PS02.03.09 UNIQUE PHASE PROBLEM SOLUTIONS FROM REDUCED DENSITY MATRICES: ARE THEY CORRECT? Douglas M. Collins*, Laboratory for the Structure of Matter, 6030 Naval Research Laboratory, Washington DC 20375-5341, *Permanent address: Geo-Centers, Inc., 10903 Indian Head Highway, Fort Washington MD 20744

The general phase problem is solved uniquely in a quantum mechanical formulation constructed to display explicitly the main idea of the Hohenberg-Kohn theorem (HKT) [(1964) Phys. Rev. 136, B864-B871]. An informal summary of HKT is that electron density alone suffices to delimit fully the ground state of a nondegenerate electronic system. Our focus is on a quantum mechanical representation from which the dependence on spin and all the electrons but one has been removed by integration. Such a representation is a one-particle reduced density matrix (ODM). The fundamental requirement of N-representability is satisfied with the necessary and sufficient condition on ODM eigenvalues that they all lie in the closed interval [0,1] and sum to N, the number of electrons; the admissible ODM set is convex. HKT requires there be an admissible ODM reconstruction from density. Entropy (a function of eigenvalues only) on an ODM is a concave functional, hence entropy's one and only stationary point is at its global maximum where the eigenvalues are stationary in the parameters of reconstruction, and the corresponding ODM is uniquely determined. Thus maximization of entropy on an admissible ODM necessarily yields a unique solution to the phase problem.

Is the solution correct if structure moduli are known but phases are variables of the reconstruction? Clearly, if two or more structures have identical structure moduli, only by chance can a direct method select a particular result, but this is a most improbable situation. Can this method generate a reasonable and well-behaved density which does not correspond to an acceptable quantum-mechanical system, i.e., will it generate a non-physical structure? Probably not. This will be discussed.

PS02.03.10 INTEGRATED DIRECT METHOD WITH ANOMALOUS SCATTERING: TRIPLETS - SECOND NEIGHBOURHOOD. D. Velmurugan and D. Subhashini, Department of Crystallography and Biophysics, University of Madras, Madras - 600 025, India

Hauptman in the year 1982, integrated the Traditional Direct Method's formalism with the Anomalous Scattering methods for the case of triplets in their first neighbourhood. The applications of this new theory on the error free data of macromolecules show promising results. This instilled an encouragement in us in going on for the conditional probability distribtion of triplets in its second neighbourhood in the presence of anomalous scattering.

PS02.03.11 INTEGRATED DIRECT METHOD WITH ISOMORPHOUS REPLACEMENT - SECOND NEIGHBOURHOOD OF QUINTETS. D.Subhashini and D.Velmurugan, Department of Crystallography and Biophysics, University of Madras, Madras - 600 025, India

Hauptman in 1982, worked out the probabilistic theory of three phase invariant in P1 space group for structurally isomorphous pair. Ability to use the isomorphous sets of observed magnitudes by increasing the number of unknowns, facilitates the solution of phase problem for macromolecules. Initiated with the derivation of the joint probability distribution of 30 structure factors where H+K+L+M+N=0, we present the conditional probability distsribution of the five phase structure invatiants given the 30 magnitudes in the second neighbourhood of the quintets.It remains to be tested on error-free real data.

PS02.03.12 INTEGRATED DIRECT METHOD WITH ANOMALOUS SCATTERING: SEXTETS. S.Banumathi, D.Subhashini and D.Velmurugan. Department of Crystallography and Biophysics, University of Madras, Madras - 600 025, India

Advances in integrating the Traditional Direct methods with Anomalous Scattering methods was formalised in 1982 by Hauptman. The promising results in the application of this theory enthused us in working out the conditional probability distribution of sextets in the presence of Anomalous scattering.

PS02.03.13 CRUNCH: SOLVING STRUCTURES USING KARLE-HAUPTMAN MATRICES. R.A.G. de Graaff, Leiden Institute of Chemistry, Gorlaeus Laboratories, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands and R. de Gelder, Department of Inorganic Chemistry, Nijmegen SON Research Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Crunch is a system of programs aimed at solving difficult structures by direct methods in a completely automatic way. Phase determination is by construction and concurrent maximization of Karle-Hauptman determinants. Trial models obtained in this way are extended to the complete model by intelligent Fourier recycling.

The Generalized Maximum Determinant Rule states that from all possible sets of phases of the reflections contained in a given Karle-Hauptman matrix, the most probable set maximizes the determinant of this matrix.

Methods of construction of suitable matrices, as well as ways of maximizing the determinant as a function of the phases, have been developed. The program has been very successful in solving the phase problem, even in cases where other, commonly available, programs failed.

The perhaps best known example is the structure put on the Internet by Dr Huffman, which was solved by K. Goubitz and M. Numan of the University of Amsterdam, using Crunch in default settings.

References:

Automatic determination of Crystal Structures using Karle-Hauptman matrices, *Acta Cryst* A49 (1993), pp 287-293, R. de Gelder, R.A.G. de Graaff & H. Schenk.

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PS02.03.14 JOINT PROBABILITY DISTRIBUTIONS OF STRUCTURE FACTORS IN CASE OF INCOMMENSURATELY DISPLACIVE MODULATIONS. R. Peschar, Laboratory for Crystallography, Amsterdams Instituut voor Moleculaire Studies, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

The derivation of a joint probability distribution of structure factors is discussed, taking the presence of a one-dimensional incommensurately displacive modulation into account [1]. The mathetical technique is based on the availability of the (approximate) average structure, as determined by means of the main reflections. Furthermore, it is shown that an appropriate choice of the primitive random variables is required. It will be discussed that next to the structure factor expression as commonly used in the refinement of satellite structure factors in incommensurately modulated compounds, a different formulation of the structure factor is possible, that seems to be more appropriate when the joint probability distribution of structure factors is aimed at. Tests of the various expressions that result from these two approaches are in progress [2] and some preliminary results will be discussed.

References

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