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## Optimization of Counting Times in Computer-Controlled X-Ray and Neutron Single-Crystal Diffractometry

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An on-line computer-controlled X-ray or neutron single-crystal diffractometer with background count times and scan speeds under the control of the computer not only makes possible the optimum division of counting time between background and scan to maximize the precision of the intensity measurement but also permits the total amount of counting time available for the structure determination or re-determination to be so distributed among the reflections as to obtain maximum precision in any desired combination of least-squares refined parameters. The precision of any such combination is maximized variationally with respect to the reflection weights (of which the parameters refined by least-squares are explicit functions) subject to the constraint that the sum of the counting times, on which the weights depend, is fixed. The existence of a stationary maximum depends on the assumption that the measurements of  $\Delta F$  are subject not only to counting errors but to other random errors which effectively set a point of diminishing returns so far as further improvement of parameter precision by additional counting is concerned. Results of this study indicate that unless the amount of time available is far beyond the point of diminishing returns, substantial numbers of reflections should not be counted at all, except to the bare minimum amount necessary for the determination of the trial structure. For optimizing the precision of positional parameters the counting time should be concentrated on the high-angle reflections; for thermal parameters low-angle reflections are also required.

### Introduction

An on-line computer-controlled X-ray or neutron single-crystal diffractometer *with background count times and scan speeds under the control of the computer* should offer certain advantages over conventional fixed-time or fixed-count procedures in enabling variances of the measured intensities and structure factors to be approximately specified and even optimized. As is already known (Parrish, 1956; Mack & Spielberg, 1958) the time available for a given reflection can be divided between background and scan so as to minimize the variance of the intensity, and the times allotted to counting or counts allotted to timing the various reflections can be specified so as to give within reason any desired precision mode in the measured quantities: constant absolute precision in intensity, constant absolute precision in the structure factor, constant relative

precision, or other (for references, see Parrish, 1962).

However, it should also be possible to divide the total amount of instrument (counting) time available for the entire determination among the various reflections so as best to accomplish the particular objectives of the structure determination or redetermination (apart from the elucidation of a correctly refinable trial structure): minimization of the variances of the positions of all atoms or of some group of atoms or of specified functions of the positional parameters, perhaps even the precise determination of a single interatomic distance, even conceivably (but not likely) maximization of the precision of certain specified thermal parameters. This amounts to the specification of the optimum weights for the various reflections, upon which the required counting times depend and which are used in the least-squares refinement.

In the case of powder diffractometry, the possibility of distributing the total available counting time among the various observations so as to minimize the variance

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of parameters derived from the line profiles has been pointed out by Wilson, Thomsen & Yap (1965) and Wilson (1967), who give equations for the optimum counting times for fixed-time counting and the optimum counts for fixed-count timing. They also mention the virtual necessity of an on-line computer (or equivalent) for continually adjusting times or counts. Our approach resembles theirs in the use of the variational method, but the applications and results are rather different.†

Since the division of counting time between scan and background or among different reflections depends on the magnitudes of the intensities themselves, these procedures might seem well suited to a structure *re-determination*, where intensities sufficiently accurate for this purpose are already known; in this case the computations can be done off-line. With an on-line computer and in the absence of such prior information, the counts for each reflection may be taken in two consecutive 'passes', separated by a rapid on-line computation, each pass consisting of background counts on both sides of the peak and a scan between. During the first pass enough counts are obtained in pre-fixed times to permit the calculation of the total optimum counting times for the background and scan and during the second pass counting is done for the remaining balances of these optimum times.

The division of time will depend on approximate knowledge of the magnitudes of various kinds of uncertainty in the experimental work and in the fit to the structure model. We shall limit ourselves here to a consideration of random errors, assumed normally distributed, although it may become possible to consider limits of systematic error in a somewhat similar context. In our mathematical model, we shall assume that there are random errors of three main types: counting errors (*c*) in the intensity measurements, errors of experimental origin (*e*) which affect the net intensity approximately in proportion to its magnitude (but may be a function of scattering angle also), and 'random' errors (*f*) in the atomic form factors (remaining after compensation by adjustment of temperature factors, which of course subjects the latter to 'systematic' errors) to an extent that depends primarily on the scattering angle and only weakly on the structure factor magnitude if (as we shall assume) we have a roughly equal-atom structure with no atoms in special positions. Thus the variance in  $\Delta F$  may be expressed

$$\sigma_{\Delta F}^2 = \frac{1}{(2 \text{Lp}F)^2} (\sigma_c^2 + \sigma_e^2) + \sigma_f^2. \quad (1)$$

