Some Simple Examples of Correlated Multielectron States Determined by Single Electron States

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Independent--particle states (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, one can introduce a class of correlated states that generalize the IPS model, that explicitly contain a description of correlation effects, in the sense that multi-electron states and their energies are determined by one-electron quantities. These are energy optimized Antisymmetrized Geminal Power (AGP) states. In this presentation I will

- display some simple examples that explicitly show that this one particle theory is more general than a First Order Reduced Density Operator (FORDO) one
  and
- discuss methods of optimization tailored towards such states.

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