### Analytic solution

A formal solution of (10) is $\mathbf{V}=(\mathbf{U}'\mathbf{U})^{1/2}$, and $\mathbf{R}=\mathbf{V}\mathbf{U}^{-1}$, but this leaves the signs of the square roots undefined and fails when $\mathbf{U}$ is singular. ($\mathbf{U}'$ is the transpose of $\mathbf{U}$)

More generally consider the matrices $\mathbf{U}'\mathbf{U}$ and $\mathbf{U}\mathbf{U}'$. They are both symmetric and positive definite. Also the diagonal sums of $(\mathbf{U}'\mathbf{U})^n$ and $(\mathbf{U}\mathbf{U}')^n$ are the same, and it can be shown that both matrices have the same eigenvalues. Therefore orthogonal matrices $\mathbf{H},\mathbf{K}$ exist, with determinant $+1$, such that

$$\mathbf{U}\mathbf{U}'=\mathbf{H}^{-1}\mathbf{D}^2\mathbf{H}\,,\quad \mathbf{U}'\mathbf{U}=\mathbf{K}^{-1}\mathbf{D}^2\mathbf{K} \tag{16}$$

where $\mathbf{D}^2$ is a diagonal matrix with positive elements. The matrix

$$\mathbf{M}=\mathbf{H}\mathbf{U}\mathbf{K}^{-1} \tag{17}$$

has the property that

$$\mathbf{M}\mathbf{M}'=\mathbf{M}'\mathbf{M}=\mathbf{D}^2 \tag{18}$$

and commutes with $\mathbf{D}^2$. Hence, if $\mathbf{D}^2$ is nondegenerate, $\mathbf{M}$ is already diagonal. If $\mathbf{D}^2$ is degenerate, with eigenvalues $D_\lambda^2$, $\mathbf{M}$ and $\mathbf{M}'$ are block-diagonal, each block being of the form $M_\lambda=d_\lambda Q_\lambda$, where $d_\lambda^2=D_\lambda^2$ and $Q_\lambda Q_\lambda'=I_\lambda$. Thus $Q_\lambda$ is orthogonal, with determinant $\pm 1$. The matrix $\mathbf{Q}^{-1}\mathbf{M}=\mathbf{d}$ is therefore diagonal, and

$$\mathbf{V}_1=(\mathbf{K}^{-1}\mathbf{Q}^{-1}\mathbf{H})\mathbf{U}=\mathbf{K}^{-1}\mathbf{d}\mathbf{K} \tag{19}$$

is symmetric. However, the transformation $\mathbf{Q}$ derived by this procedure may have determinant $-1$, and the signs of the elements $d_\lambda$ may not maximize the diagonal sum of $\mathbf{V}_1$. To correct this we now construct a matrix $\mathbf{P}$ with all its diagonal elements $\pm 1$, such that Det $\mathbf{P}\mathbf{Q}=1$ and form the diagonal matrix $\mathbf{D}=\mathbf{P}\mathbf{d}$, with $D_\lambda=\pm d_\lambda$. The correct solution is then

$$\mathbf{V}=(\mathbf{K}^{-1}\mathbf{P}\mathbf{Q}^{-1}\mathbf{H})\mathbf{U}=\mathbf{K}^{-1}\mathbf{D}\mathbf{K} \tag{20}$$

$$\mathbf{R}=\mathbf{K}^{-1}\mathbf{P}\mathbf{Q}^{-1}\mathbf{H} \tag{21}$$

and

$$v=D_1+D_2+D_3\,.$$

This is unique unless $\mathbf{U}$ is a singular matrix of rank 1, for the subspace belonging to the eigenvalue $D_\lambda^2=0$ is then of dimension 2, and the rotation is undefined. This happens when the atoms of either set lie on a line.

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## The *a priori* optimization of diffractometer data to achieve the minimum average variance in the electron density.

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A discussion is given of the relationship between diffractometer data accuracy and the average variance of the electron density.

A consideration of constant-count-per-reflexion diffractometer experiments such as those performed, for example, by the Siemens AED System, has led Killean (1967) to show that to obtain data capable of yielding an $R$ index of 0·10 the total number of counts per reflexion need not exceed twenty-five, for low background reflexions, or one-hundred and twenty-five counts for a peak to background ratio of three to two. Clearly in view of these small counts no problem exists in the high-speed collection of data required only for stereochemical determination or conformation. The collection of data becomes more time consuming when the data is to be used for deductions requiring highly accurate electron densities. This paper is concerned with the mode of data collection likely to make the most efficient use of the diffractometer time available.

The approach to the problem is entirely *a priori* and, as such, represents a basic planning approach to single-crystal diffractometry. It assumes low background counts and consequently it is likely that a monochromator would be used in the experiment. The separate, but related, attempts of Hamilton (1967) and Shoemaker (1968) to optimize the collection of data for least squares analysis are *a posteriori* in that they require that the structure must have been solved before the data can be optimally recollected with respect to, for Hamilton's treatment, the variance of one positional or one thermal parameter and, for Shoemaker's analysis, a linear combination of the weights of the various parameters.

