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Short Communications

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On weights for a least-squares refinement.

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The determination of the probable errors

The object of a least-squares refinement is the minimization of a quantity such as

$$\Sigma w(hkl)\{F_{obs}(hkl)-F_{calc}(hkl)\}^2$$

in which the weight $w(hkl)$ of each term should be taken inversely proportional to the square of the probable error of the corresponding F_{obs} (see *e.g.* Lipson & Cochran, 1957); F_{obs} and F_{calc} stand here and in the following for their moduli. The essential problem in the determination of weights is therefore how to get an estimate of the probable errors in the measurements. There are three basically different methods of doing this, which are briefly discussed.

One way is to determine experimentally the probable error in F_{obs} by repeated measurements. This determination is complicated, however, by the presence of various kinds of systematic error.

Another method is to calculate the probable error in F_{obs} on the basis of theoretical considerations (*e.g.* Evans, 1961). Here the systematic errors constitute an even larger problem.

The third method is to refine the structure first, using some arbitrary weighting scheme (*e.g.* the same weight for all reflexions), and next to take $F_{obs}-F_{calc}$ as a measure for the error in F_{obs}.

None of these methods is quite correct. The first two for the reason that the weights as defined above are generally not those one really wants, for the deviations in F_{calc} due to approximations in the model (*e.g.* the omission of hydrogen atoms or the use of incorrect atomic scattering factors) should also be taken into account for the calculation of the weights (Kroon, 1962). The third method is not quite correct because errors in F_{calc} due to incorrect parameter values should not be included in the calculation of the weights,

and because the deviations in F_{obs} and F_{calc} one wants to find may be partly obscured by incorrect 'refinement'.

The probable errors as functions of I and θ.

We confine ourselves here to the first and the last of the above mentioned methods, and we designate the probable errors as estimated for the individual reflexions by δ and the values obtained by averaging δ's by σ.

It has been generally assumed that σ can be considered as only a function of the magnitude of F_{obs}, though some authors have been aware of the influence of the Lorentz-polarization factor (*e.g.* Feil, 1961; Cruickshank *et al.*, 1960). Since maximum accuracy can be obtained with the least-squares method only when the weights assigned to the observations are correct (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1960), it was considered worth while to study this problem in some more detail.

From the formula $F_{obs} = \sqrt{I_{obs}/\mathrm{Lp}}$ it follows that

$$\text{error in } F_{obs} = \frac{\text{error in } \sqrt{I_{obs}}}{\sqrt{\mathrm{Lp}}},$$

and from this formula it is seen that the error in F_{obs} may be expected to be a function of I_{obs} and of θ (De Vries, 1963). It will be a function of I_{obs} because the accuracy of the measurement is generally a function of the measured intensity. It will be a function of θ since

(*a*) the error in F_{obs} is a function of the magnitude of the Lorentz-polarization factor;
(*b*) the error in I_{obs} will be a function of θ, *e.g.* through the $\alpha_1-\alpha_2$ separation which increases with θ.

Deviations in F_{calc} due to approximations in the model will also be a function of θ.

The correct way, therefore, to deal with the variation of σ is not to regard it as a function of F or as a function of F and θ, but as a function of I and θ.

The determination of φ(θ) and ψ(I).

Since in most cases there will not be enough data to determine σ directly as a function of two variables, we shall make the plausible assumption that the I-dependence of σ is not influenced by θ or *vice versa*, in the formula:

$$\sigma = \varphi(\theta) \times \psi(\mathrm{I}) .$$

This way it will be possible, after making an initial assumption about, say, $\varphi(\theta)$ (*e.g.* $\varphi(\theta) = 1/\sqrt{\mathrm{Lp}}$; compare below), to use all δ values in each I range to determine $\psi(I)$; this $\psi(I)$ is then used to obtain a better $\varphi(\theta)$, and so on. Thus the number of data over which averaging is performed each time will be large enough, and reliable estimates of $\varphi(\theta)$ and $\psi(I)$ can be obtained.

The interpretation of φ(θ) and ψ(I).

Both $\varphi(\theta)$ and $\psi(I)$ have physical significance, so these functions may be of use not only for the calculation of weights but also as a check on the measurements and on the refinement.

From its definition it follows that $\psi(I)$ gives the variation of σ with I_{obs} when θ is constant, and since it does not seem likely that the error in F_{calc} could be a function of I, this variation of σ can always be attributed completely to the variation of the error in F_{obs}. So, a plot of $\psi(I)$ will give the variation of the error in $\sqrt{I_{obs}}$ with I_{obs} (for constant θ). For instance, for counter data the statistical counting error gives a constant contribution to $\psi(I)$, but, owing to the influence of errors in the measurement of the background scattering on the one hand and extinction, absorption and scaling errors on the other, one may expect an increase of $\psi(I)$ both for low and high values of I.

The interpretation of $\varphi(\theta)$ depends upon the method used to determine the δ's, since also the errors in F_{calc} vary with θ. Restricting ourselves for the moment to the influence of errors in F_{obs}, we get (for I_{obs} = constant):

$$\begin{aligned}\text{error in } F_{obs} &= c \times \varphi(\theta)\\ \text{error in } I_{obs} &= 2c \times \mathrm{Lp} \times F_{obs} \times \varphi(\theta)\\ &= 2c \times \sqrt{\mathrm{Lp}} \times \sqrt{I_{obs}} \times \varphi(\theta)\\ &= c' \times \sqrt{\mathrm{Lp}} \times \varphi(\theta).\end{aligned}$$

Thus we find the following interpretation for $\varphi(\theta)$: a plot of $\sqrt{\mathrm{Lp}} \times \varphi(\theta)$ gives the variation of the error in the intensity measurement with the Bragg angle (for constant I_{obs}). A variation of this kind may be caused for instance by the $\alpha_1-\alpha_2$ separation, the varying breadth of the diffracted beam, slight misalignment of the crystal or absorption effects.

The θ-dependence of various errors in F_{calc} will be discussed in another article.

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The Mo $K\alpha_1$/Cu $K\alpha_1$ wavelength ratio.

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The commonly used values of the wavelength of X-radiation were determined by Siegbahn (1931) and are based on the cleavage spacing of calcite. Cohen & DuMond (1963), in redetermining the value of Avogadro's number, have analyzed 16 X-ray lattice constant determinations. They found that the value of λ determined from measurements made with copper radiation is 76 ± 25 ppm larger than the value determined with molybdenum radiation,