}$ for an n-dimensional summation, it turns out that Luzzati's σ^2 is related to it by

$$\sigma^2 = \overline{|\Delta r|^2_1} = \tfrac{1}{2}\overline{|\Delta r|^2_2} = \tfrac{1}{3}\overline{|\Delta r|^2_3},$$

so that his σ^2 is identical with the r.m.s. error *per coordinate*, designated by 'Δ' in our analysis. It follows that Luzzati's $D = \exp[-2\pi^2|S|^2\sigma^2]$ becomes

$$D = \exp[-\tfrac{1}{2}4\pi^2\Delta^2/d^2] = \exp[-\tfrac{1}{2}u^2] \quad (|S| \equiv 1/d_{hkl})$$

in our notation, and *a single curve* in terms of 'u' is obtained for 1, 2 and 3-dimensional summations.

after substitution for Γ_a, (da_t/dt), etc., and simplification.

The equation can be solved numerically if the value of W^2f is known. Since it was found in preceding analyses (Qurashi, 1953; Qurashi & Vand, 1953) that the form,

$$W^2f^2 = d^\nu \quad \text{with} \quad \nu \sim n+2\,,$$

is the most suitable* weighting function for the least-squares refinement of an n-dimensional summation, we shall use a corresponding form (cf. the factor $1/f$ in equation (6)) for the present analysis, viz.

$$W^2f = d^\nu \propto u^{-\nu} \quad \text{with} \quad \nu \sim n+2;$$

and shall work with two values of ν, viz. $\nu = n+2$, and $\nu = n+1$, for comparison with the corresponding cases of the refinement by least squares. Also, we shall use the symbol $\bar{\eta}^{n,\nu}_{F.S.}$ to denote the value of $\bar{\eta}_{F.S.}$ for an n-dimensional Fourier synthesis with $W^2f = d^\nu$. We need only consider the one-dimensional case, since it can be shown that the expression for $\bar{\eta}_{F.S.}$ is the same for a given value of $(\nu-n)$; cf. Part I, § 5(*b*), where it is proved that

$$\eta_F^{3,\nu} \equiv \eta_F^{2,\nu-1} \equiv \eta_F^{1,\nu-2}\,.$$

5. Evaluation of $\bar{\eta}_{F.S.}$

On replacing the summations by integrations, which is always valid since $\Delta/a < 0{\cdot}1$, i.e. the r.m.s. error per coordinate is less than 1/10th of the cell dimension (cf. Part I, § 5), we obtain (in one dimension),

$$\begin{aligned}&\frac{\pi}{2}t_m\int_{u_0}^{U} u^{2-\nu}\exp\left[-t_m^2u^2/2\right]du\\ &=\int_{u_0}^{U} u^{2-\nu}du\{t_m\exp\left[-t_m^2u^2/2\right]\tan^{-1}(\exp\left[u^2\right]-1)^{\frac{1}{2}}\\ &+(1-t_m)\exp\left[-(1-t_m)^2u^2/2\right](1-\exp\left[-u^2\right])^{\frac{1}{2}}\},\end{aligned}\tag{12a}$$

where the limits of integration are clearly related to the minimum and maximum indices, h_0 and H, of the summations as follows:

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

For small U, the integrands can be expanded in power series to give

$$\begin{aligned}&\frac{\pi}{2}t_m\int_{u_0}^{U}\left(u^{2-\nu}-\frac{t_m^2}{2}u^{4-\nu}+\ldots\right)du\\ &=\int_{u_0}^{U}u^{2-\nu}\left[t_m\left\{u-u^3\left(\frac{t_m^2}{2}+\frac{1}{12}\right)+\ldots\right\}\right.\\ &\left.+(1-t_m)\left\{u-u^3\left(\frac{(1-t_m)^2}{2}+\frac{1}{4}\right)+\ldots\right\}\right]du\\ &=\int_{u_0}^{U}\left[u^{3-\nu}-\left\{\frac{(1-t_m)^3+t_m^3}{2}+\frac{1}{3}\right\}u^{5-\nu}+\ldots\right]du\,,\end{aligned}$$

whence

$$\begin{aligned}&(t_m)_\nu\left(1-t_m^2\frac{U^2}{2}\frac{3-\nu}{5-\nu}+\ldots\right)\\ &=\frac{2}{\pi}\frac{\int_{u_0}^{U}u^{3-\nu}du}{\int_{u_0}^{U}u^{2-\nu}du}\left\{1-\frac{5}{6}\frac{4-\nu}{6-\nu}U^2(1+\Phi^2)+\ldots\right\}\,,\end{aligned}\tag{12b}$$

so that

$$\left.\begin{aligned}\bar{\eta}^{n,n+1}_{F.S.} &= \bar{\eta}^{1,2}_{F.S.} = 1-(t_m)_{\nu=2}\\ &= 1-\frac{U}{\pi}(1+\Phi)\{1-\tfrac{5}{12}U^2(1+\Phi^2)+\ldots\}\,,\\ \bar{\eta}^{n,n+2}_{F.S.} &= \bar{\eta}^{1,3}_{F.S.} = 1-(t_m)_{\nu=3}\\ &= 1-\frac{U}{\pi}\frac{2(1-\Phi)}{\log 1/\Phi}\{1-\tfrac{5}{18}U^2(1+\Phi^2)+\ldots\}\,.\end{aligned}\right\}\tag{13}$$

These results are seen to be very close to the corresponding equations (13) in Part I of this paper, thus confirming the idea that $\eta_{F.S.} \simeq \eta_F$. For very large U, when $\eta \to 0$ (i.e. $t_m \to 1$), it is desirable to transpose the first term on the right-hand side of equation 12(*a*). This gives

$$\begin{aligned}&t_m\int_{u_0}^{U}u^{2-\nu}\exp\left[-t_m^2u^2/2\right]\left\{\frac{\pi}{2}-\tan^{-1}(\exp\left[u^2\right]-1)^{\frac{1}{2}}\right\}du\\ &=(1-t_m)\int_{u_0}^{U}u^{2-\nu}\exp[-(1-t_m)^2u^2/2](1-\exp[-u^2])^{\frac{1}{2}}du,\end{aligned}$$

whence it follows that $(1-t_m) > 0$, since t_m and the integrands on both sides are always positive. We can solve the above integral equation for large U (actually, $u_0 > 1$) by expanding some of the functions in powers of $\exp\left[-u^2\right]$, viz.

$$\begin{aligned}&t_m\int_{u_0}^{U}u^{2-\nu}\exp\left[-t_m^2u^2/2\right]\\ &\qquad\times\{\exp\left[-u^2/2\right]/(1-\exp\left[-u^2\right])^{\frac{1}{2}}\ldots\}du\\ &=(1-t_m)\int_{u_0}^{U}u^{2-\nu}\exp\left[-(1-t_m)^2u^2/2\right]\\ &\qquad\times\{1-\tfrac{1}{2}\exp\left[-u^2\right]+\ldots\}du\,,\end{aligned}$$

whence

$$\bar{\eta}^{1,\nu}_{F.S.}/(1-\bar{\eta}^{1,\nu}_{F.S.}) = \frac{1-t_m}{t_m} \simeq \int_{u_0}^{U}u^{2-\nu}\exp\left[-(1-\bar{\eta}^{1,\nu}_{F.S.})u^2\right]du \Big/ \int_{u_0}^{U}u^{2-\nu}\exp\left[-(\bar{\eta}^{1,\nu}_{F.S.})^2u^2/2\right]du\,.$$

* It is to be noted that, for $u = 2\pi\Delta/d < 1{\cdot}0$, the error, $\overline{||F_o|-|F_c||} \div \overline{|F_c|}$, varies as $1/d$, and the summands in equation (11) are of the form $W^2f \times u^2$ and $W^2f \times u^3$, so that the effects of high- and low-angle reflexions are best equalized by using a power law for W^2f rather than the exponential form, $\exp\left[-K(\sin\theta/\lambda)^2\right]$.