In the counting error (*c*) we include not only the counting errors proper as estimated from statistics, but also the short-term errors in the source intensity or the estimate of them that is used in the calculations. When

† After this paper had been submitted it came to my attention that Hamilton (1967) and V. Schomaker (unpublished) had independently investigated aspects of the problem here treated, apparently with an approach similar to mine.

a monitor counter is used, as is common in neutron diffraction, counting statistics may be used directly for these short-term errors. Even when there is no monitor we may expect that rapid short-term fluctuations in the source intensity (due to electrical 'noise' in the X-ray generator regulation circuitry) will have properties closely analogous to counting statistics. The experimental errors (*e*) include, perhaps among others, contributions from long-term variations in source intensity, effect of an inhomogeneous beam as the crystal rotates or moves in it, and perhaps residual absorption after estimation and correction. These errors are partly systematic (not completely independent from reflection to reflection) but we shall assume that they have in effect a random part that we can discuss here. Much the same can be said for the errors in the form factors, but we shall assume that these are sufficiently well randomized by the signs of the individual terms in the summation for the structure factor if we have a many-atom structure that is not too strongly dominated by one or a few atoms. This division of errors between random and systematic admittedly may not be very satisfactory, but we need it here for a starting point and we may hope that it will be further clarified later if the need arises. [The problem of estimating variances in intensities and structure factors has been discussed by Abrahams & Reddy (1965)].

Secondary extinction and multiple scattering are difficult to deal with here because their functional dependences on intensity and scattering angle are very complicated, and because errors due to their neglect or incomplete correction are not normally distributed around a zero mean. It seems best here to assume that secondary extinction has been eliminated or accurately corrected for by the methods of Zachariasen (1963, 1967) and multiple scattering has been sufficiently minimized by avoidance of crystal orientations that give rise to systematic multiple diffraction (Zachariasen, 1965; Burbank, 1965) and/or estimated and corrected for as suggested by Coppens (1968). Coppens's procedure also is best accomplished with an on-line computer, and perhaps could be integrated with the procedures here discussed.

The following treatment assumes that the least-squares procedure minimizes  $\sum_j w_j (|F_o| - |F_c|)^2$ , but adaptation of it to minimization of  $\sum_j w'_j (|F_o|^2 - |F_c|^2)^2$  should present no difficulties.

The intensity of the reflection is given by

$$I = k\omega \left( C_S - \frac{t_S}{t_B} C_B \right) = k\Delta\psi \left( \frac{C_S}{t_S} - \frac{C_B}{t_B} \right) = k\Delta\psi (R_S - R_B), \quad (2)$$

where *k* is a constant for the experiment,  $\omega$  is the angular scanning speed (assumed uniform for a given reflection),  $\Delta\psi$  is the angular range of scan,  $C_S$  and  $C_B$  are the total scan and background counts respectively,  $t_S$  and  $t_B$  are the respective effective counting times (taken proportional to the monitor counts in

neutron work), and  $R_S$  and  $R_B$  are the respective average counting rates. In the terms above discussed, the variance in  $I$  is

$$\begin{aligned} \sigma_I^2 &= (k\Delta\psi)^2 \left[ \frac{C_S}{t_S^2} + \frac{C_B}{t_B^2} + \frac{M_S}{M_S^2} \cdot \frac{C_S^2}{t_S^2} + \frac{M_B}{M_B^2} \cdot \frac{C_B^2}{t_B^2} \right. \\ &\quad \left. + s_e^2 \left( \frac{C_S}{t_S} - \frac{C_B}{t_B} \right)^2 \right] \\ &= (k\Delta\psi)^2 \left[ \frac{R_S}{t_S} + \frac{R_B}{t_B} + \frac{1}{\varrho} \left( \frac{R_S^2}{t_S} + \frac{R_B^2}{t_B} \right) + s_e^2 (R_S - R_B)^2 \right] \end{aligned} \quad (3)$$

where  $M_S$  and  $M_B$  are monitor counts during scan and background,  $\varrho$  is the measured mean monitor counting rate in the case of neutrons (and an empirical constant in the case of X-ray measurements without monitor), and  $s_e = \sigma_e/I$ . We have here made use of the fact that the variance in the number of counts is equal to the number of counts itself.

