Exploiting Energetic and Spatial Structure in the Subtractive Manufacturing of Wave Functions

In approximating solutions to the many-electron Schrödinger equation, one typically exploits simplifying structural elements within the wave function. A famous example of this approach is the hierarchy of Hartree-Fock, density functional, Møller-Plesset, and coupled cluster theories that exploit the energetic structure present in the natural stratification of orbital energies in order to build the wave function up from a single Slater determinant. We discuss an alternative approach, in which a highly accurate approximation emerges subtractively through the elimination of unphysical terms from an initially very poor wave function form. In addition to energetic structure, this ansatz also exploits spatial structure by fusing together elements of coupled cluster theory, tensor network wave functions, valence bond theory, and quantum Monte Carlo. Preliminary tests in small molecule bond dissociations suggest that this ansatz is both more accurate and more compact than either coupled cluster theory or complete active space perturbation theory, delivering faithful treatments of both strong and weak electron correlations for a cost scaling polynomially as the fifth power of the system size. These findings provide a first step towards a new paradigm of electronic structure methods that subtract from, rather than add to, an initial starting point in order to more thoroughly exploit the simplifying structures that exist in nature’s wave functions.

Monday, November 17, 2014
4:00 P.M.
2033 Young Hall

Contact: Carol Canedo at (310) 206-4956 or carol@chem.ucla.edu for more information.