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Dissertation Defense

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THE SELF-CONSISTENT FIELD ENERGY LANDSCAPE AND ITS APPLICATION TO DESCRIBING ELECTRON CORRELATION

ABSTRACT:

Global elucidation of self-consistent-field (SCF) solutions is an extension of global optimization in which the goal is to identify stationary points of the Hartree-Fock equations. The value of identifying multiple SCF solutions is to use as reference wavefunctions in post-Hartree-Fock wavefunction theories, such as in those recently developed by the research group -- difference projected double-hybrid density functional theory,[1] nonorthogonal configuration interactions (NOCI),[2] or nonorthogonal multiconfigurational SCF (NOMCSCF).[3] Recent work has indicated that different SCF solutions may indicate how correlation in strongly correlated systems can be partitioned into weakly correlated subspaces.[4] However, the high-dimensional space over which to search and the relatively high cost of local optimization in Hartree-Fock (HF) models require new models to search over the entire SCF space efficiently. This work uses a Lie algebraic description of electronic structure combined with a stochastic basin hopping approach to address the technical issues of high-dimensionality and nonlinearity.[5] Having developed robust techniques for determining self-consistent field solutions, I subsequently discuss how SCF solutions can be categorized according to their connections to an exact electronic state. Using a symmetry-based graphical approach, I describe how symmetry-adapted SCF solutions and symmetry-broken SCF solutions are connected and how the topology of self-consistent field solution space encodes the mechanisms of electron correlation that must be considered for accurate evaluation of the wavefunction. Finally, I apply the ability to identify different SCF solutions to develop new real-time time-dependent wavefunction methods, with application to the study of molecular processes at ultrafast timescales. The orbital relaxation in the SCF field solutions allows an improved description of electron correlation in the ground state of configuration interaction singles calculations without increasing the computational cost of the time propagation. Configuration interaction singles exhibits overpolarization in response to an applied electric field owing to the absence of correlation in the ground state. I will describe the development of the nonorthgonal configuration interaction model and test the electronic response properties to determine whether the use of nonorthogonality can improve the performance of real-time simulations.

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