#### Division of counting time between scan and background

The problem of maximization of the precision of the difference between two counting rates by appropriately dividing the available time between them has been discussed in connection with powder diffractometry by Parrish (1956) and Mack & Spielberg (1958); these authors also give several references to prior solutions of the same problem for use in radiochemical counting applications. Their solution is equivalent to

$$t_S = \frac{R_S^{1/2}}{R_S^{1/2} + R_B^{1/2}} t, \quad t_B = \frac{R_B^{1/2}}{R_S^{1/2} + R_B^{1/2}} t, \quad (4)$$

where the terms in  $1/\varrho$  have been neglected. [A similar result has been reported independently by Hamilton (1967)]. These equations are obtained by minimizing  $\sigma_I^2$  [equation (3)] with respect to  $t_S$  and  $t_B$  with the constraint  $t_S + t_B = t$ . Inclusion of the terms in  $1/\varrho$  gives

$$t_S = \frac{R_S'^{1/2}}{R_S'^{1/2} + R_B'^{1/2}} t, \quad t_B = \frac{R_B'^{1/2}}{R_S'^{1/2} + R_B'^{1/2}} t, \quad (5)$$

where

$$R_S' = R_S(1 + R_S/\varrho), \quad R_B' = R_B(1 + R_B/\varrho). \quad (6)$$

Substitution into equation (3) gives

$$\sigma_I^2 = (k\Delta\psi)^2 \left[ \frac{1}{t} (R_S'^{1/2} + R_B'^{1/2})^2 + s_e^2 (R_S - R_B)^2 \right]. \quad (7)$$

With

$$F = (I/Lp)^{1/2} = K^{1/2}(R_S - R_B)^{1/2}, \quad \sigma_F = \sigma_I/(2LpF), \quad (8)$$

where  $Lp$  is the Lorentz-polarization factor and  $K = k\Delta\psi/Lp$ , we obtain for the variance in  $\Delta F = F_o - F_c$ :

$$\sigma_{\Delta F}^2 = \frac{K}{4} \left[ \frac{1}{t} \frac{(R_S'^{1/2} + R_B'^{1/2})^2}{R_S - R_B} + s_e^2 (R_S - R_B) \right] + \sigma_f^2. \quad (9)$$

The terms  $R_S/\varrho$  and  $R_B/\varrho$  will ordinarily be quite small, especially when a monitor is used as in neutron work; it is possible however that they could be of significance

in X-ray work without a monitor. From this point on we will neglect them, and drop the primes. We then obtain

$$\begin{aligned} \sigma_{\Delta F}^2 &= \frac{K}{4} \left[ \frac{1}{t} \left( \frac{R_S^{1/2} + R_B^{1/2}}{R_S^{1/2} - R_B^{1/2}} \right) + s_e^2 (R_S - R_B) \right] + \sigma_f^2 \\ &= \frac{K}{4t} \left[ 1 + \frac{2K^{1/2}R_B^{1/2}}{|F|} \left( 1 + \frac{KR_B}{F^2} \right)^{1/2} + \frac{2KR_B}{F^2} \right] \\ &\quad + \frac{1}{4}s_e^2 F^2 + \sigma_f^2. \end{aligned} \quad (10)$$

Equation (9) or (10) may be used for calculating weights for the least-squares refinement if counting times have been apportioned between scan and background in accordance with equations (6) or (4).

#### Two-pass counting

For specified precision in the intensity  $I$  or structure factor  $F$  or structure factor difference  $\Delta F$ , we solve the appropriate equation (equation (7) in the case of  $I$ ; (9) or (10) in the case of  $\Delta F$ ) for the total time  $t$ . Provisional values of  $R_S$  and  $R_B$ , if not known beforehand, must be obtained from the first of two passes. The times  $t_{S1}$  and  $t_{B1}$  chosen for scan and background counting during the first pass should not exceed the times appropriate to  $R_S$  and  $R_B$  and should therefore be taken as the minimum values possible for any conceivable values of  $R_S$  and  $R_B$ .

For specified absolute precision in the intensity, the value assigned to  $\sigma_I$  must be such that

$$\sigma_I^2 > (k\Delta\psi)^2 s_e^2 (R_S - R_B)_{\max}^2. \quad (11)$$

On solving equations (7) and (5) for  $t_S$  and  $t_B$  in terms of  $R_S$  and  $R_B$  we find that we are in no danger of exceeding the optimum value of  $t_S$  and  $t_B$  if we take provisionally  $R_S = R_B = R_{\min}$  (where  $R_{\min}$  is the smallest possible value for  $R_B$ ) in calculating  $t_{S1}$  and  $t_{B1}$ ; we find  $t_{S1} = t_{B1} = t_1/2$ , where  $t_1$  is the total time for the first pass.

In the case where  $R_B$  and  $s_e^2 (R_S - R_B)^2$  are negligible in comparison with  $R_S$ , specification of absolute precision in the intensity amounts to specifying a fixed count  $C_S$ .

