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The symmetry of the normal equations for least squares.

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In a least-squares refinement applied to all three co-ordinates of n atoms simultaneously, the normal equations may be written in the form

$$\begin{pmatrix} A_{ij} & L_{ij} & M_{ij} \\ L'_{ij} & B_{ij} & N_{ij} \\ M'_{ij} & N'_{ij} & C_{ij} \end{pmatrix} \cdot \begin{pmatrix} \Delta x_i \\ \Delta y_i \\ \Delta z_i \end{pmatrix} = \begin{pmatrix} X_i \\ Y_i \\ Z_i \end{pmatrix} (i, j = 1, 2, \ldots, n) , \quad (1)$$

where the matrix of coefficients consists of nine blocks (A_{ij}, etc.) and each of these blocks has n^2 terms with the following typical elements:

$$\left.\begin{aligned} a_{ij} &= \Sigma \frac{\partial F}{\partial x_i} \cdot \frac{\partial F}{\partial x_j}; \quad b_{ij} = \Sigma \frac{\partial F}{\partial y_i} \cdot \frac{\partial F}{\partial y_j}; \quad c_{ij} = \Sigma \frac{\partial F}{\partial z_i} \cdot \frac{\partial F}{\partial z_j} \\ l_{ij} &= \Sigma \frac{\partial F}{\partial x_i} \cdot \frac{\partial F}{\partial y_j}; \quad m_{ij} = \Sigma \frac{\partial F}{\partial x_i} \cdot \frac{\partial F}{\partial z_j}; \quad n_{ij} = \Sigma \frac{\partial F}{\partial y_i} \cdot \frac{\partial F}{\partial z_j} \\ l'_{ij} &= \Sigma \frac{\partial F}{\partial y_i} \cdot \frac{\partial F}{\partial x_j}; \quad m'_{ij} = \Sigma \frac{\partial F}{\partial z_i} \cdot \frac{\partial F}{\partial x_j}; \quad n'_{ij} = \Sigma \frac{\partial F}{\partial z_i} \cdot \frac{\partial F}{\partial y_j} \end{aligned}\right\} (2)$$

The column matrices in (1) have been written for brevity in terms of sub-matrices. Thus Δx_i stands for the column sub-matrix

$$\{\Delta x_1 \ \Delta x_2 \ \Delta x_3 \ \ldots \ \Delta x_n\} ,$$

and similarly for Δy_i, Δz_i, and X_i, Y_i, Z_i. The typical elements of X_i, Y_i and Z_i are

$$X_i = \Sigma \frac{\partial F}{\partial x_i} \cdot (F_o - F_c); \quad Y_i = \Sigma \frac{\partial F}{\partial y_i} \cdot (F_o - F_c); \quad Z_i = \Sigma \frac{\partial F}{\partial z_i} \cdot (F_o - F_c) . \quad (3)$$

The summations in (2) and (3) are over all the structure factors used, and unit weight has been assumed.

The matrix of the coefficients is, of course, symmetric, since

$$a_{ij} = a_{ji}; \ b_{ij} = b_{ji}; \ c_{ij} = c_{ji}; \ l_{ij} = l'_{ji}; \ m_{ij} = m'_{ji}; \ n_{ij} = n'_{ji}; \quad (4)$$

but with the normal equations met with in crystal determination, further symmetry is possible. Thus for a crystal possessing only a centre of symmetry the expression for the structure factor is

$$F = 2 \sum_r f_r \cos 2\pi(hx_r/a + ky_r/b + lz_r/c) , \quad (5)$$

for which the following relations are readily verified:

$$\frac{\partial F}{\partial x_r} \cdot \frac{\partial F}{\partial y_s} = \frac{\partial F}{\partial x_s} \cdot \frac{\partial F}{\partial y_r}; \quad \frac{\partial F}{\partial x_r} \cdot \frac{\partial F}{\partial z_t} = \frac{\partial F}{\partial x_t} \cdot \frac{\partial F}{\partial z_r}; \quad \frac{\partial F}{\partial y_s} \cdot \frac{\partial F}{\partial z_t} = \frac{\partial F}{\partial y_t} \cdot \frac{\partial F}{\partial z_s} , \quad (6)$$

whence it follows that

$$l_{ij} = l_{ji}; \ m_{ij} = m_{ji}; \ n_{ij} = n_{ji} , \quad (7)$$

with similar relations for the dashed quantities. Thus each of the nine blocks in the matrix of coefficients is separately symmetric, the total number of independent coefficients being $3n(n+1)$.

If, however, the crystal possesses a mirror plane in addition to a centre, i.e. space group $P12/m1$, the expression for the structure factor is

$$F = 4 \sum_r f_r \cos 2\pi(hx_r/a + lz_r/c) \cos 2\pi k y_r/b , \quad (8)$$

and the relations corresponding to (7) become

$$l_{ij} \neq l_{ji}; \ m_{ij} = m_{ji}; \ n_{ij} \neq n_{ji} , \quad (9)$$

i.e. only blocks M and M' are now separately symmetric. The symmetry of the dashed blocks is, of course, the same as that of the corresponding undashed blocks. The number of independent coefficients is now $2n(2n+1)$.

Lastly, for space groups with symmetry higher than that of the monoclinic system, all the additional symmetry of the matrix of coefficients disappears, and there are $3n(3n+1)/2$ independent coefficients. It is, of course, the reduction of the general expression for the structure factor by summation over the equivalent points which causes this elimination of symmetry in the matrix.

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On the use of slope and curvature maps in refinement of crystal structures.

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Difference maps have been used increasingly in last-stage-refinement of crystal structures, and the theory underlying this method has been set out in numerous papers by several authors. The results can, for our present purpose, be summarized in the following synopsis:

On assuming spherical electron-density distribution near an atomic centre, the displacement Δx from the near-correct input parameter x to the better approximation $x+\Delta x$ will be

$$\Delta x = -(\delta \Delta \varrho / \Delta x) / (\delta^2 \varrho_c / \Delta x^2) ,$$

and similar expressions for other coordinates;

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