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 function, 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 representation is a one-particle reduced density matrix (ODM). Our in progress [2] and some preliminary results will be discussed.

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 mathematical 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