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On the scaling of X-ray photographs*.

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A simple general procedure is given for scaling X-ray photographs. The method avoids some of the approximations and difficulties of earlier procedures and should be more economical of computer time.

The scaling of X-ray photographs from intersecting reciprocal lattice planes has been the subject of recent papers (Hamilton, Rollett & Sparks, 1965; Fox & Holmes, 1966), in which references to earlier work are also given. The purpose of the present note is to point out a simple method of obtaining the best intensity values for reflections and to avoid the approximations and difficulties introduced in the earlier papers.

We follow the notation of Hamilton, Rollett & Sparks. Here F^2_{hl} is the observed intensity corrected for Lorentz, polarization, and other effects, h is the abbreviation for the Miller indices, l refers to the lth film, F^2_h is the true intensity of the reflection, G_l is the inverse scale factor of the lth film, and $\sqrt{w_{hl}}$ is the weight associated with a given observation F^2_{hl} and is chosen as the reciprocal of the standard deviation σ_{hl} in that observation.

We are then really interested in obtaining the best set of F^2_h from the measurements and only incidentally are we interested in the inverse scale factors G_l. To obtain this best set, the sum

$$\psi = \sum_{h,l} (F^2_{hl} - G_l F^2_h)^2 / \sigma^2_{hl} \tag{1}$$

over all observed reflections is minimized† with respect to the G_l and F^2_h by setting $\partial\psi/\partial G_l = 0$ and $\partial\psi/\partial F^2_h = 0$. This yields the normal equations which we can transpose to get

$$G_l = \sum_h (F^2_h F^2_{hl}/\sigma^2_{hl}) / \sum_h (F^2_h/\sigma_{hl})^2 \tag{2}$$

and

$$F^2_h = \sum_l (G_l F^2_{hl}/\sigma^2_{hl}) / \sum_l (G_l/\sigma_{hl})^2 \,. \tag{3}$$

Now letting $F^2_h(\varrho)$ be the ϱth iterative solution of equation (3), we have

$$F^2_h(\varrho) = \sum_l [G_l(\varrho-1) F^2_{hl}/\sigma^2_{hl}] / \sum_l [G_l(\varrho-1)/\sigma_{hl}]^2 \,,$$

where $G_l(\varrho-1)$ is the $(\varrho-1)$th iterative solution obtained from (2). The values of $F^2_h(\varrho)$ will be arbitrary to within a common factor. We repeat these calculations until the fractional change in any $F^2_h(\varrho)$ is less than a predetermined quantity ε, *i.e.*, until

$$\left| \frac{F^2_h(\varrho) - F^2_h(\varrho-1)}{F^2_h(\varrho)} \right| \le \varepsilon \,.$$

We take these final values as our scaled intensities.

This procedure avoids making any approximations such as were made in the work of Fox & Holmes and of Hamilton *et al.* It can be shown that the method of these earlier authors will converge to the same results as the one obtained here.

We also wish to remark that the most reasonable estimate of the errors in the measurements of intensities from X-ray photographs is that the fractional error in each determination is constant; in other words, each intensity above a certain minimum value is determined with the same percentage error. With this assumption the equations can be further simplified because it amounts to saying that the weight is given by $w_{hl} = 1/\sigma^2_{hl} = 1/(\alpha F^2_{hl})^2$, where α is the constant fractional error. Equations (2) and (3) then become

$$F^2_h = \sum_l (G_l/F^2_{hl}) / \sum_l (G_l/F^2_{hl})^2$$

and

$$G_l = \sum_h (F^2_h/F^2_{hl}) / \sum_h (F^2_h/F^2_{hl})^2 \,.$$

These latter equations have been used in a computer program (Bush & Gvildys, 1963) written for the IBM 704 and adapted to the CDC 3600 computer. The program initially assumes $G_l = 1$. Reflections on each film are treated as independent observations, thus avoiding accumulated errors which might arise if the scaling within each film pack were done separately. The scaling is based only on reflections which are well determined, with observed values greater than a specified limit. The program also estimates the standard deviations of the F^2_h. The final scale factors are used to obtain values of F^2_h for the weaker reflections. This program has been used in connection with the determination of the structure of fluoromalic acid by one of us (Schiffer, 1964), who used 1751 well-determined reflections from 78 films. The convergence criterion with $\varepsilon = 0{\cdot}003$ was satisfied after 64 iterations. The final value of χ^2 [which is equivalent to the ψ of equation (1) if errors are normally distributed] corresponded to a 7% standard deviation in the original observations. The average fractional change in F^2_h at the last iteration was $\sim 0{\cdot}0002$.

It seems probable that the present method is more economical in terms of computer time than the methods described in earlier papers.

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† It can easily be shown that this is equivalent to minimizing $\sum_{h,l} (K_l F_{hl}{}^2 - F_h{}^2)^2/\sigma_{hl}{}^2$, where $K_l = 1/G_l$, but only if $\sigma_{hl} \propto K_l$. If this is not so, then only (1) is the statistically meaningful quantity to minimize, and not the latter expression.

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