For $\nu = 2, 3$, this gives, for $\Phi U = u_0 > 1$,

$$\left.\begin{aligned} \bar{\eta}_{F.S.}^{1,2} &\simeq \tfrac{1}{2}\Phi \exp\left[-\Phi^2U^2\right]/(\Phi^2U^2)\,, \\ \bar{\eta}_{F.S.}^{1,3} &\simeq \frac{1}{2\log 1/\Phi} \exp\left[-\Phi^2U^2\right]/(\Phi^2U^2)\,. \end{aligned}\right\} \quad (14)$$

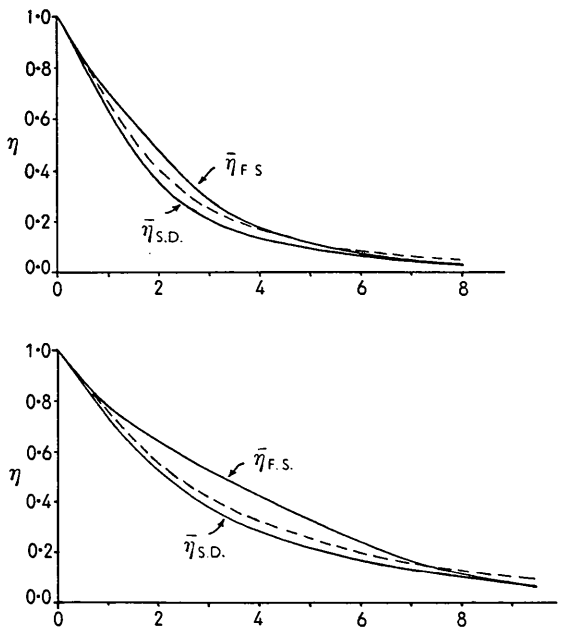

Fig. 2. Curves for $\bar{\eta}_{F.S.}$, $\bar{\eta}_{S.D.}$ and η_F (broken line) against $U = 2\pi\Delta/d_{\min.}$ for optimum weighting, viz. (*a*) $W^2f = d^{n+1}$, (*b*) $W^2f = d^{n+2}$, for an n-dimensional Fourier synthesis.

The corresponding results for η_F are again similar, viz.

$$\eta_F^{1,2} \simeq \frac{2}{\pi}\Phi \exp\left[-\tfrac{1}{2}\Phi^2U^2\right]/(\Phi^2U^2)$$

and

$$\eta_F^{1,3} \simeq \frac{2}{\pi\log 1/\Phi} \exp\left[-\tfrac{1}{2}\Phi^2U^2\right]/(\Phi^2U^2)\,,$$

whence it is seen that for large U, $\bar{\eta}_{F.S.} < \eta_F$ with corresponding weighting. For intermediate values of U, the integral equation can be solved by numerical methods.

The solution is most conveniently carried out by fixing the values of t_m and of $\Phi = u_0/U$, and then tabulating the integrals on either side of equation (12*a*) for a series of values of U; from these tabulated values it is a simple matter to find the particular value of U which fits the equation, i.e. makes the two sides equal.* This has been done for both $\nu = 2$ and $\nu = 3$, using a value of $\Phi = 1/10$, and the results are shown graphically in Fig. 2, together with the corresponding curves for η_F and $\bar{\eta}_{S.D.} = \eta_F \times \bar{\eta}_{T,\beta}$. The variation of the curves with Φ is small, cf. Part I, Fig. 1; therefore only one value of Φ has been used.

6. Discussion of results and applications

It is evident from the figure that curves for $\bar{\eta}_{F.S.}$ follow the corresponding ones for η_F closely, the two being practically coincident for $\eta > \frac{3}{4}$. Also interesting is the fact that for very large U, $\bar{\eta}_{F.S.} < \eta_F$, while for moderately large U, $\bar{\eta}_{F.S.} > \eta_F$. However, when the comparison is made with $\bar{\eta}_{S.D.}$ (which is the quantity of practical interest), it is seen that $\bar{\eta}_{F.S.} > \bar{\eta}_{S.D.}$ for all values of U, and the two approach each other for very small and very large values of U; in the range of moderately large U (corresponding to $0{\cdot}6 < \eta < 0{\cdot}2$), $\bar{\eta}_{F.S.}$ is greater than $\bar{\eta}_{S.D.}$ by about 25–40%, which difference can be of considerable advantage in the convergence of a rather poor approximation to the correct structure. Apart from this feature, the curves are so similar that the discussion of the corresponding curves in Part I (§§ 5, 6, 7) will apply here also. Curves for $\bar{\eta}_{F.S.}$ against U_c are shown in Fig. 3(*a*), where

$$U_c = \bar{\eta}_{F.S.} \times U = 2\pi(\Delta \times \bar{\eta}_{F.S.})/d_{\min.} = 2\pi\Delta_c/d_{\min.}\,,$$

Δ_c being the r.m.s. *correction* per coordinate given by the one refinement. As before, the curves give two values of η for each value of U_c or Δ_c, the lower value being for an approximation far removed from the correct structure. To determine which value of η is

* It turns out that for $t_m < \frac{1}{2}$, there are two solutions for each value of t_m. One solution is that given by the approximation (12*b*), while the other occurs at $U > 20$. The latter solution is, however, ruled out because it gives a maximum value of R (i.e. the second derivative $\partial^2 R/\partial t^2$ is negative).

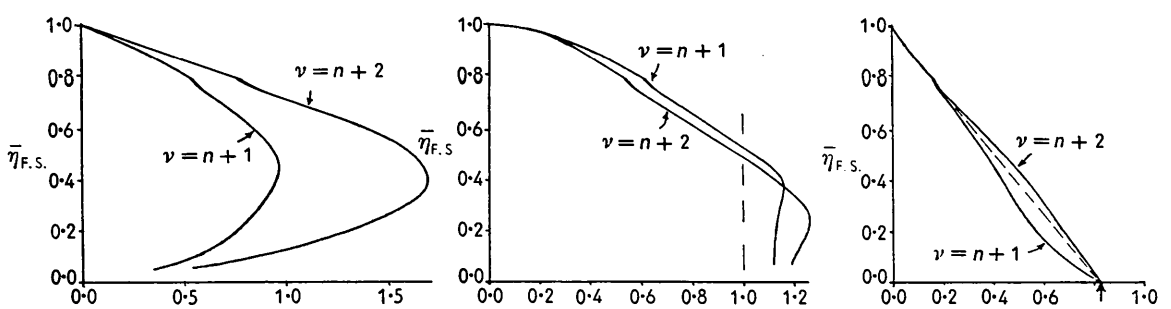

Fig. 3. Curves for $\bar{\eta}_{F.S.}$ (for an optimally weighted synthesis) against (*a*) $U_c = \bar{\eta}_{F.S.} \times U = 2\pi\Delta_c/d_{\min.}$, (*b*) the convergence ratio, $\bar{\varrho} = (\Delta_c)_2/(\Delta_c)_1$, for two successive refinements, (*c*) the integral reliability index, $R_I = \Sigma W^2||F_o|-|F_c||\div\Sigma W^2|F_c|$; the broken line is $\bar{\eta} = 1-R_I/0{\cdot}828$.

