17.2–4 EFFECT OF THE QUALITY OF INVARIANTS IN THE RANDOM PHASES - LINEAR EQUATIONS METHOD

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In the YZARC method (Baggio et al., Acta Cryst. (1978) A34, 883-892), triple-phase invariants treated as linear equations are used to refine a set of initially random phases, the resulting 70 or so phases being used as a starting point for the tangent formula. In matrix notation these equations can be written as

$$\underset{\sim}{A}\underset{\sim}{\phi} + \underset{\sim}{b} \approx \underset{\sim}{h} \qquad (1)$$

where phases ϕ are in cycles and $\underset{\sim}{b}$ is a vector of phase shifts. In the absence of structural information the right-hand-sides h of these equations are assumed to have integer values n, whence the least squares solution for the phases is

$$\underset{\sim}{\phi} = (\underset{\sim}{A}^T\underset{\sim}{A})^{-1}\underset{\sim}{A}^T(\underset{\sim}{n}-\underset{\sim}{b}) \qquad (2)$$

In practice the true invariant values will deviate from integer by an amount t and each of the phases found will deviate from its true value by an amount $\delta\phi$. Analysis shows that for certain classes of solution the vector of phase errors $\underset{\sim}{\delta\phi}$ is given by

$$\underset{\sim}{\delta\phi} = (\underset{\sim}{A}^T\underset{\sim}{A})^{-1}\underset{\sim}{A}^T\underset{\sim}{t} = \underset{\sim}{C}\,\underset{\sim}{t} \qquad (3)$$

Where a structure is known, Eqn. 3 provides a theoretical limitation on the quality of solution obtainable from a particular set of equations. In the absence of phase information a statistical argument yields individual expected phase errors $\langle\delta\phi_i^2\rangle^{\frac{1}{2}}$ where

$$\langle\delta\phi_i^2\rangle = \sum_j^{NINV} c_{ij}^2 \langle t_j^2\rangle \qquad (4)$$

and $\langle t_j^2\rangle$ is obtained from Cochran statistics.

The application of Eqns. 3 and 4 to several real structures is presented and the results are discussed in the light of approximations necessary to obtain these expressions. The implications of Eqn. 4 in the choice of phase set for the linear equations method is investigated with a view to improving upon the present method of choosing reflexions for the random phases approach.

17.2–5 DETERMINATION OF THE PHASE SEMINVARIANTS OF FIRST RANK VIA THE HARKER SECTIONS.

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It is well known that a general correspondence exists between the Patterson and direct methods. In practice they are used as two separate approaches for solving crystal structures. If there are few heavy atoms in the molecule the Patterson function is often calculated and the complete crystal structure is found by successive Fourier syntheses. Direct methods are by far preferable for equal atom molecules.
In this communication some algebraic and probabilistic considerations are given which allow the use of the information contained in the Harker sections of the Patterson map. Some applications are also described in order to show the advantages of the new approach.

17.2–6 DIRECT METHODS AND SUPERSTRUCTURES.

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A-priori information, when available, facilitates the crystal structure solution. Sometimes such an a-priori information is only indirectly available; for example, it may be provided by inspection of the intensity distributions. Indeed when pseudosymmetry occurs the mean intensities of the measured structure factors are different for distinct classes of reflexions. Often difficulties occur for the solution of structures showing pseudosymmetry.
An important kind of pseudosymmetry occurs when a not negligible amount of the electron density fulfil a pseudotranslation. In this communication we describe a statistical approach which is able to produce normalized structure factors by taking explicitly into account the structural regularities arising from the presence of one or more pseudotranslations. A probabilistic theory of triplet invariants is also described, particularly devoted to the solution of crystal structures having superstructure effects.