The case of specified absolute precision in the structure factor  $F$  or structure factor difference  $\Delta F$  is more complicated. The value assigned to  $\sigma_{\Delta F}$  must be such that

$$\sigma_{\Delta F}^2 \geq \sigma_f^2 + \frac{1}{4} K s_e^2 (a R_S - R_B)_{\max}, \quad a > 1. \quad (12)$$

The values assigned to  $R_S$  and  $R_B$  for calculating the values of  $t_{S1}$  and  $t_{B1}$  here depend on the value of  $a$ . If  $a \geq (R_{\max}/R_{\min})^{1/2}$  in calculating  $t_{S1}$  and  $a \geq 3$  in calculating  $t_{B1}$  (where  $R_{\max}$  is the largest possible value of  $R_S$ ), we should take  $R_S = R_{\max}$  and  $R_B = R_{\min}$  for calculating these times. The contrary cases are more complicated, requiring the finding of the minimum times by differentiation and solution of the resulting quadratic and cubic equations; it is perhaps better to try two or three trial values for  $R_S$ , keeping  $R_B = R_{\min}$ , and employ the smallest times obtained.

For specified relative precision

$$\sigma_{\Delta F}^2/F^2 > s_e^2/4 + \sigma_f^2/K(R_S - R_B)_{\min} \quad (13)$$

we should take  $R_S = R_{\max}$  and  $R_B = R_{\min}$  in calculating  $t_{S1}$  and  $t_{B1}$ .

In all cases, from the counts we obtain in the first pass we calculate new provisional values of the counting rates  $R_S$  and  $R_B$ , with which to calculate new times  $t$ ,  $t_S$ , and  $t_B$  with equations given. Then we carry out the second pass with  $t_{S2} = t_S - t_{S1}$ ,  $t_{B2} = t_B - t_{B1}$  and combine the counts and times for the two passes.

However, these procedures do not exhaust the potentialities of variable counting times. We show now how we propose to divide the total instrument counting time available for the determination among the various reflections  $j=1, 2, \dots, m$ , so as to best accomplish the particular objectives of a structure determination.

### Optimization of parameter precision

Let there be  $n$  refinable parameters  $\xi_i$ . Now it might be desired to maximize

$$\Omega \equiv \sum_{i=1}^n W_i \omega_i \quad (14)$$

where  $\omega_i$  is the weight (reciprocal variance) of  $\xi_i$  and  $W_i$  is an assigned weight representing the relative importance of precision in  $\xi_i$  in the mind of the investigator. For example,  $W_i$  could be set equal to unity for all position parameters and zero for all thermal parameters. The weight  $\omega_i \equiv 1/\sigma_i^2$  of  $\xi_i$  is given by

$$\omega_i = \frac{1}{B_{ii}} w_1,$$

where

$$1/w_1 \equiv \sigma_1^2 = \frac{1}{m-n} \sum_{j=1}^m w_j (\Delta F_j)^2$$

is the 'variance of an observation of unit weight'. Here the  $\Delta F_j$  are the residuals at the end of refinement and  $w_j = 1/\sigma_{\Delta F}^2$  are the weights estimated from the experiment and used in the refinement. If our assumptions have been correct and the magnitudes of the error parameters  $s_e$  and  $\sigma_f$  have been properly assigned we should expect  $\sigma_1$ , the 'goodness of fit', to be unity; *i.e.* that  $w_1 = 1$ . (Even if  $w_1$  is not actually unity we will at least assume that it is constant with respect to variation of the  $w_j$ ). Taking  $w_1 = 1$  we have

$$\omega_i = 1/B_{ii} \quad (15)$$

where

$$(\mathbf{B}) = (\mathbf{A})^{-1} \quad (16)$$

and  $(\mathbf{A})$  is the normal equations matrix.

We wish to maximize  $\Omega$  with respect to variation of the weights  $w_j$ , upon which depend the times  $t_j$  for which the reflections must be counted, subject to the constraint

$$\sum_j t_j = T, \quad (17)$$

where  $T$  is the total available counting time for all reflections. We may write equations (9) and (10) in the form

$$t_j = \frac{\lambda_j}{1/w_j - \kappa_j^2} \quad (18)$$

where  $1/w_j = \sigma_{\Delta F_j}^2$  and

$$\lambda_j = \frac{K(R_S^{1/2} + R_B^{1/2})^2}{4(R_S - R_B)} \simeq \frac{K}{4} \left[ 1 + \frac{2K^{1/2}R_B^{1/2}}{|F|} \left( 1 + \frac{KR_B}{F^2} \right)^{1/2} + \frac{2KR_B}{F^2} \right] \quad (19)$$

$$\kappa_j^2 = \frac{1}{4} K s_e^2 (R_S - R_B) + \sigma_f^2 = \frac{1}{4} s_e^2 F^2 + \sigma_f^2. \quad (20)$$

Equation (19), second part, reduces to

$$\lambda = \frac{1}{4} K = K \Delta \psi / 4 L p \quad (19a)$$

when the background counting rate is negligible. Equation (20) represents that part of the variance in  $\Delta F$  that is due to sources other than counting statistics.