Cruickshank (1960) has summarized the requirements that must be satisfied for an accurate structure determination. It is assumed in the following analysis that these conditions are to be satisfied.

Cruickshank (1949) has derived an expression for the variance on the electron density for centrosymmetric space groups and Killean & Lawrence (1969*b*) have modified his approach to take account of random errors in the phase angles of the structure factors for non-centrosymmetric space groups. Essentially when the average variance in the electron density is to be considered it is sufficient to use Cruickshank's form for $P\bar{1}$

$$\langle\sigma^2(\varrho)\rangle=\tfrac{1}{2}\left(\frac{2}{V}\right)^2\sum\sigma^2(\mathbf{h}) \tag{1}$$

where $\sigma^2(\mathbf{h})$ = variance of the structure factor.

Let

$$|F(\mathbf{h})|^2 = \frac{KI(\mathbf{h})}{\mathrm{Lp}\, t(\mathbf{h})}$$

assuming negligible background counts and where $I(\mathbf{h})$ is the total counts accumulated in time $t(\mathbf{h})$. Define

$$R(\mathbf{h}) = \frac{I(\mathbf{h})}{t(\mathbf{h})}.$$

The variance of $F(\mathbf{h})$ due to counting statistics is

$$\sigma_1^2(\mathbf{h}) = \frac{|F(\mathbf{h})|^2}{4R(\mathbf{h})t(\mathbf{h})}.$$

It has been suggested (*e.g.* Grant, Killean & Lawrence, 1969; Killean & Lawrence, 1969*a*) that additional terms must be added to this variance to give a satisfactory weighting scheme for least-squares analysis but it is open to question whether these terms represent mainly random or mainly systematic errors in the data. The subsequent analysis does not involve these terms since they are independent of $t(\mathbf{h})$ and consequently their form is unimportant for *a priori* optimization. Let these terms be denoted by $A(\mathbf{h})$. The variance of the structure factor may be estimated as

$$\sigma^2(\mathbf{h}) = \sigma_1^2(\mathbf{h}) + A(\mathbf{h}) = \frac{|F(\mathbf{h})|^2}{4R(\mathbf{h})t(\mathbf{h})} + A(\mathbf{h}) \qquad (2)$$

and

$$\sigma^2(\varrho) = \tfrac{1}{2}\left(\frac{2}{V}\right)^2 \sum \left\{\frac{|F(\mathbf{h})|^2}{4R(\mathbf{h})t(\mathbf{h})} + A(\mathbf{h})\right\}. \qquad (3)$$

The measuring time for the diffractometer experiment, ignoring circle setting time, is

$$T = \sum t(\mathbf{h})$$

and the *a priori* optimal time for any $t(\mathbf{h})$ is given by solving

$$\frac{\partial \psi}{\partial t(\mathbf{h})} = 0$$

for $t(\mathbf{h})$, where

$$\psi = \langle \sigma^2(\varrho) \rangle - \lambda\{T - \sum t(\mathbf{h})\},$$

*i.e.*

$$t(\mathbf{h}) = \left(\frac{1}{\mathrm{Lp}}\right)^{1/2} \left(\frac{K}{4\lambda}\right)^{1/2}. \qquad (4)$$

The fraction of the experiment time to be spent on any reflexion is

$$\frac{t(\mathbf{h})}{T} = \frac{\left(\frac{1}{\mathrm{Lp}}\right)^{1/2}}{\sum \left(\frac{1}{\mathrm{Lp}}\right)^{1/2}} \qquad (5)$$

and the time spent measuring each reflexion is independent of the magnitude of the reflexion but depends on the geometry of the diffractometer and the wavelength of the X-radiation.

Define

$$G^2 = \frac{\sum \sigma_1^2(\mathbf{h})}{\sum |F(\mathbf{h})|^2} = \frac{1}{4T} \cdot \frac{\left\{\sum \left(\frac{1}{\mathrm{Lp}}\right)^{1/2}\right\}^2}{\sum \frac{R(\mathbf{h})}{\mathrm{Lp}}} \qquad (6)$$

and, assuming that the random errors are due only to counting statistics

$$T = \frac{\sum |F(\mathbf{h})|^2}{2\langle \sigma^2(\varrho) \rangle V^2} \cdot \frac{\left\{\sum \left(\frac{1}{\mathrm{Lp}}\right)^{1/2}\right\}^2}{\sum \frac{R(\mathbf{h})}{\mathrm{Lp}}}. \qquad (7)$$

In order to evaluate $T$ for a given $\langle \sigma^2(\varrho) \rangle$ it is necessary to estimate the average variation of $R(\mathbf{h})$ with $(\mathbf{h})$ and the height of the origin of the Patterson function $(\sum |(F(\mathbf{h})|^2)$.

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## On the diffraction enhancement of symmetry. Erratum.

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A correction is given to Iwasaki, H. (1972). *Acta Cryst.* A**28**, 253.

In a previous paper of the above title (Iwasaki, 1972), equation (25) (p. 256) should read:

$$I_p(hkl) = I_p(k\bar{h}l).$$

### Reference

IWASAKI, H. (1972). *Acta Cryst.* A**28**, 253.