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Weighting factors for single-crystal X-ray diffraction intensity data. By HOWARD T. EVANS, JR.,*

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Ever since the introduction of the methods of least-squares analysis for the refinement of crystal structures by Hughes (1941), scientists who use the method have been concerned over the problem of assigning proper weight to each of the data. Obviously each datum has a different reliability, but rarely is the standard deviation of each intensity measurement actually measured. The crystallographer must either assume unit weight for all data, as he usually does for the Fourier methods, or some arbitrary function such as the one Hughes (1941) used, namely, $|w = 1/|F|$. Fortunately, until recently, the choice of weighting function has had little effect on the results of crystal-structure studies, first because the structure problem is often overdetermined by a factor of 10 or more, and secondly, because few attempts have been made to reach the limit of accuracy of structure determination inherent in the diffraction data. Nowadays the need for increased accuracy of refinement requires that more attention be paid to the question of proper weighting of the data.

The weighting of data measured from film depends on the function relating the intensity of the X-ray beam and the quantity measured, the density of film blackening. At low densities, this function may be assumed to be linear:

$$D = kI/q, \quad (1)$$

where D is the density, I the beam intensity, k a proportionality factor and q a filter factor, the factor by which the intensity is reduced by the use of multiple-film technique or filters to record the stronger reflections in the linear range of the film. At high densities the function may be assumed to be logarithmic:

$$D = \gamma \log I/q + \log I_t/q \\ = \gamma \log I + [\log I_t - (1 + \gamma) \log q], \quad (2)$$

where γ is the photographic characteristic, I_t is the threshold intensity, and the quantity in brackets is constant. We may derive the appropriate weights for the structure factors F from these functions, making use of the relation between the standard deviations:

$$\sigma_{|F|} = (d|F|/dD)\sigma_D \quad (3)$$

and the intensity function:

$$I = KALp|F|^2, \quad (4)$$

where K is a scale factor, A the transmission factor (ratio of intensity with absorption to that expected without absorption) and Lp is the Lorentz and polarization correction.

For the linear case (letting $k=1$ if I is relative intensity), by differentiating (1) and (4) we readily obtain

$$\sigma_{|F|} = q\sigma_D/(2KALp|F|). \quad (5)$$

For the logarithmic case, from (2) and (4),

$$dD/dI = \gamma/I \\ \sigma_{|F|} = (|F|/2\gamma)\sigma_D. \quad (6)$$

Since the weighting functions of F in least-squares analysis have only relative significance, we may obtain them by inverting $\sigma_{|F|}$ and neglecting constant terms including σ_D :

$$\begin{aligned} |w = (ALp/q)|F|, & \quad \text{linear photographic case;} \\ |w = 1/|F|, & \quad \text{logarithmic photographic case.} \end{aligned}$$

These functions have been commonly used in crystal-structure refinement, except that in the linear case the factors ALp/q are usually neglected. In the common technique where a calibrated strip is prepared on film in which each exposure has a fixed ratio to its neighbor, D is measured on the arbitrary scale of this strip and the logarithmic function holds, regardless of what the true nature of the film may be. It is well known that for X-rays the true function is usually linear over a wide range, so that when photometric methods are used to measure film densities the linear weighting function is probably the most generally applicable. Just which function, if either, is appropriate to any particular group of reflections is a question which may be difficult to answer.

When counter techniques are used, it is possible to base the weighting of the structure factors on actual observational statistics. The intensity of a reflection is measured by:

$$I = q(T - B) = q(1 - b)T, \quad (7)$$

where T is the total number of counts in a peak, B is the number of counts corresponding to the background and b is a background ratio, $b = B/T$. The filter factor q includes any factors resulting from changes in conditions of measurement from one reflection to another, such as length of counting time, primary X-ray beam intensity and number of filter foils. With equation (4) we have

$$T = KALp|F|^2/(q(1 - b)). \quad (8)$$

The standard deviation of the structure factor is

$$\sigma_{|F|} = (d|F|/dP)\sigma_P, \quad (9)$$

where P is the number of counts corresponding to the area under a peak, that is, $P = (1 - b)T$. From (8),

$$(d|F|/dP) = q/(2KALp|F|). \quad (10)$$

By normal counting statistics, and (8):

$$\begin{aligned} \sigma_P &= [T + P]^{\frac{1}{2}} = [(1 + b)T]^{\frac{1}{2}} \\ &= \{[(1 + b)/q(1 - b)]KALp|F|^2\}^{\frac{1}{2}}. \end{aligned} \quad (11)$$

Combining (10) and (11) in (9):

$$\sigma_{|F|} = \frac{1}{2}[q(1 + b)/(KALp(1 - b))]^{\frac{1}{2}}. \quad (12)$$

As before, we may set down the relative weighting factor from the standard deviation as follows:

$$|w = [ALp(1 - b)/q(1 + b)]^{\frac{1}{2}}, \quad \text{pulse-counter case.}$$

Reference

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1731-1752.

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