to be used, we can make use of the convergence ratio, $\bar{\varrho} = (\Delta_c)_2/(\Delta_c)_1$, for two successive refinements, labelled (1) and (2). Curves for $\bar{\eta}_{F.S.}$ against $\bar{\varrho}$ are shown in Fig. 3(*b*). The region, $\bar{\varrho} < 1$, corresponds to the upper branch of the curves of Fig. 3(*a*), and in this region, the precise value of $\bar{\eta}_{F.S.}$ to be used can be read off accurately from the curves. For $\bar{\varrho} \gtrsim 1$, (corresponding to the lower branch in Fig. 3(*a*)), a precise determination is difficult because of the rapid variation of $\bar{\eta}_{F.S.}$ with $\bar{\varrho}$ and the somewhat large error inherent in the estimation of $\bar{\varrho}$. However, we have $\bar{\eta}_{F.S.} < \frac{1}{2}$ in this region, so that we can safely multiply all the calculated corrections by 2, or even a little more, as in the case of the corresponding curves for $\bar{\eta}_{S.D.}$ in Part I.

In the region of small η, the following device can be used advantageously to determine an accurate value of η. A comparison of the graphs of Fig. 2 with the corresponding curves for the reliability factor, R_I, in Fig. 1, shows that the variation of η with U is very similar to that of $(1-R_I/0{\cdot}828)$; so that we can expect a one-to-one relationship between η and R_I. The graphs for $\bar{\eta}_{F.S.}$ against R_I for the cases of $\nu = n+2$ and $\nu = n+1$ are shown in Fig. 3(*c*), and it is notable that the straight line, $\bar{\eta}_{F.S.} \simeq 1-R_I/0{\cdot}828$, is a good approximation, particularly for the optimum index, $\nu = n+2$. Thus, if R_I is calculated *for the reflexions used* in the Fourier synthesis, the appropriate value of $\bar{\eta}_{F.S.}$ can be read off from Fig. 3(*c*). However, it must be remembered that the value of R_I calculated from the observed data is always greater than the theoretical value, owing to the effect of observational errors, etc., which may be of the order of 0·15 or so. Thus the curves of Fig. 3(*c*) can be used with satisfactory precision only for $R_I \sim 0{\cdot}3$ or more, i.e. for $\eta < 0{\cdot}6$. When $R_I < 0{\cdot}4$, it is definite that $\eta > 0{\cdot}45$, and therefore the upper branch of the curves of Fig. 3(*a*) can be used.* In Appendix 3 we consider the effect of overlapping atoms and of statistical fluctuations (in the averages in equation (7)) on the smallest *useful* value of η. For properly weighted syntheses, this limit is of the order of 0·2 or less.

Finally, we must note that the above curves for $\bar{\eta}_{F.S.}$ have been calculated for optimum weighted Fourier syntheses with $W^2 f \propto d^\nu$ and $\nu \sim n+2$ for an n-dimensional summation. It is usual, however, to work with unweighted syntheses, i.e. to put $W^2 =$ constant. For this case, we must clearly replace $u^{-\nu} \propto d^\nu$ by 'f' in the integrals of equation (12*a*). We consider only the case of 2- and 3-dimensional summations. For a 2-dimensional summation, the index of 'u' in equation (12*a*) is to be increased by unity (because the summations over h and k are replaced by the integration in polar coordinates, cf. § 5, Part I); so that the integrands involved are of the type

$$u^3 \times f = (2\pi\Delta/d)^3 \times f \propto f/d^3.$$

* Graphs for $\bar{\eta}_{S.D.}$ against R_I can be used similarly in conjunction with the curves for $\bar{\eta}_{S.D.}$ against U_c in Fig. 3, Part I. These graphs are very like those in Fig. 3(c) here.

Now, Fig. 4 shows the curve for f/d^3 against $\sin\theta/\lambda$ $(= 1/2d)$ for a sodium atom with a temperature factor

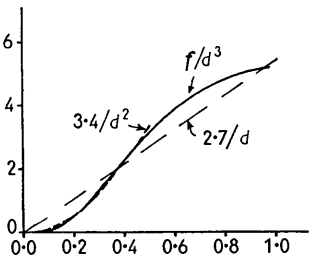

Fig. 4. Curves for $(f_0)_{\mathrm{Na}} \exp[-1\times(\sin\theta/\lambda)^2]/d^3$ against $\sin\theta/\lambda$, together with the approximations, $3{\cdot}4/d^2$ and $2{\cdot}7/d$.

of $\exp[-1\times(\sin\theta/\lambda)^2]$, and it is apparent that $3{\cdot}4/d^2$ is an excellent approximation to f/d^3 for $\sin\theta/\lambda < 0{\cdot}5$, while $2{\cdot}7/d$ is a fairly good approximation, for the purposes of the integrations, in the range $0 < \sin\theta/\lambda < 1{\cdot}1$. Thus, to a good approximation for our purpose, we can put

$$f \propto d^\mu \propto u^{-\mu}, \qquad 1 \leqslant \mu \leqslant 2\,.$$

The calculations of $\bar{\eta}_{F.S.}$ have accordingly been repeated for the 2- and 3-dimensional cases with both $\mu = 1$ and $\mu = 2$, and the curves are shown in Fig. 5. It is seen that the differences between the curves with $\mu = 1$ and $\mu = 2$ are small, and therefore a mean value of $\mu = 1{\cdot}5$ has been used to derive the curves for $\bar{\eta}_{F.S.}$.

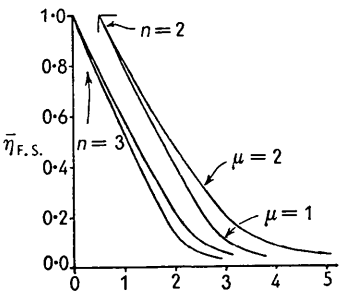

Fig. 5. Curves for $\bar{\eta}_{F.S.}$ against U for 2- and 3-dimensional unweighted syntheses, using the two approximations to f/d^3 shown in Fig. 4.

against U_c and against the convergence ratio, $\bar{\varrho}$; cf. Fig. 6(*a*) and (*b*). It is clear that the fall of efficiency with increasing U is considerably more rapid than for $\bar{\eta}_{F.S.}$ (or $\bar{\eta}_{S.D.}$) with optimum weighting. Also, this fall is more rapid for a 3-dimensional summation than for a 2-dimensional one, confirming the belief that the radii and rates of convergence of 3-dimensional Fourier syntheses are a little less than those of 2-dimensional ones. Another noteworthy feature is that the maximum value of $U_c = 2\pi\Delta_c/d_{\min.}$ is only about 0·6 for the unweighted Fourier syntheses, as against 1·7 for the Fourier syntheses with optimum weighting. The smaller figure corresponds to