It is necessary to differentiate  $\Omega$  with respect to the  $w_j$ . The derivative of the normal equations determinant  $A$  with respect to  $w_j$  is

$$\frac{\partial A}{\partial w_j} = \sum_k \sum_l a_{j,kl} \bar{A}_{kl}, \quad (21)$$

where

$$a_{j,kl} = \frac{\partial (\Delta F)_j}{\partial \xi_k} \cdot \frac{\partial (\Delta F)_j}{\partial \xi_l} \quad (22)$$

and  $\bar{A}_{kl}$  is the cofactor of element  $A_{kl}$  in the determinant  $A$  (obtained by deleting the  $k$ th row and the  $l$ th column of  $A$ , evaluating the result as a determinant and multiplying by  $(-1)^{k+l}$ ; if  $A$  has only a single element, its cofactor is  $+1$ ). From

$$B_{st} = \bar{A}_{ts} / A \quad (23)$$

we obtain by differentiation

$$\frac{\partial B_{st}}{\partial w_j} = \frac{1}{A^2} \sum_k \sum_l a_{j,kl} (A \bar{A}_{klts} - \bar{A}_{kl} \bar{A}_{ts}), \quad (24)$$

where  $\bar{A}_{klts}$  is the determinant obtained by deleting rows  $k$  and  $t$  and columns  $l$  and  $s$  of  $A$  and multiplying by  $(-1)^{k+l+t+s}$ ; it vanishes if  $k=t$  and/or  $l=s$ ; for  $A$  of order 2 it has as a possible non-zero value only  $+1$ ; for  $A$  of order 1 it is zero. From this result and equations (15) and (23) we obtain

$$\Omega_{i,j} \equiv \frac{\partial \omega_i}{\partial w_j} = \frac{1}{\bar{A}_{ii}^2} \sum_k \sum_l a_{j,kl} (\bar{A}_{kl} \bar{A}_{ii} - A \bar{A}_{klit}). \quad (25)$$

We can of course be more general, and elect to maximize a linear combination

$$\Omega' = \sum_{k=1}^{n'} W'_k \omega'_k \quad (26)$$

of the weights of linear (or linearizable) functions  $\eta_k$  of the  $\xi_i$  (*e.g.* interatomic distances):

$$\eta_k = \sum_i P_{ik} \xi_i + c_k. \quad (27)$$

Now

$$\omega'_k = 1/Q_{kk}, \quad (28)$$

where  $(\mathbf{Q})$  is an  $n' \times n'$  matrix,

$$(\mathbf{Q}) = (\tilde{\mathbf{P}})(\mathbf{B})(\mathbf{P}); \quad Q_{kk} = \sum_s \sum_t P_{sk} P_{tk} B_{st}. \quad (29)$$

Corresponding to equation (25) we may write

$$\Omega'_{k,j} \equiv \frac{\partial \omega'_k}{\partial w_j} = \frac{1}{A^2 Q_{kk}} \sum_s \sum_t P_{sk} P_{tk} \sum_k \sum_l a_{j,kl} (\bar{A}_{klls} - A \bar{A}_{klls}). \quad (30)$$

We now write

$$\Omega_j \equiv \frac{\partial \Omega}{\partial w_j} = \sum_i W_i \Omega_{i,j}; \quad \Omega'_j \equiv \frac{\partial \Omega'}{\partial w_j} = \sum_k W'_k \Omega'_{k,j}. \quad (31)$$

The variational equation may now be written in either the unprimed form or the primed form (we will confine ourselves henceforth to the former)

$$\delta(\Omega - \alpha^2 T) = \sum_j \delta w_j \left( \Omega_j - \alpha^2 \frac{dt_j}{dw_j} \right) = 0, \quad (32)$$

where  $\alpha^2$  is a Lagrangian multiplier. For arbitrary and independent variations of  $w_j$  the quantity in the second parenthesis must vanish for each term in the sum; from equation (18) we obtain

$$\Omega_j = \alpha^2 \frac{\lambda_j}{(1 - w_j \kappa_j^2)^2}.$$

Taking the positive square roots ( $w_j$  may not exceed  $1/\kappa_j^2$ ) we obtain

$$w_j = \frac{1}{\kappa_j^2} \left[ 1 - \alpha \frac{\lambda_j^{1/2}}{\Omega_j^{1/2}} \right]. \quad (33)$$

