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The correlation of intersecting layers of X-ray intensity data.

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The various observed intensity values for X-ray reflections on a single reciprocal-lattice layer, obtained by the multiple-film Weissenberg or precession-camera technique, can usually be reduced to a common arbitrary scale straightforwardly and with little error.

The next stage is the reduction of a set of intersecting layers to a single arbitrary scale. Kraut (1958) and Dickerson (1959) have both suggested a method of approximating the solution to the normal equations of the least-squares analysis of this problem which can give grossly incorrect results. We outline below a derivation of the normal equations for a simple case, describe the method of using them which we find unsatisfactory, explain how more accurate answers may be obtained, and, by tabulating the results for a practical example, illustrate the size of the errors which can occur. Finally we suggest a means of weighting the observations in more general cases.

We consider first the case in which data are collected by rotation (or precession) about two axes only, so that any one reflection appears on at most two layers. In general each layer about the one axis will intersect all layers about the other and vice versa.

Where two layers on independent arbitrary scales intersect, an estimate can be made of their relative scales. Let

K_i be the scale factor by which F^2 values from layer i must be multiplied to place them on the common scale.

(F^2_{hi}) be the value of F^2_h derived from layer i (h is written throughout for hkl).

Then for an h lying on both of layers a and b we have:

$$(F^2_{ha})K_a-(F^2_{hb})K_b=0\,. \qquad (1)$$

Hence we can derive a set of observational equations which will usually be more numerous than the K_i (this will usually still be true if all the observational equations derived from a single reciprocal-lattice line of intersection are combined into one equation by forming $\Sigma(F^2_{ha})$ and $\Sigma(F^2_{hb})$, summing over those h appearing on both layers). The observational equations should be prepared (Whittaker & Robinson (1944), p. 244) by multiplying them by the square roots of their weights W_h so that the uncertainties in the differences may all be expected to be of the same size. It is then possible to use the observational equations to calculate the normal equations, which are:

$$\begin{array}{l}\sum\limits_h W_h(F^2_{ha})^2K_a-\ldots-\sum\limits_h W_h(F^2_{ha})(F^2_{hb})K_b-\ldots=0\\ \qquad\vdots\qquad\qquad\qquad\qquad\vdots\\ -\sum\limits_h W_h(F^2_{ha})(F^2_{hb})K_a-\ldots+\sum\limits_h W_h(F^2_{hb})^2K_b-\ldots=0\,.\\ \qquad\vdots\qquad\qquad\qquad\qquad\vdots\end{array}$$

For the ith square term the summation $\sum$ includes one term for each reflection occurring both on layer i and on some other layer. For the ij cross term the summation includes one term for each reflection appearing on both layer i and layer j.

There is in general no exact solution of the observational equations, except the trivial one with all K_i equal to zero. As a result it is impossible to satisfy all of these homogeneous normal equations exactly except with $K_i=0$. Since one is able to obtain only the ratios of the K_i rather than their absolute values, there is a temptation to try to obtain an approximate solution by setting one of the K_i equal to unity and by deleting one normal equation, solving the remainder for the other K_i. The unsatisfactory nature of this solution may be demonstrated by repeating it with a different deleted equation. The larger the errors in the observational equations the more the answers will be found to differ.

It is possible to find a non-trivial set of K_i subject to the reasonable normalising condition $\sum\limits_i K_i^2=1$ which will minimise the weighted sum of squares of discrepancies for the observational equations. This is equivalent to solving the normal equations with the zero right-hand sides replaced by the values of λK_i where λ is a constant. If there are n scale factors then there are n values of λ for which the equations can be solved and it is the smallest of these which gives the minimum weighted sum of squares of discrepancies. This value of λ and the corresponding set of K_i are the smallest latent root and the corresponding latent vector respectively of the matrix of the normal equations and they can be determined by any of the standard methods which are now available. In this laboratory we have found Givens' process fast, convenient and accurate for this purpose on the Ferranti Mercury computer; but, since the smallest root of a scaling matrix of this type is usually very different from any other root, inverse iteration would probably be quite rapid and easier to program if a standard subroutine for solving linear simultaneous equations is available. This iteration involves solving the normal equations with the zero right-hand sides replaced either by equal numbers or by estimates of the K_i. The solution is then normalised

Table 1. *Scale factors for a system of fifteen mutually intersecting layers by two different methods*

Axis and layer	Scale factors (i)	Scale factors (ii)	Ratio (i):(ii)
*a*0	1·0000	1·0000	1·000
*a*1	1·5336	1·2196	1·258
*a*2	1·9258	1·5564	1·237
*a*3	1·0260	0·8202	1·251
*a*4	1·2478	0·9972	1·251
*a*5	1·3141	1·0466	1·256
*a*6	1·1827	0·9322	1·269
*a*7	0·5546	0·4409	1·258
*c*0	0·3363	0·2704	1·244
*c*1	0·8277	0·6918	1·240
*c*2	0·7384	0·5913	1·249
*c*3	1·0311	0·8122	1·270
*b*0	0·9353	0·7341	1·274
*b*1	1·3500	1·0675	1·265
*b*2	1·5120	1·2171	1·242

and used in the next iteration in place of the original right-hand sides. When successive normalised solutions agree to a sufficient number of figures the answers can be accepted.