$$\Delta_c = d_{\min.} \times U_c/2\pi = 0{\cdot}074 \text{ Å}\,,$$

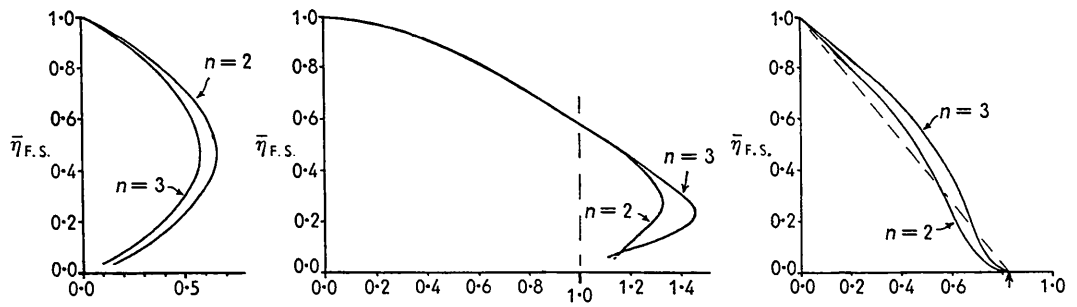

Fig. 6. Curves for $\bar{\eta}_{F.S.}$ (for unweighted syntheses) against (*a*) $U_c = \bar{\eta}_{F.S.} \times U = 2\pi\Delta_c/d_{\min.}$, (*b*) the convergence ratio, $\bar{\varrho} = (\Delta_c)_2/(\Delta_c)_1$, for two successive refinements, (*c*) the integral reliability index, $R_I = \Sigma||F_o|-|F_c|| \div \Sigma|F_c|$.

for the limiting sphere of Cu $K\alpha$ radiation. This is the maximum value of the r.m.s. refinement per coordinate to be expected in unweighted Fourier syntheses.

Finally, graphs for $\bar{\eta}_{F.S.}$ against R_I have also been recalculated (Fig. 6(*c*)). These also approximate to the linear relation $\bar{\eta}_{F.S.} = 1-R_I/0{\cdot}828$, and, as discussed previously, they can be used advantageously when $\bar{\eta}_{F.S.} < 0{\cdot}6$. However, when $\bar{\eta} \leqslant 0{\cdot}5$, fluctuations in η are of the order of η (cf. Appendix 3), and can therefore produce large errors. A calculated value of $R_I < 0{\cdot}5$ can be taken as an indication that $\bar{\eta}_{F.S.} > 0{\cdot}5$, and in this case use can be made of the upper branch of the curves of Fig. 6(*a*). The above considerations provide some justification for the bias against working up approximate structures with $R_I > 50\%$.

7. Conclusions

The main results of the foregoing analysis are:

1. Analytical expressions have been obtained for the mean value, $\bar{\eta}_{F.S.}$, of the efficiency of convergence of the method of Fourier synthesis. $\bar{\eta}_{F.S.}$ is ultimately expressed as a function of $U = 2\pi\Delta/d_{\min.}$, where Δ is the r.m.s. *error per atomic coordinate.*

2. It is found (in agreement with the indications in Part I) that $\bar{\eta}_{F.S.} \simeq \bar{\eta}_{S.D.}$, where $\bar{\eta}_{S.D.}$ is the efficiency of the correspondingly weighted methods of steepest descents and least squares. However, two important features are that (*a*) $\bar{\eta}_{F.S.} > \bar{\eta}_{S.D.}$ always, but $\bar{\eta}_{F.S.} \rightarrow \bar{\eta}_{S.D.}$ for both small and large U, and that (*b*) in the range of moderately large errors (corresponding to $0{\cdot}2 < \eta < 0{\cdot}6$), $\bar{\eta}_{F.S.}$ is greater than $\bar{\eta}_{S.D.}$ by a factor of about 1·3.

3. Since the r.m.s. *correction*, Δ_c, per coordinate *given by any refinement* is different from the *actual error*, Δ, graphs are drawn for $\bar{\eta}_{F.S.}$ against $U_c = 2\pi\Delta_c/d_{\min.}$, and also against the convergence ratio, $\bar{\varrho} = (\Delta_c)_2/(\Delta_c)_1$, of two successive refinements. The graphs of $\bar{\eta}_{F.S.}$ against U_c show a maximum value of U_c, and are therefore double-valued; the ϱ curves can be used to overcome the consequent ambiguity.

4. It is also shown that for discriminating between the two branches of the η against U_c curves, it is sometimes advantageous to use the practically linear graphs for η against R_I, where R_I is the correspondingly weighted reliability factor,

$$\sum_{hkl} W^2||F_o|-|F_c|| \div \sum_{hkl} W^2|F_c| ,$$

calculated *for the reflexions used* in the Fourier synthesis. It is found that $\eta > \frac{1}{2}$ when $R_I < 0{\cdot}45$, approximately.

5. As an incidental to these calculations, R_I is also graphed as a function of U for various values of the weighting function, W^2. These graphs should be useful for estimating the error, Δ ($= d_{\min.} \times U/2\pi$) from a *single* calculation of R_I (cf. Luzzati, 1952).

6. For comparison with the results of Part I on the methods of steepest descents and least squares, we have used the optimum value of the weighting function, which is, in this case, $W^2 f \propto d^\nu$, $\nu \sim n+2$ for n-dimensional summations. However, because Fourier syntheses are usually not weighted, all the calculations have also been carried out for the case of $W^2 =$ constant, for both two- and three-dimensional summations. The $\bar{\eta}_{F.S.}$ curves for these cases fall much more rapidly than for optimum weighting; the curves for $\bar{\eta}_{F.S.}$ against R_I are an exception, the linear approximation, $\eta \simeq 1-R_I/0{\cdot}828$, being still valid. For unweighted syntheses, values of $\eta < \frac{1}{2}$ (corresponding to $R_I > 50\%$) cannot be used with any confidence.

7. It is perhaps pertinent to point out that, in view of general considerations of 'contact' of atoms, and also the analysis for overlap of atoms in projection, etc. (Qurashi & Vand, 1953), the foregoing analysis is meaningful only if $\sqrt{3}.\Delta < \frac{1}{2} \times$(mean interatomic distance)$\simeq 0{\cdot}7$–$1{\cdot}0$ Å, i.e. if Δ is less than about 0·5 Å. With Cu $K\alpha$ radiation, this gives $U_{\max.} \simeq 4$. It is seen from the graphs that, for values of U between 2 and 4, $\bar{\eta}_{F.S.}$ for unweighted refinement is of the order of 0·1, whereas when optimum weighting is used, the corresponding values are of the order of 0·5; this very significant improvement in the initial stages of refinement should outweigh the increased labour of properly weighting the Fourier synthesis or other refinement technique used.

APPENDIX 1

Probability distribution of φ_{ct} when φ_o and φ_c are given

The distribution is bounded by two conditions, viz.

$$(\varphi_{ct})_{t=0} = \varphi_o, \quad (\varphi_{ct})_{t=1} = \varphi_c .$$

However, φ_o and φ_c are mutually correlated, as can be seen by calculating $\overline{\varphi_o\varphi_c}$:

$$\overline{\varphi_o\varphi_c} = \overline{(2\sum_j N_j \cos v_{jo})(2\sum_j N_j \cos (v_{jo}-\delta v_{jo}))}$$
$$= 2\sum_j N_j^2 \overline{\cos \delta v_{jo}} = 2\sum_j N_j^2(1-2\overline{\sin^2 \tfrac{1}{2}\delta v_{jo}}) \neq 0 .$$

