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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 coordinates of n atoms simultaneously, the normal equations may be written in the form

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

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:

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

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

$$X_i = \sum \frac{\partial F}{\partial x_i} \cdot (F_o - F_c) ; \quad Y_i = \sum \frac{\partial F}{\partial y_i} \cdot (F_o - F_c) ;$$

$$Z_i = \sum \frac{\partial F}{\partial z_i} \cdot (F_o - F_c) . \qquad (3)$$

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

$$a_{ij} = a_{ji};\; b_{ij} = b_{ji};\; c_{ij} = c_{ji};\; l_{ij} = l'_{ji};$$

$$m_{ij} = m'_{ji};\; n_{ij} = n'_{ji}; \qquad (4)$$

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

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

for which the following relations are readily verified:

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

whence it follows that

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

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

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

and the relations corresponding to (7) become

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

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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$$\Delta\varrho = \varrho_o - \varrho_c ,$$

and we have therefore obtained the shift, compensated for termination-of-series effects.

The slopes and curvatures may be computed either by direct summation at the given point from the relevant expressions, or else from a difference synthesis map. In the latter case it is customary to assume that the curvatures $\delta^2\varrho_c/\delta x^2$ are to all practical purposes equal to $\delta^2\varrho_o/\delta x^2$, and this statement holds in all cases (last-stage-refinement) where it is proposed to use it.

From the Gaussian shape of peak-density-distributions another helpful expression can be derived:

$$\varrho_r = Z.(p/\pi)^{3/2}.\exp(-pr^2) ,$$

where p is a constant, Z the total number of electrons in the peak considered, and ϱ_r the electron density at a distance r from the summit. From this the compensated shift may now be written:

$$\Delta x = -(\delta\Delta\varrho/\delta x)/2p.\varrho_s .$$

Both p and the electron density of the summit, ϱ_s, can conveniently be derived from the F_o syntheses maps. It will not usually be necessary to know either value to a very high degree of precision since, in the polishing stages of refinement, slopes become small quantities and limited variations in the denominator of the given formula do not change Δx significantly.

When many atoms are involved in the refinement, as will be the case when a large molecule is found to be in general position, the evaluation of shifts by purely arithmetical means becomes a formidable undertaking and is hardly ever attempted without the aid of sophisticated machinery. The ΔF map is less unwieldy but even with careful contour plotting yields slope values of rather limited accuracy.

Another approach to this predicament (not in itself novel) was found to be practical since it involves only standard punched-card equipment for Beevers–Lipson summations.

The slope values are plotted as a function of the coordinates, and for the most general centrosymmetrical case, space group $P\bar{1}$, the slope in the x direction is given by the relation

$$\delta\Delta\varrho/\delta x = -(4\pi/aA).\Sigma\Sigma h.\Delta F.\sin(hx+ky)$$

in the abbreviated notation, where $\Delta F = F_o - F_c$. This expression can, of course, be expanded in the usual way to be handled by one-dimensional summation. Similar relations hold for the shifts in the direction of the other axes.

For a single projectional refinement two slope maps are therefore necessary. The input parameters for the atomic positions may be drawn in the slope maps, and the slope values at these points found by simple interpolation techniques. It was found that whereas the slopes, deduced from very carefully drawn difference maps, would vary within 15% of the numerically accurate values, the slopes found from slope maps would give only a 6% maximum discrepancy.

The necessity for curvature maps, analogous to the slope maps, will not as a rule arise, but they could of course be prepared in extreme cases; the same holds for the cross-term derivatives when the assumption of orthogonality and sphericity will not hold to a good approximation.

The refinement procedure outlined above was used for a carotenoid compound containing 43 atoms in general position, so as to obtain simultaneous compensated shifts. The ΔF difference map was used for a general assessment of scaling and temperature-factor adjustment in this stage. The method was found to be relatively fast and of satisfactory accuracy.

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Phase relations in the plagioclase felspars: composition range An_0 to An_{70}.

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This communication summarizes recent observations on materials covering nearly the whole plagioclase series.

(1) Cole, Sörum & Taylor (1951) observed no departure from the low-temperature albite-type structure in plagioclase samples containing up to about 30% An. The coexistence of two plagioclases in this composition range was first reported by Laves (1951), and later confirmed by one of us (J. V. S., in collaboration with Dr W. S. MacKenzie, Geophysical Laboratory, unpublished). Laves (1954) has concluded that 'low-temperature' plagioclases within the range An_5 to An_{17} consist of two phases.

We also have examined a number of specimens in the region An_0–An_{20} from low-temperature environments (both specimens showing schiller ('peristerites'; Böggild, 1924) and specimens devoid of schiller). In agreement with Laves we have found that all the specimens in the region An_5–An_{17} are unmixed. The lattice angles of the two phases agree closely with those found by Laves and the compositions deduced from the curves of lattice parameters determined by Smith (1954) are $An_{3\pm2}$ and $An_{23\pm2}$. The failure of previous workers, using powder methods, to detect this type of unmixing in albite-oligoclases is not surprising in view of the poor resolution of the powder method.

In spite of this evidence, which suggests that all low-temperature oligoclases are unmixed, some evidence (not regarded as conclusive) has been obtained by one of us (J. V. S., in collaboration with Dr W. S. MacKenzie, Geophysical Laboratory) which suggests that the two-phase region lies below the high–low inversion and that homogeneous crystals may exist in the low-temperature state. This point is under further examination.

(2) For the range An_{50}–An_{70}, further measurements have confirmed that the separation of the pairs of sub-