17.2–15
THE ROLE OF THE ONE-PHASE SEMINVARIANTS IN THE CONVERGENCE / DIVERGENCE PROCEDURE

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The use of the one-phase seminvariants is a particular useful instrument in the phase-extention procedure.
Generally the one-phase seminvariants, used as known phases in the "starting set", are frequently displayed at the top of divergence map or at the bottom of convergence map. In this case the seminvariants play a fundamental role in the phasing process.
Sometimes the one-phase seminvariants, used as known phases in the "starting set", do not work in the first step of the phase development.
In this case, the role in the phase extention is not so evident, but an important action is produced during the convergence / divergence process connecting particular groups of reflections with final advantageous results.
Examples of the two possibilities are reported.

17.2–16 SAYRE'S EQUATION AND ENTROPY MAXIMIZATION. By D.M. Collins, Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA.

Sayre's equation and similar relationships of different origin are the present mainstay of direct methods. These relationships suggest an approximate idempotence which can be displayed explicitly in a density matrix upon which entropy is a maximum.

The number representation of a suitably constructed density matrix in the Fourier basis has initial entries

$$G(\underset{\sim}{h}_i-\underset{\sim}{h}_j) = p^{-1}\, F(\underset{\sim}{h}_i-\underset{\sim}{h}_j),$$

where F is a structure factor and p^{-1} is an occurrence weighting. Jaynes gives as the entropy of a density matrix

$$S = -\Sigma\lambda_i \ell n\lambda_i,$$

where λ is an eigenvalue of G. When S is an absolute maximum the eigenvalues are equal and

$$G \backsim GG, \text{ or } G(\underset{\sim}{h}_i-\underset{\sim}{h}_j) \sim \Sigma G(\underset{\sim}{h}_i-\underset{\sim}{h}_k)G(\underset{\sim}{h}_k-\underset{\sim}{h}_j)$$

which corresponds to the Sayre equation. In a direct methods calculation only the phase of an element of G would be allowed to change. Entropy maximization requires change in the magnitude as well.

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17.2–17 ESTIMATING INVARIANT PHASE SUMS FROM A NEW JOINT PROBABILITY DISTRIBUTION OF STRUCTURE FACTORS. By R. Peschar and H. Schenk.

A new joint probability distribution of structure factors has been derived in order to estimate invariant phase sums. The derivation joins the methods for the calculation of j.p.d.'s of real-valued structure factors (Naya, Nitta & Oda (1964) Acta Cryst. A17, 421) and complex-valued structure factors (Naya, Nitta & Oda (1965) Acta Cryst. A19, 734), so all types of structure factors are allowed. The distribution, in which space group symmetry has been included as well as the presence of different atom types, appears in a series expansion, containing Laguerre and/or Hermite polynomials, depending on the presence of complex-valued and/or real-valued structure factors. The process of deriving a particular distribution has been automated: for a specific choice of the reflections and symmetry operations, a computer program calculates the distribution, without using actual values for the structure factors and type and number of atoms. Employing numerical data and the generated distribution, theoretical estimation of the triplet and quartet phase sums has been made. In particular, the influence of higher order terms symmetry and special structure factors on the reliability of the estimations has been investigated. Testresults in spacegroup P1 show that the reliability of the triplet phase sum estimates depends in a more intricate way on the structure factor magnitudes and the number of atoms present in the unit cell than indicated by the widely used Cochran-distribution for the triplet phase sum (Cochran (1955), Acta Cryst. 8, 473).

17.2–18 A POWERFUL NEW TANGENT FORMULA. By T.Debaerdemaeker, Sektion fur Rontgen-und Elektronenbeugung, Universitat Ulm, W.Germany and C.Tate & M.M.Woolfson, Department of Physics, University of York, York, YO1 5DD.

A tangent formula for phase determination involving quartets as well as triplets has been derived from the system of Sayre's equations for the set of reflexions that would be used in a direct methods structure determination. The algebraic derivation involves only a relatively small sample of the possible quartets but the sample includes (typically) a few thousand which are most likely to be negative as well as a similar number most likely to be positive; and the derivation provides for appropriate weighting of these contributions. An additional feature is the emergence of a new figure of merit for the reliability of a set of phases. A computer program based on this derivation is giving correct structure determinations more frequently than either MULTAN or RANTAN. The improvement in performance is particularly striking for structures without translational symmetry for which, with this formula, trivial solutions are never found.