To make the conditions independent and symmetrical, we replace them by two linear combinations of φ_o and φ_c, putting $\frac{1}{2}(v_{jo}+v_{jc}) = v_{jm}$:

$$\varphi_{\sin} = \tfrac{1}{2}(\varphi_\varrho-\varphi_c) = 2\sum_j N_j \tfrac{1}{2}(\cos v_{jo}-\cos v_{jc})$$
$$= -2\sum_j N_j \sin v_{jm} \sin \tfrac{1}{2}\delta v_{jo} ,$$

$$\varphi_{\cos} = \tfrac{1}{2}(\varphi_o+\varphi_c) = 2\sum_j N_j \tfrac{1}{2}(\cos v_{jo}+\cos v_{jc})$$
$$= 2\sum_j N_j \cos v_{jm} \cos \tfrac{1}{2}\delta v_{jo} .$$

It is easily verified that $\overline{\varphi_{\sin}\varphi_{\cos}} = \frac{1}{4}\overline{(\varphi_o^2-\varphi_c^2)} = 0$, so that $\varphi_{\sin}$ and $\varphi_{\cos}$ are independent boundary values for the distribution of φ_{ct}. If we put $(\frac{1}{2}-t)\delta v_{jo} = \Delta v_{jt}$, then φ_{ct} can be written as

$$\varphi_{ct} = 2\sum_j N_j \cos v_{jct} = 2\sum_j N_j \cos (v_{jm}+\Delta v_{jt})$$
$$= -2\sum_j N_j \sin v_{jm} \sin \Delta v_{jt} + 2\sum_j N_j \cos v_{jm} \cos \Delta v_{jt}$$
$$= a_t\varphi_{\sin}+b_t\varphi_{\cos}$$
$$+2\sum_j N_j[\sin v_{jm}(a_t \sin \tfrac{1}{2}\delta v_{jo}-\sin \Delta v_{jt})$$
$$+\cos v_{jm}(\cos \Delta v_{jt}-b_t \cos \tfrac{1}{2}\delta v_{jo})] . \qquad (15)$$

Because $\varphi_{\sin}$ and $\varphi_{\cos}$ are not correlated, we have to adjust a_t and b_t independently so as to minimize the r.m.s. value of the third term in the above expression. Noting that $\overline{\sin v_{jm} \cos v_{jm}} = 0$, the condition for this becomes:

$$\overline{\sin^2 v_{jm} \sin \tfrac{1}{2}\delta v_{jo}(a_t \sin \tfrac{1}{2}\delta v_{jo}-\sin \Delta v_{jt})} = 0$$
$$= \overline{\cos^2 v_{jm} \cos \tfrac{1}{2}\delta v_{jo}(\cos \Delta v_{jt}-b_t \cos \tfrac{1}{2}\delta v_{jo})} ,$$

i.e. $$a_t\overline{\sin^2 \tfrac{1}{2}\delta v_{jo}}-\overline{\sin \tfrac{1}{2}\delta v_{jo} \sin \Delta v_{jt}} = 0$$
$$= b_t\overline{\cos^2 \tfrac{1}{2}\delta v_{jo}}-\overline{\cos \tfrac{1}{2}\delta v_{jo} \cos \Delta v_{jt}} ,$$

which is equivalent to

$$a_t\overline{\sin^2 \tfrac{1}{2}\delta v_{jo}} = \overline{\sin \tfrac{1}{2}\delta v_{jo} \sin (\tfrac{1}{2}-t)\delta v_{jo}},$$
$$b_t\overline{\cos^2 \tfrac{1}{2}\delta v_{jo}} = \overline{\cos \tfrac{1}{2}\delta v_{jo} \cos (\tfrac{1}{2}-t)\delta v_{jo}} .$$

Because the distribution of δv_{jo} is closely Gaussian (Part I, Appendix 2), these expressions can be evaluated as follows (on putting $\delta v_{jo} = \mu$, and $\sqrt{(\overline{\mu^2})} = u$):

$$\overline{\cos a\mu} = \int_0^\infty \cos a\mu \exp\left[-\frac{\mu^2}{2u^2}\right] d\mu \Big/ \int_0^\infty \exp\left[-\frac{\mu^2}{2u^2}\right] d\mu$$
$$= \exp[-\tfrac{1}{2}a^2u^2] ,$$

so that

$$a_t = \overline{\sin \tfrac{1}{2}\mu \sin (\tfrac{1}{2}-t)\mu} \Big/ \overline{\sin^2 \tfrac{1}{2}\mu}$$
$$= (\overline{\cos \mu t}-\overline{\cos (1-t)\mu}) / (1-\overline{\cos \mu})$$
$$= (\exp[-\tfrac{1}{2}u^2t^2]-\exp[-\tfrac{1}{2}u^2(1-t)^2]) /$$
$$(1-\exp[-\tfrac{1}{2}u^2]) , \qquad (16a)$$

$$b_t = \overline{\cos \tfrac{1}{2}\mu \cos (\tfrac{1}{2}-t)\mu} \Big/ \overline{\cos^2 \tfrac{1}{2}\mu}$$
$$= (\overline{\cos \mu t}+\overline{\cos (1-t)\mu}) / (1+\overline{\cos \mu})$$
$$= (\exp[-\tfrac{1}{2}u^2t^2]+\exp[-\tfrac{1}{2}u^2(1-t)^2]) /$$
$$(1+\exp[-\tfrac{1}{2}u^2]) . \qquad (16b)$$

It is readily seen that these values of a_t and b_t give the mean value of φ_{ct}, so that the complete expression for φ_{ct} can be written

$$\varphi_{ct} = a_t\tfrac{1}{2}(\varphi_o-\varphi_c)+b_t\tfrac{1}{2}(\varphi_o+\varphi_c)\pm c_t\sqrt{(\overline{\varphi^2})}$$
$$= b_t\varphi_o+\tfrac{1}{2}(a_t-b_t)(\varphi_o-\varphi_c)\pm c_t\sqrt{(\overline{\varphi^2})} , \qquad (17)$$

where the third term has a random distribution, and

$$c_t^2 = \overline{(a_t \sin \tfrac{1}{2}\mu-\sin (\tfrac{1}{2}-t)\mu)^2}+\overline{(\cos (\tfrac{1}{2}-t)\mu-b_t \cos \tfrac{1}{2}\mu)^2}.$$

c_t is a maximum for $t = \frac{1}{2}$, i.e. when the structure (corresponding to φ_{ct}) is exactly half-way between those corresponding to φ_o and to φ_c. For this special case, $a_{\frac{1}{2}} = 0$, so that $\varphi_{c\frac{1}{2}} = b_{\frac{1}{2}}\cdot\frac{1}{2}(\varphi_o+\varphi_c)\pm c_{\frac{1}{2}}\sqrt{(\overline{\varphi^2})}$, where

$$b_{\frac{1}{2}} = 2\exp[-u^2/8]/(1+\exp[-u^2/2]) \simeq 1+u^2/8$$
for small u ,

$$c_{\frac{1}{2}} = \{1-2\exp[-u^2/4]/(1+\exp[-u^2/2])\}^{\frac{1}{2}} \simeq \sqrt{2}\,.\,u^2/8$$
for small u .