Substituting this into equation (18) we obtain

$$t_j = \frac{\lambda_j}{\kappa_j^2} \left( \frac{\Omega_j^{1/2}}{\alpha \lambda_j^{1/2}} - 1 \right), \quad (34)$$

and on summing [equation (17)] we get

$$\alpha = \frac{\sum_{j=1}^m \lambda_j^{1/2} \Omega_j^{1/2} / \kappa_j^2}{T + \sum_{j=1}^m \lambda_j / \kappa_j^2}. \quad (35)$$

Once the particular combination of parameters to be optimized is chosen (*i.e.* the  $W_i$  or  $W'_k$  are specified), we propose that equations (33) and (34) be used to calculate the desired weights  $w_j$ , and the required counting times  $t_j$  which can be further divided between scan and background with equations (4) or (5).

### Discussion

If the structure factor derivatives needed are already approximately known (from a previous determination), their values can be used in calculating the quantities

required in equations (25) and (30); otherwise it will be necessary to use expectation values of their squares and products:

$$\langle a_{j,kl} \rangle = \left\langle \frac{\partial(\Delta F)_j}{\partial \xi_k} \frac{\partial(\Delta F)_j}{\partial \xi_l} \right\rangle. \quad (22a)$$

The expectation value will be roughly equal to an average taken over a group of similar parameters (*e.g.* coordinates of roughly equal atoms), and its use would involve little disadvantage relative to the true values when equal weights  $W_i$  are assigned to a group of such parameters.

Provisional values for the weights are necessary in general; we might for example take  $w_j^0 = C/F_j^2$  where  $C$  is a constant [this is equivalent to neglecting  $\sigma_j^2$  in equation (20) and ignoring the bracketed quantity in equation (33)]. In principle, once having got weights from equations (33) and (35) we can put them into the equations for a second approximation, but as a practical matter this may not be necessary; in any case it would require prior knowledge of approximate intensities before data collection.

Some observations are in order concerning equations (33)–(35). The second term in the denominator of (35) has the dimensions of time; we may indeed write

$$T^0 = \sum_{j=1}^m t_j^0, \quad t_j^0 = \lambda_j / \kappa_j^2, \quad (36)$$

where  $t_j^0$  represents a counting time that would give a variance due to counting statistics equal to  $\kappa_j^2$ . Thus, we see that the 'point of diminishing returns' is reached when  $T$  is of the order of  $T^0$ ; increases in total counting time beyond  $T^0$  produce smaller and smaller increases in  $w_j$ . We also see that when  $\Omega_j$  is large (*i.e.* the structure factor is sensitive to the parameters chosen),  $w_j$  is almost equal to  $1/\kappa_j^2$ , not surprisingly. When  $\Omega_j$  is small (structure factor insensitive to the chosen parameters) the value of  $w_j$  may be small or zero. An apparent negative value means that the reflection should be left out altogether; *any time spent on it is wasted* because that time has to be taken from reflections that are more sensitive to the parameters. Reflections with  $w_j \leq 0$  will be said to have zero weight. After eliminating such reflections we may 'renormalize' by omitting the corresponding terms from the summations in equation (35). The renormalization may result in a few more reflections needing to be dropped, but ordinarily the process should be expected to converge rapidly, and again as a practical matter the renormalization may not be necessary.

To illustrate further the behavior of these equations, let us imagine a hypothetical (but unlikely) situation where  $\lambda_j = \lambda$ ,  $\kappa_j^2 = \kappa^2$ ,  $\lambda$  and  $\kappa^2$  being constants for all reflections. Equations (33) and (35) then combine to give

$$w_j = \frac{1}{\kappa^2} \left[ 1 - \frac{T^0}{T + T^0} \frac{\langle \Omega_j^{1/2} \rangle}{\bar{\Omega}_j^{1/2}} \right], \quad (37)$$

where  $\langle \Omega_j^{1/2} \rangle$  is the average of  $\Omega_j^{1/2}$  over all reflections. If for example we take the 'point of diminishing re-

turns' at  $T=T^0$ , then we should in principle omit all reflections for which  $\Omega_j^{1/2} < \langle \Omega^{1/2} \rangle / 2$ .

