Preliminary Calculations with Correlated Single Particle States.

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This presentation describes the continuation of work presented at the Sanibel Symposia of 2008, which described the generalization of the Independent Particle State (IPS) Model of molecular and solid state structure. IPS's have proved to be a mainstay of molecular multi-particle quantum mechanics both in qualitative interpretation and numerical applications for many decades and are fundamental to the understanding of chemical reactions. The major attraction of these states lies in the conceptually concrete and chemically understandable pictures of molecular structure and properties that they provide. It is often the case, however, that the IPS model is not sufficiently accurate to predict or explain the finer details of chemical reaction mechanisms or spectroscopic observations. In order to achieve this, one must take into account electron-electron correlation. Traditionally this is accomplished by methods that increase numerical accuracy at the cost of a clear, tangible, chemical model of the molecular system. Thus one cannot use chemical intuition to construct reaction pathways or picture the structure of molecules.

However, a class of correlated states have been discovered[1] that

- generalize the IPS model
- explicitly contain a description of correlation effects
- are the most general states that produce a one--particle theory of electrons in the sense that multi-particle states are determined by one--particle quantities.

These are the Antisymmetrized Geminal Power (AGP) states. In order to obtain the best picture of molecules in terms of these states one must optimize them. In this presentation I will discuss the development of computer programs needed to optimize such states and initial numerical results obtained from them.

[1] B. Weiner and J. V. Ortiz "Correlated One-Electron Wave Functions", Int. J. Quantum Chem, 104, 299-327 (2005).