$b_{\frac{1}{2}}$ and $c_{\frac{1}{2}}$ are plotted as functions of u in (Fig. 7*a*),

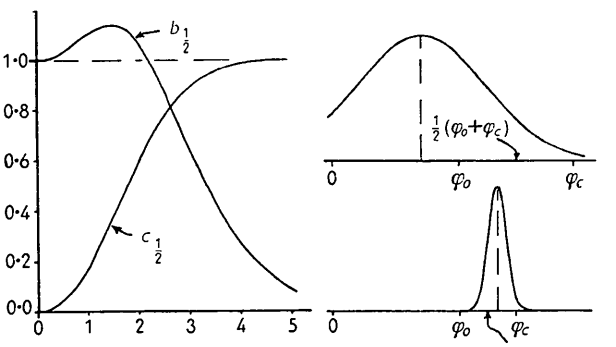

Fig. 7. (*a*) Curves for $b_{\frac{1}{2}}$ and $c_{\frac{1}{2}}$ as functions of $u = 2\pi\Delta/d$. Note the initial rise of $b_{\frac{1}{2}}$ to a maximum at $u \simeq 1{\cdot}5$.
(*b*) Typical probability distributions of φ_{ct} for small and large u.

and two typical distributions of φ_{ct} are shown in Fig. 7(*b*), one for small u and the other for large u.

It is interesting to note that whereas $c_{\frac{1}{2}}$ is a monotonic increasing function of u, $b_{\frac{1}{2}}$ first increases (approximately as $1+u^2/8$) for small u, and then (for large u) decreases as $2\exp[-u^2/8]$. Thus $b_{\frac{1}{2}}$ attains a maximum value of 1·140 at $u=(2\log 3)^{\frac{1}{2}}=1{\cdot}48$; the initial increase is a consequence of the fact that

$$\cos\tfrac{1}{2}(A+B)\simeq\tfrac{1}{2}(\cos A+\cos B)(1+(A-B)^2/8)\,,$$

while the exponential drop for large u is caused by the increasing randomness of the φ and $\delta\varphi$ distributions.

Finally, we evaluate the first derivatives of a_t and b_t since these are required in minimizing the residual, $R(t)$. We get

$$\left.\begin{aligned}-\frac{da_t}{dt}&=\{u^2/(1-\exp[-\tfrac{1}{2}u^2])\}\\&\quad\times\{t\exp[-\tfrac{1}{2}u^2t^2]+(1-t)\exp[-\tfrac{1}{2}u^2(1-t)^2]\},\\-\frac{db_t}{dt}&=\{u^2/(1+\exp[-\tfrac{1}{2}u^2])\}\\&\quad\times\{t\exp[-\tfrac{1}{2}u^2t^2]-(1-t)\exp[-\tfrac{1}{2}u^2(1-t)^2]\}.\end{aligned}\right\}\quad(18)$$

APPENDIX 2

Evaluation of $\overline{(\sum_{hkl}{}' \varphi_o\varphi_{ct}/\sum_{hkl}1)_\theta}=\chi(t)$

We first obtain

$$\chi(1)=\overline{\left(\sum_{hkl}{}'\varphi_o\varphi_c/\sum_{hkl}1\right)_\theta}\,.$$

The probability distribution of φ_o is

$$\frac{1}{(2\pi)^{\frac{1}{2}}\sigma}\exp[-\varphi_o^2/(2\sigma^2)]d\varphi_o\,,$$

and, given φ_o, the distribution of $\delta\varphi=(\varphi_o-\varphi_c)$ is

$$\frac{1}{(2\pi)^{\frac{1}{2}}\sigma\gamma_2}\exp[-(\delta\varphi-\gamma_1\varphi_0)^2/(2\sigma^2\gamma_2^2)]d(\delta\varphi)\,,$$
$$\gamma_1=(1-\exp[-\tfrac{1}{2}u^2]),\quad\gamma_2=(1-\exp[-u^2])^{\frac{1}{2}}\,,$$

cf. Part I, Fig. 7 and equation (8*d*). It follows, on putting $\varphi_o=y$ and $\delta\varphi=z_1$, and therefore $\varphi_c=(y-z_1)$, that

$$\begin{aligned}\chi(1)&=\frac{2}{(2\pi)^{\frac{1}{2}}\sigma(2\pi)^{\frac{1}{2}}\sigma\gamma_2}\int_{y=0}^{\infty}\exp[-y^2/(2\sigma^2)]\\&\quad\times\left(\int_{z_1=y}^{\infty}y(y-z_1)\exp[-(z_1-\gamma_1y)^2/(2\sigma^2\gamma_2^2)]dz_1\right)dy\\&=\frac{1}{\pi\sigma^2\gamma_2}\left(\int_{y=0}^{\infty}\exp[-y^2/(2\sigma^2)]\int_{z'=y(1-\gamma_1)}^{\infty}(y^2-\gamma_1y^2)\right.\\&\quad\times\exp[-(z')^2/(2\sigma^2\gamma_2^2)]dz'dy\\&\quad-\int_{y=0}^{\infty}\exp[-y^2/(2\sigma^2)]\int_{z'=y(1-\gamma_1)}^{\infty}yz'\\&\quad\left.\times\exp[-(z')^2/(2\sigma^2\gamma_2^2)]dz'dy\right)\qquad(z'=z_1-\gamma_1y)\\&=\frac{1}{\pi\sigma^2\gamma_2}\left((1-\gamma_1)\int_{y=0}^{\infty}y^2\exp[-y^2/(2\sigma^2)]\int_{z''=y(1-\gamma_1)/(2)^{\frac{1}{2}}\gamma_2\sigma}^{\infty}\right.\\&\quad\times\exp[(-z'')^2](2)^{\frac{1}{2}}\gamma_2\sigma dz''dy\\&\quad\left.-\gamma_2^2\sigma^2\int_{y=0}^{\infty}y\exp[-y^2/(2\sigma^2)-(1-\gamma_1)^2y^2/(2\sigma^2\gamma_2^2)]dy\right)\\&\qquad\qquad(z''=z'/(2)^{\frac{1}{2}}\gamma_2\sigma)\,.\end{aligned}$$

Making use of the relations,

$$\gamma=\gamma_2/(1-\gamma_1),\quad\gamma_2^2=\gamma^2/(1+\gamma^2)\,,$$

and putting

$$y\frac{1-\gamma_1}{(2)^{\frac{1}{2}}\gamma_2\sigma}=\frac{y}{(2)^{\frac{1}{2}}\gamma\sigma}=y'\,,$$

we get

$$\begin{aligned}\chi(1)&=\frac{\gamma_2}{\pi}\left(4\gamma^2\sigma^2\int_{y'=0}^{\infty}(y')^2\exp[-\gamma^2y'^2]\right.\\&\quad\left.\times\int_{y'}^{\infty}\exp[-z''^2]dz''dy'-\int_{y=0}^{\infty}y\exp[-y^2/(2\gamma_2^2\sigma^2)]dy\right)\\&=\frac{\gamma_2\sigma^2}{\pi}\left[\left\{-2\left|\exp[-\gamma^2y'^2]y'\int_{y'}^{\infty}\exp[-z''^2]dz''\right|_{y'=0}^{\infty}\right.\right.\\&\quad+2\int_{y'=0}^{\infty}\exp[-\gamma^2y'^2]\left(\int_{y'}^{\infty}\exp[-z''^2]dz''\right)dy'\\&\quad\left.\left.-2\int_{y'=0}^{\infty}y'\exp[-\gamma^2y'^2-y'^2]dy'\right\}-\gamma_2^2\right]\\&=\frac{\gamma_2\sigma^2}{\pi}\{0+(\tan^{-1}\gamma)/\gamma-1/(1+\gamma^2)-\gamma_2^2\}\,,\end{aligned}$$

cf. derivation of equation (10*a*) in Part I.