If we suppose that the  $\kappa_j^2$  are very small,  $T^0/(T+T^0)$  approaches unity and only those reflections for which  $\Omega_j^{1/2} > \langle \Omega^{1/2} \rangle$  will have non-zero weights. Renormalization will throw out about half of the reflections, the next renormalization will throw out about half of those left, and so on until self-consistency is reached where the number of those remaining is small enough to enable the times given to them to be as large as  $\lambda/\kappa^2$  in order of magnitude. In the limit of vanishingly small  $\kappa_j^2$  this would ultimately lead to only one reflection remaining, to which all of the counting time must be assigned; however, some of the approximations in the treatment are invalid when  $m$  is not large in comparison with  $n$ . (A treatment of this case without any approximations should give the result that the number  $m$  of reflections to be counted should be reduced to equality with the number  $n$  of refinable parameters. The selection of the  $n$  most appropriate reflections and the division of counting time among them presents a very different problem which we have not treated, as it would appear to have little or no practical importance in the present context.) We may conclude that the existence of random errors not due to counting but of roughly the same order of magnitude as the counting errors is essential to the validity of the treatment as carried out here. Indeed, an attempt to maximize  $\Omega$  in the case where the  $\kappa_j^2$  vanish will result in the finding that no stationary maximum with respect to weights  $w_j$  or counting time  $t_j$  exists.

The equations obtained by Wilson *et al.* (1965) do not show the behavior here described. A major difference is that in their treatment the function for which the variance is minimized is not an explicit function of the weights, as it is here owing to the use of weights in the least-squares refinement of an overdetermined problem.

The computation of the  $\lambda_j$  and  $\kappa_j^2$  requires approximate knowledge of the magnitude of the intensity or structure factor and of the background counting rate for each reflection, so a two-pass procedure is again necessary (unless data from a previous determination can be used). For preliminary estimate of the weight so that  $t_{B1}$  and  $t_{S1}$  can be specified one might set  $F^2$  in equation (20) to some large value, perhaps  $F_{\max}^2$ , and set the bracketed quantity in equation (33) to some fraction, say 0.10, if it is not possible or desirable to calculate it. This, of course, will result in collection of data for some reflections for which  $w_j$  will turn out to be zero, but the amount of counting time assigned to these reflections will be inconsiderable, and moreover some data for *all* reflections may be needed for the determination of the trial structure anyway.

The machine computation of the  $\Omega_j$  or  $\Omega_j^2$  can in many cases precede the data collection, and should not be as formidable as it looks because with expectation values for the  $a_{j,ik}$  many elements  $A_{ik}$  will be zero. In view of other approximations involved it may be

justifiable to assume that **(A)** is diagonal or at least block diagonal. Positional parameters in an orthogonal lattice generally have small matrix elements with each other and with other parameters, and in the absence of previous structure information the expectation values of such elements are zero; in this case equation (25) reduces to

$$\Omega_{i,j} = a_{j,ii} = \left[ \frac{\partial(\Delta F)_j}{\partial \xi_i} \right]^2, \quad (38)$$

the expectation value of which can easily be estimated. For the  $x$  parameter of atom  $v$  it is for reflection  $j$

$$\langle a_{j,v,x} \rangle = 8\pi^2 f_v^2 \cdot h_j^2 \quad (39)$$

in space group  $P\bar{1}$ . Since for positional parameters these values are quadratic in the Miller indices it may be expected that a substantial body of reflections at low and medium scattering angles may turn out to have zero values of  $w_j$ .

When (i) the background counting rate is assumed negligible, (ii)  $\sigma_e^2$  in equation (1) is assumed proportional to the square of the intensity (*i.e.*  $s_e^2 = \text{constant}$ ), (iii)  $\sigma_f^2$  is neglected, (iv)  $\sigma_c^2$  is assumed small in comparison with  $\sigma_e^2$ , (v) the normal equation matrix is assumed diagonal, and (vi) optimization is limited to a single parameter  $\xi_i$ , then equation (34) reduces to an equation presented by Hamilton (1967), derived independently in what appears to be an essentially similar way. In our notation his equation is

$$t_j \propto (\text{Lp})^{-1/2} \left| \frac{\partial |F_j|^2}{\partial \xi_i} \right| \cdot \frac{1}{|F_j|^3}$$

(In Hamilton's abstract the Lp factor has instead the exponent  $+\frac{1}{2}$ , because he defines Lp as  $F^2/I$ .)