The 15 scale factors listed below were obtained (i) by finding the latent root and vector and (ii) by setting $K_{a0}=1{\cdot}0$ and solving for the other 14 values. It can be seen that the primary effect of method (ii) is to exaggerate K_{a0} in relation to the others, but that variations of several percent also occur between the remaining ratios.

When it is desired to extend the method to the case in which more than two layers on independent arbitrary scales intersect at the same h the observational equations can be derived in the following way. Let F_h^2 be the weighted average of the scaled F_h^2 occurring on all the layers. Then the observational equation for F_{hi}^2 will be:

$$(F_{hi}^2)K_i - F_h^2 = 0 ,$$

where

$$F_h^2 = \sum_j (W_{hj}K_jF_{hj}^2)/\sum_j W_{hj} ,$$

hence

$$(F_{hi}^2)K_i - \sum_j W_{hj}(F_{hj}^2)K_j/\sum_j W_{hj} = 0 . \qquad (2)$$

The weight to be given to equations (2) is W_{hi}.* Where m layers intersect at h, all m of the equation (2) must be included to weight the observations correctly, although one equation is dependent on the other $m-1$. When only two layers intersect at h a pair of equations (2) can be reduced to the form of equation (1) with weight $W_h = W_{ha}W_{hb}/(W_{ha}+W_{hb})$.

The latent vector solution given above is the multidimensional analogue of the methods described by Schomaker, Waser, Marsh & Bergman (1959) for the similar problem of fitting least-squares lines and planes to given sets of points.

* It has been pointed out by the referee that the use of equations (2) is equivalent to the minimisation of

$$\sum_{hi} W_{hi}(K_iF_{hi}^2 - F_h^2)^2,$$

where the summation includes one term for each observation of any reflection appearing on more than one layer. The minimisation is, of course, subject to the restriction that

$$\sum_i K_i^2 = 1 .$$

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Extension of the *M* function tables for a hindered rotator of Lipscomb and King.

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King & Lipscomb (1950) have derived an expression for the structure amplitude from a crystal containing rotating groups for the particular case of the hindered rotator. Under the assumptions made by these authors they have derived a modifying function such that the scattering amplitude is written

$$F = \sum_i f_i \exp[2\pi i\mathbf{h}\cdot\mathbf{k}_i] M_{n_i}^{\gamma_i}(a_i, b_i)$$

where

$$M_n^{\gamma}(a, b) = \sum_{p=0}^{\infty} \varepsilon_p i^{pn} J_{pn}(a) I_p(b) \cos pn\gamma / I_0(b) ,$$

where

n = the number of potential minima,
γ = the rotation angle corresponding to a potential minimum,
a = $2\pi|\mathbf{h}||\mathbf{v}|\sin\psi$,
b = $V_0/2kT$,
V_0 = the height above the minimum of the barrier to rotation,
$\mathbf{v}$ = the vector from the center of rotation to the instantaneous position of the atom,
$\mathbf{h}$ = the reciprocal lattice vector
ψ = the angle between $\mathbf{h}$ and the normal to the plane of rotation of the atom.

We have evaluated the M function for the following values:

(1) a = 0 to 4 in intervals of 0·1,
(2) b = 0·5 to 6 in intervals of 0·5 and ∞,
(3) n = 2, 3, 4, 6,
(4) γ = 0, $\pi/16$, $\pi/8$, $3\pi/16$, $\pi/4$ when n = 2, 4,
γ = 0, $\pi/12$, $\pi/6$ when n = 3, 6.

For the case $n=3$ the M function will have real and imaginary parts and writing

$$M_3^{\gamma}(a, b) = x + iy .$$

The tabular values are listed as $(x^2+y^2)^{\frac{1}{2}}$ with the sign of x.

The evaluation of the M function was accomplished on the IBM type 650 digital computer. The computation time required for one value of the M function was between 0·5 sec. and 10 sec. depending on the number of terms required for convergence.

A few minor changes in the present computer program would allow it to be used as a subroutine in another program which requires the M function. This subroutine is available for the IBM 650 only.

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The tables can be obtained from the American Documentary Inst.; microfilm copies of the tables and copies of the program for computing the M function on an IBM 650 can be obtained, upon request, from the authors.