When the value of t is different from unity, we must replace $\varphi_c=(y-z_1)$ in the above calculation by

$$\begin{aligned}\varphi_{ct}&=b_t\varphi_o+\tfrac{1}{2}(a_t-b_t)(\varphi_o-\varphi_c)\pm c_t(\overline{\varphi^2})^{\frac{1}{2}}\ \text{after equation (17)}\\&=b_ty+\tfrac{1}{2}(a_t-b_t)z_1\pm c_t\sigma\,.\end{aligned}$$

In carrying out the very first integration with respect to z_1, the effect of the term $\pm c_t\sigma$ disappears, and after further simplifications (as for $\chi(1)$), we finally get

$$\begin{aligned}\chi(t)&=\frac{\gamma_2\sigma^2}{\pi}\left[\frac{a_t-b_t}{2}\gamma_2^2\right.\\&\quad\left.+\left(b_t+\gamma_1\frac{a_t-b_t}{2}\right)\frac{1}{1-\gamma_1}\left(\frac{\tan^{-1}\gamma}{\gamma}-\frac{1}{1+\gamma^2}\right)\right]\\&=\frac{\sigma^2}{2\pi}\left[a_t\left\{\gamma_2\frac{\gamma^2}{1+\gamma^2}-\gamma_1\left(\frac{\gamma}{1+\gamma^2}-\tan^{-1}\gamma\right)\right\}\right.\\&\quad\left.-b_t\left\{\gamma_2\frac{\gamma^2}{1+\gamma^2}+\left(\frac{\gamma}{1+\gamma^2}-\tan^{-1}\gamma\right)(2-\gamma_1)\right\}\right]\\&=\frac{\sigma^2}{2\pi}\left[a_t\left\{\gamma_2\frac{\gamma^2}{1+\gamma^2}+\left(\frac{\gamma_2}{\gamma}-1\right)\left(\frac{\gamma}{1+\gamma^2}-\tan^{-1}\gamma\right)\right\}\right.\\&\quad\left.-b_t\left\{\gamma_2\frac{\gamma^2}{1+\gamma^2}+\left(\frac{\gamma_2}{\gamma}+1\right)\left(\frac{\gamma}{1+\gamma^2}-\tan^{-1}\gamma\right)\right\}\right]\end{aligned}$$

$$= \frac{\sigma^2}{2\pi}\left[a_t\left\{\gamma_2\left(1-\frac{\tan^{-1}\gamma}{\gamma}\right)+\left(\tan^{-1}\gamma-\frac{\gamma}{1+\gamma^2}\right)\right\}\right.$$
$$\left.-b_t\left\{\gamma_2\left(1-\frac{\tan^{-1}\gamma}{\gamma}\right)-\left(\tan^{-1}\gamma-\frac{\gamma}{1+\gamma^2}\right)\right\}\right]$$
$$= \frac{\sigma^2}{2\pi}[a_t\Gamma_a+b_t\Gamma_b]\,, \qquad (19a)$$

where

$$\left.\begin{aligned}\Gamma_a &= \{(1-\exp[-u^2])^{\frac{1}{2}}-\exp[-u^2/2]\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}\}\\ &\quad+\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}-\exp[-u^2/2](1-\exp[-u^2])^{\frac{1}{2}}\}\\ &= (1-\exp[-u^2/2])\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}\\ &\quad+(1-\exp[-u^2])^{\frac{1}{2}}\}\,,\\ \Gamma_b &= (1+\exp[-u^2/2])\{\tan^{-1}(\exp[u^2]-1)^{\frac{1}{2}}\\ &\quad-(1-\exp[-u^2])^{\frac{1}{2}}\}\,.\end{aligned}\right\} \qquad (19b)$$

APPENDIX 3

In the discussion of the curves for $\bar{\eta}_{F.S.}$ against U, $\bar{\varrho}$, etc., we have ignored the influence of (1) statistical fluctuations in the averages used for calculating the residual, $R(t)$, and (2) 'diffraction effects' due to neighbouring atoms, which can also be treated as series-termination errors.

The first effect corresponds to that discussed in Part I, Appendix 2(*d*), and can be represented by a fluctuation $(\Delta\eta)_1$, where, for a 2-dimensional summation with N terms,

$$\{\overline{(\Delta\eta)_1^2}\}^{\frac{1}{2}} \simeq \{3(1-\eta)/N\}^{\frac{1}{2}} \simeq 1{\cdot}45u_0/U \qquad (\eta < \tfrac{1}{2})\,.$$

An exact treatment of the second effect is a little difficult, but if we make use of the discussion (cf. Qurashi & Vand, 1953, § 3) for atoms overlapping in projection, and take $\bar{\delta}$ ($\sim 1{\cdot}5$ Å) as the average distance (in projection) of an atom from its six nearest neighbours, the uncertainty $(\Delta\eta)_2$ due to this cause can be estimated as*

$$\{\overline{(\Delta\eta)_2^2}\}^{\frac{1}{2}} \simeq 2C/U(\bar{\delta}) = 2Cd_{\min.}/(2\pi\bar{\delta}) = 2C(\Delta/\bar{\delta})/U\,,$$

where $C \simeq 1$ for optimally weighted Fourier syntheses ($W^2 f \propto d^\nu$, $\nu = n+1$, or $n+2$), and $C \simeq 2{\cdot}5$ for unweighted syntheses. Thus the total uncertainty, $\Delta\eta$, for a 2-dimensional synthesis is given by

$$\{\overline{(\Delta\eta)^2}\}^{\frac{1}{2}} = \{\overline{(\Delta\eta)_1^2}+\overline{(\Delta\eta)_2^2}\}^{\frac{1}{2}} \simeq \{(1{\cdot}45u_0/U)^2 + 4C^2(\Delta/\bar{\delta})^2/U^2\}^{\frac{1}{2}}$$
$$= (1{\cdot}45/U)(u_0^2+C^2\Delta^2)^{\frac{1}{2}} \quad (\bar{\delta} = 1{\cdot}4 \text{ Å})\,.$$

Now, we can take $\{\overline{(\Delta\eta)^2}\}^{\frac{1}{2}} \leqslant \bar{\eta}$ as a limiting criterion for reliable convergence, because this gives 85% probability that $(\bar{\eta}+\Delta\eta)$ still has the sign of $\bar{\eta}$. Application of this criterion gives the following results:

(*a*) $\nu = n+2$

$$\bar{\eta} \simeq (1{\cdot}3-u_0)^2(u_0/U)^{\frac{1}{2}} \simeq K(u_0/U)^{\frac{1}{2}} \quad (\bar{\eta} < 0{\cdot}7\,,\ K \sim 1)\,,$$

whence the limiting condition is

$$K(u_0/U)^{\frac{1}{2}} \geqslant (1{\cdot}45/U)(u_0^2+\Delta^2)^{\frac{1}{2}} = 1{\cdot}45(u_0/U)(1+(\Delta/u_0)^2)^{\frac{1}{2}},$$

whence

$$(u_0/U)^{\frac{3}{2}} \leqslant (K/1{\cdot}45)/(1+(\Delta/u_0)^2)^{\frac{1}{2}},$$

so that

$$\bar{\eta} = K(u_0/U)^{\frac{1}{2}} \leqslant (K^3/1{\cdot}45)^{\frac{1}{2}}(1+(\Delta/u_0)^2)^{-\frac{1}{4}}.$$

Since $u_0 = (2\pi/d_{\max.})\Delta \sim \Delta$ with $d_{\max.} \sim 8$ Å, we finally get

$$\bar{\eta} \leqslant K^{3/2}/(\sqrt{1{\cdot}45}\times\sqrt{1{\cdot}41}) \simeq \sqrt{\tfrac{1}{2}}K^{3/2} \sim 0{\cdot}7\,,$$

which is always satisfied when there are a large number of terms in the summation. It is interesting to note that there is no lower limit to the useful values of $\bar{\eta}$ in this case, although of course u_0 is limited to being less than unity (approximately), which corresponds to $\Delta < 1$ Å, a needlessly generous limit.