The use of equation (38) is not in general permissible with thermal parameters because of their strong correlation with the scale factor. To illustrate, let us consider the normal equations matrix to be block diagonal, one block of which **(A)** is a  $2 \times 2$  matrix for the overall isotropic temperature factor  $B$  and the scale factor  $k$ . Equation (25) reduces, for the temperature factor, to

$$\Omega_{B,j} \equiv \frac{\partial \omega_B}{\partial w_j} = \frac{1}{A_{kk}^2} \{ [A_{BB} A_{kk} - (A_{BB} A_{kk} - A_{kB}^2) \cdot 1] a_{j,kk} - 2A_{Bk} A_{kk} a_{j,kB} + A_{kk}^2 a_{j,BB} \}. \quad (40)$$

Now if we write the Debye-Waller factor as  $\exp(-BH_j^2/4)$ , where  $H_j = (2 \sin \theta_j)/\lambda$ , then  $\partial F_j / \partial B = \partial \Delta F_j / \partial B = -H_j^2 F_j / 4$ ,  $\partial \Delta F_j / \partial k = F_j$ , and

$$a_{j,BB} = F_j^2 H_j^4 / 16, \quad a_{j,Bk} = a_{j,kB} = -F_j^2 H_j^2 / 4, \quad a_{j,kk} = F_j^2. \quad (41)$$

Summing over (say) a hemisphere in the reciprocal lattice to obtain matrix elements we get for example

$$A_{BB} = \sum_j w_j a_{j,BB} \simeq V_c \cdot \frac{1}{16} 2\pi \int_0^{H_{\max}} w F^2 H^6 dH,$$

where  $V_c$  is the unit-cell volume. For simplicity we assume here that provisionally  $w = C/F^2$ , where  $C$  is a constant, as suggested earlier. Then

$$A_{BB} = \frac{3}{112} \gamma H_{\max}^4, \quad A_{Bk} = A_{kB} \\ = - \frac{3}{20} \gamma H_{\max}^2, \quad A_{kk} = \gamma, \quad (42)$$

where

$$\gamma = C \cdot V_c \frac{2\pi}{3} H_{\max}^3 = C \cdot N, \quad (43)$$

where  $N$  is the number of reciprocal lattice points summed over. Substitution into equation (40) gives

$$\Omega_{B,j} = \frac{H_{\max}^4}{400} F_j^2 \left[ 3 - 5 \left( \frac{H_j}{H_{\max}} \right)^2 \right]^2. \quad (44)$$

The squared quantity in brackets decreases from a maximum value of 9 at  $H_j=0$  to a minimum value of zero at  $H_j/H_{\max}=(3/5)^{1/2}=0.755$  and increases to a value of 4 at  $H_j/H_{\max}=1$ . Thus, the data at small angles are as important as those at high angles in establishing the value of  $B$ , while those at intermediate angles are of little or no use. Neglect of the off-diagonal elements  $A_{kB}=A_{Bk}$  results in the loss of the first term in the brackets and leads to the unreasonable result (but nevertheless a result that is suggested by the fact that the structure factor derivative is quadratic in  $H_j$ ) that only the very high angle reflections are important in determining the temperature factor. Indeed, Cruickshank (1960) has presented an equation which would appear to indicate that data at large angles would be particularly valuable in determining vibration parameters, but he points out that that equation neglects the very serious correlation between the scale factor and the vibration parameters.

The equation corresponding to equation (44) in the case of the scale factor is

$$\Omega_{k,j} = \frac{1}{25} F_j^2 \left[ 5 - 7 \left( \frac{H_j}{H_{\max}} \right)^2 \right]^2. \quad (45)$$

The squared quantity in brackets here goes from a maximum of 25 at  $H_j=0$  to a minimum of zero at  $H_j/H_{\max}=(5/7)^{1/2}=0.845$  and increases to 4 at  $H_j/H_{\max}=1$ . The data at low angles are relatively more important in determining the scale factor (though some data at high angles are needed because of the connection with the temperature factor). Neglect of off-diagonal elements here results in the loss of the second term in the brackets and leads to the unreasonable result that, at a given  $F^2$  level, data at all angles are equally important in determining the scale factor.

It is perhaps not likely that the primary objective of a structure determination or redetermination would be the accurate evaluation of thermal parameters. Even if it were, these parameters are the ones most subject to systematic errors such as uncorrected absorption. Accordingly, the utility of equation (44), like

that of (45), may be limited to expressing more precisely what is already known intuitively from the properties of a Wilson plot.

In most cases the primary objectives of a structure determination are to obtain an atomic arrangement that is correct and positional parameters and interatomic distances and angles that are as precise as possible. If the burden of work on a diffractometer is such that counting time available for a given determination must be limited, consideration should be given to limiting the counting of low- and medium-angle reflections to the bare minimum needed to determine the trial structure and to concentrating the bulk of the time on high-angle reflections. However, Cruickshank (1956, 1960) has pointed out that with room-temperature data the proper calculation of bond lengths from positional parameters involves consideration of thermal vibration effects and knowledge of the values of thermal parameters. Therefore, if data collection is to be concentrated at high angles, serious consideration should be given to his recommendation (Cruickshank, 1960) that the crystal be maintained at a low temperature ( $<100^\circ\text{K}$ ).

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