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An extension of the inequalities method of sign determination by means of negative-density transforms. By M. M. QURASHI, *National Research Council, Ottawa, Canada*

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The Harker-Kasper and other related analytical methods, when applied to structure determination, give the signs (or phases) of a certain fraction (say a set S_1) of the observed structure factors; this fraction (Hughes, 1949) decreases as the number of atoms in the asymmetric unit increases. It is therefore of interest to explore methods for determining the signs of additional structure factors when those of the set S_1 are known. The problem is somewhat similar to that discussed by Goedkoop, MacGillavry & Pepinsky (1951). One such method, which has proved successful in solving the structure of the mineral metahewettite ($\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), uses an extension of the physical principle of non-negative electron density.

Consider a centric three-dimensional Fourier synthesis. A synthesis using only the set S_1 of structure factors will contain some regions, $R_{(-)}$, of negative electron-density, situated between the peaks. If the remaining structure factors comprise a set, S_2 , and we put

$$\left. \begin{aligned} \varrho_{S_1}(x, y, z) &= \frac{1}{V} \sum_{S_1} F_{hkl} \cos 2\pi(hx + ky + lz), \\ \varrho_{S_2}(x, y, z) &= \frac{1}{V} \sum_{S_2} F_{hkl} \cos 2\pi(hx + ky + lz), \end{aligned} \right\} \quad (1)$$

the condition for non-negative electron-density becomes

$$\begin{aligned} \varrho_{S_1}(x, y, z) + \varrho_{S_2}(x, y, z) &= \varrho(x, y, z) \\ &= \frac{1}{V} \sum_{S_1+S_2} F_{hkl} \cos 2\pi(hx + ky + lz) \geq 0, \end{aligned} \quad (2)$$

whence it follows that

$$\varrho_{S_2}(x, y, z) \geq -\varrho_{S_1}(x, y, z) \quad (3a)$$

$$> 0 \text{ when } (x, y, z) \text{ lies in } R_{(-)}. \quad (3b)$$

Also, we have

$$\begin{aligned} F_{hkl} &= \iiint_{\text{cell}} (\varrho_{S_1}(x, y, z) + \varrho_{S_2}(x, y, z)) \cos 2\pi(hx + ky + lz) dx dy dz \\ &= \iiint_{\text{cell}} \varrho_{S_2}(x, y, z) \cos 2\pi(hx + ky + lz) dx dy dz \\ &\quad \text{if } (hkl) \text{ is in } S_2. \end{aligned}$$

The problem then is to determine $\varrho_{S_2}(x, y, z)$ over the whole cell. As a first approximation, within the regions of negative density $R_{(-)}$, we can use the sign of equality in equation (3a). Thus, for (x, y, z) in $R_{(-)}$,

$$\varrho_{S_2}(x, y, z) \simeq -\varrho_{S_1}(x, y, z). \quad (4)$$

(The approximation will in general be fairly good as these regions lie between positive peaks, which probably form the atomic peaks in the ultimate structure, and

these fall rapidly to zero in a short distance.) Over the rest of the cell ($R_{(+)}$), the simplest approximation is to put $\varrho_{S_2}(x, y, z) \simeq -K$, where K is such that

$$\iiint_{R_{(+)}} K dx dy dz + \iiint_{R_{(-)}} \varrho_{S_1}(x, y, z) dx dy dz = 0; \quad (5)$$

this ensures correct scaling of the structure factors. We finally have for hkl in the set S_2 ,

$$\begin{aligned} F_{hkl} &\simeq -K \iiint_{R_{(+)}} \cos 2\pi(hx + ky + lz) dx dy dz \\ &+ \iiint_{R_{(-)}} -\varrho_{S_1}(x, y, z) \cos 2\pi(hx + ky + lz) dx dy dz. \end{aligned} \quad (6)$$

With this relation, we can determine the signs of the reflections in the set S_2 by successive approximations. The integrals of the Fourier transforms can be replaced by summations with sufficient accuracy, and these can then be performed with Beavers-Lipson strips or more readily with an analogue computer like the X-RAC. With the latter, this method can be used advantageously in the usual technique of refinement by trial and error to minimize background ripple in a projection, if the projection does not have much overlap of atoms.

For the metahewettite structure, a start was made with fifteen $h0l$ structure factors, whose signs were determined by Harker-Kasper inequalities. The above method of negative-density transforms then yielded a sufficiently good $h0l$ projection to identify all the atoms and to determine the number of water molecules in the cell, although six atoms overlap in the projection. Because of the approximations involved, the expression (6) gives small 'corrections' to the F 's comprising the already determined set, and a criterion for estimating their significance is easily set up. The technique can then be used to correct some doubtful signs obtained from the inequalities, which may have been vitiated by incomplete fulfilment of the assumptions made in the theory. The method proposed above shows some interesting similarities with that suggested by Zachariassen (1952).

Since in a structure composed of close-packed spherical atoms only about three-quarters of the volume is occupied by the atoms, it is easy to show that the 'efficiency of convergence' of equation (6) to the correct structure is of the order of $\frac{1}{4}\alpha$, where $1 < \alpha < 2$; for a two-dimensional projection with no overlap, it should be of the order of $\frac{1}{10}\alpha$, $1 < \alpha < 2$.

References

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