(*b*) $\nu = n+1$

$$\bar{\eta} \simeq 0{\cdot}55/U \qquad (\bar{\eta} < 0{\cdot}3)\,,$$

whence for the limit,

$$0{\cdot}55/U \geqslant (1{\cdot}45/U)(u_0^2+\Delta^2)^{\frac{1}{2}} \simeq (1{\cdot}45/U)(2u_0\Delta)^{\frac{1}{2}} = 1{\cdot}45(u_0/U)(d_{\max.}/\pi)^{\frac{1}{2}},$$
$$(\Delta = u_0 d_{\max.}/(2\pi) \sim u_0)\,,$$

whence

$$u_0 \leqslant (0{\cdot}55/1{\cdot}45)(\pi/d_{\max.})^{\frac{1}{2}},$$

i.e.

$$U \simeq (d_{\max.}/d_{\min.})u_0 \leqslant (0{\cdot}55/1{\cdot}45)(\pi d_{\max.})^{\frac{1}{2}}/d_{\min.}\,,$$

so that finally

$$\bar{\eta} = 0{\cdot}55/U \geqslant (1{\cdot}45/\sqrt{\pi})d_{\min.}/\sqrt{d_{\max.}} \simeq 0{\cdot}2$$

for a cell side of the order of 8 Å, and using all the reflexions observable with Cu $K\alpha$ radiation. This shows that all the region $0{\cdot}2 < \bar{\eta} < 1{\cdot}0$ gives good convergence. This lower limit for $\bar{\eta}$ quite naturally decreases as the number of reflexions used increases.

(*c*) $\nu = 1{\cdot}5$ (*unweighted synthesis*)

We can anticipate from the above results that the lower limit for $\bar{\eta}$ will be fairly high in this case.

Now,

$$\bar{\eta} \simeq \exp[-0{\cdot}7U]$$

(to within 20% in the range $0{\cdot}1 < \bar{\eta} < 1{\cdot}0$)

and for this case $C = 2{\cdot}5$, whence

$$(\overline{(\Delta\eta)^2})^{\frac{1}{2}} \simeq (1{\cdot}45/U)\{u_0^2+(2{\cdot}5\Delta)^2\}^{\frac{1}{2}} = 1{\cdot}45\times 2{\cdot}5(\Delta/U)\{1+(0{\cdot}4u_0/\Delta)^2\}^{\frac{1}{2}},$$

whence we get for the limit,

$$\bar{\eta} \geqslant 3{\cdot}62(\Delta/U)\{1+(0{\cdot}4u_0/\Delta)^2\}^{\frac{1}{2}},$$

* It is well to note that the effect will be proportionately greater if one or all of the neighbouring atoms are heavier than the atom under consideration.

i.e.

$$3{\cdot}62\Delta\{1+(0{\cdot}4u_0/\Delta)^2\}^{\frac{1}{2}} \leqslant U\times\bar{\eta} = 0{\cdot}5\pm 0{\cdot}1 \qquad (0{\cdot}15 < \bar{\eta} < 0{\cdot}75)\,,$$

whence

$$U = 2\pi\Delta/d_{\min.} \leqslant (2\pi/d_{\min.})(0{\cdot}5/3{\cdot}62)/\{1+(0{\cdot}4u_0/\Delta)^2\}^{\frac{1}{2}} \simeq 0{\cdot}8/d_{\min.}\,,$$

so that

$$\bar{\eta} = \exp[-0{\cdot}7U] \geqslant \exp[-0{\cdot}56/d_{\min.}] \simeq 0{\cdot}5\,,$$

for the reflections within the limiting sphere of Cu $K\alpha$ radiation. Now, this limit on $\bar{\eta}$ corresponds to $R_I \leqslant 45\%$, and provides some justification for the usual bias against attempting the refinement of an approximation with a reliability index greater than 50%. This is to be contrasted with the properly weighted syntheses, for which the useful upper limit of R_I is considerably higher. Similarly the upper limit of u_0 (and Δ) increases progressively as we go from case (*c*) to case (*a*) above.

Finally, we must note that the value of the fluctuation $\Delta\eta$ is not the same for all three coordinates of any one atom. This follows from the fact that only corresponding coordinates of neighbouring (or overlapping) atoms are involved in the equations for the separate shifts (cf. Qurashi & Vand, 1953, equation (9)). However, it appears that the fluctuation $(\Delta\eta)_1$ is the same for all three coordinates. Thus we get

$$\eta_x = \bar{\eta}+(\Delta\eta)_1+(\Delta\eta)_{2,x}\,,$$
$$\eta_y = \bar{\eta}+(\Delta\eta)_1+(\Delta\eta)_{2,y}\,,$$
$$\eta_z = \bar{\eta}+(\Delta\eta)_1+(\Delta\eta)_{2,z}\,.$$

Since $(\delta x)_{\text{calc.}} = \eta_x(\delta x)_{\text{obs.}}$, etc., it is readily seen that when $\{\overline{(\Delta\eta)_2^2}\}^{\frac{1}{2}}$ is comparable with $\bar{\eta}$, the calculated vector shifts can differ very considerably in direction from the actual shifts required. Since $\overline{(\Delta\eta)_2^2} \sim \overline{(\Delta\eta)_1^2}$, this effect is small within the limits of useful $\bar{\eta}$ calculated earlier, because $\{\overline{(\Delta\eta)_2^2}\}^{\frac{1}{2}} < \bar{\eta}/\sqrt{2}$.

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Calculation of Geometrical Structure Factors for Space Groups of Low Symmetry. II

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(*Received* 6 *December* 1954 *and in revised form* 14 *February* 1955)

This instrument (called SUMCOS) assists in the calculation of $\sum_j \cos(hx_j+ky_j+lz_j)$ by hand. It does this by forming $\cos(hx_j+ky_j+lz_j)$ separately for ten atoms, and simultaneously presenting the values of these ten cosines ready for addition for any given (h, k, l). The final addition must be done by hand.

The values of $\cos(hx_j+ky_j+lz_j)$ are derived from a table of $\cos hx_j$ by using a simple mechanical arrangement to shift the origin of this table by (ky_j+lz_j). The values are presented for addition by switching on a small light behind the particular value of $\cos hx_j$ on the table, which is written on translucent material. New values of $\cos(hx_j+ky_j+lz_j)$ are presented for successive h simply by turning to the next position of a 24-position switch.

1. Introduction

Part I of this paper (Radoslovich & Megaw, 1955) described a device for moving the origin of a table of cosines by any arbitrary amount $(ky+lz)$ in order to read $\cos(hx+ky+lz)$ from a table of $\cos hx$. It consisted of a box carrying a fixed scale and two tables on a movable chart, so that shifts of origin could be made easily and rapidly. The usefulness of this box in calculations for triclinic and monoclinic space groups was pointed out.

Such a box speeds up calculations dealing with one atom at a time. In most calculations, however, we are concerned with several chemically identical but crystallographically distinct atoms, and we are therefore interested in the quantity

$$\sum_{j=0}^{N} \cos(hx_j+ky_j+lz_j)\,,$$

where the summation is over N chemically similar atoms. This could be computed rapidly if the values of