17.2-04 INFORMATION THEORY AND THE MAXIMUM DETERMINANT. By P.L. Britten and D.M. Collins, Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA.

The concepts of information theory have been applied to the analysis of spatial array data in the Maximum-Entropy method (McDonough, Geophysics (1974 39, 843). This procedure is similar to Tsoucaris' Maximum Determinant method for direct phase determination.

The Maximum Determinant method utilizes correlation coefficients given by the Sayre relation:

$$U_h = \overline{E_k E_{h-k}}, \qquad (1)$$

which presumes the density is like its square. A determinant is constructed of $U(h)$, which is then maximized to obtain the phases of the structure factors simultaneously. Instead of (1) another expression may be used:

$$F_h = \phi \Sigma_k G_k G_{h-k}^* \qquad (2)$$

where $G(h)$ is the Fourier transform of $g(r)$, and the electron density $\rho(r)$ satisfies

$$\rho(r) = |g(r)|^2 \geq 0. \quad (3)$$

In one dimension, the F(h), correlation coefficients in an exact sense, yield a maximum determinant when g(r) achieves maximum configurational entropy. The three-dimensional case is the subject of continuing investigation.

17.2-05 A UNIQUELY POWERFUL PHASE RELATIONSHIP. By D.M. Collins, and M. Fredrich, Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA.

Phase-determining relationships among structure factors may be based on a requirement that electron density be a positive function. It is necessary and sufficient that Karle-Hauptman determinants be non-negative and in this sense the resulting inequalities exhaust the variety of phase-determining relationships. An order N determinant may contain among its NxN elements as many as $N(N-1)/2-1$ independent variables, or as few as (N-2); it is assumed the diagonal elements are positive constants and an origin may be set. For any order N the case of fewest variables necessarily is the case of most constraints and accordingly is a uniquely powerful phase relationship.

The fewest variable case is ensured by using $\{E(0), E(h), E(2h), ..., E((N-1)h)\}$ in the first column of a matrix which is readily employed in the probabilistic sense of Tsoucaris' maximum determinant. Such a matrix has Toeplitz structure and corresponds to a projection of electron density onto a line. In a six atom test case, $P2_12_12_1$, all phases calculated for $|E| > 1.0$ and along lines in {hk0}, {h0l}, {0kl} were correct. In the case of a small protein, $\overline{P2_12_12_1}$, many determinants were assembled for the same classes of reflections. After ordering by Gersgorin's eigenvalue bound, the first several determinants gave phase indications in the ratio of 2.3 correct for each error.

17.2-06 A NEW DETERMINANTAL THEORY FOR SOLVING THE PHASE PROBLEM USING STEREOCHEMICAL INFORMATION. By A. D. Podjarny and C. Faerman, Laboratorio de Rayos X, Depto. de Fisica,UNLP, La Plata,Argentina.

In order to improve phase prediction by determinantal methods in macromolecules at low and medium resolution, a theory has been developed which includes stereochemical information in both the normalization of structure factors and the calculation of covariances. This theory merges the determinantal approach (Tsoucaris, Acta Cryst.,(1970),A26,492-499;Castellano,Podjarny and Navaza,Acta Cryst.,(1973),A29, 609-615) with previous theories that include stereochemical information in the evaluation of the phase probability of a triple product (Main,Crystallographic Computing Techniques, (1976),pp. 97-105,edited by F.R. Ahmed;Heinerman,Acta Cryst.,(1977),A33,100-106).
The main assumption is the existence of approximately equal atomic groups of known stereochemistry repeated at random positions and orientation in the asymmetric unit (e.g., a polypeptide or polynucleotide). The theory has been tested in model cases, improving significantly the phase prediction at non-atomic resolution.

17.2-07 ESTIMATION OF RELIABLE NORMALIZED STRUCTURE FACTORS. V. Subramanian and S.R. Hall, Crystallography Centre, University of Western Australia, Nedlands 6009, Australia.

The importance of the precision of $|E(h)|$ values to the phasing process is investigated. The $|E(h)|$ values calculated from exponential (k exp Bs^2) and profile scales with overall and index rescaling schemes are compared in terms of the reliability of triplet and quartet structure invariant relationships. Estimates of $|E(h)|$ based on random-atom and Debye expectation values are also considered. Tests involved the refined phases of the 14 known structures. In every case, the combination of exponential scale, overall rescale, and random-atom expectation value provided the most reliable $|E(h)|$ values.

The use of an exponential scale in a normalization procedure requires precise values for B and k. The B values from existing Wilson plot programs were found to differ by as much as a factor of two. These differences are shown to have a significant effect on the $|E(h)|$ values and reliability of structure invariants. The use of Bayesian statistics for weak intensities, the inclusion of missing data, the application of least-squares weights, and the compensation for Debye scattering effects to the Wilson plot are examined. The last factor was found most important for reliable estimates of B, especially for structures with limited data sets. A procedure based on the selective application of least squares to predicted inflexion points of the Debye curve will be described. This procedure, in conjunction with factors discussed above, provided B estimates within 5% of the refined values.