Holomorphic Hartree-Fock Theory: A basis for multireference electronic structure

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A particular challenge in electronic structure theory is that of bond-breaking, where single reference electronic structure methods often break down producing qualitatively incorrect binding curves. Associated with the onset of the multi-reference character of these wavefunctions is the existence of multiple, often symmetry-broken, solutions to the Hartree-Fock (HF) equations which can be challenging to find with conventional methods[1]. In more complicated systems the the lowest energy Hartree-Fock state may even change discontinuously between such solutions, and theories built upon a single HF state often perform very poorly.

An potentially effective approach to remedy this is that of Non-Orthogonal Configuration Interaction (NOCI), where the Hamiltonian is expressed in the basis of these different HF solutions, and the resulting energies and wavefunctions (for both ground and excited states) can smoothly vary between the optimal HF solutions at each geometry[2] and require little computational effort to calculate.

This approach is hampered by the coalescence and disappearance of HF solutions, as typified by the Coulson-Fischer point in the dissociating hydrogen molecule, and all but renders NOCI built upon conventional HF solutions useless as disappearing HF solutions lead to discontinuities in the potential energy surface.

We have developed an alternative analytic continuation of HF theory, holomorphic Hartree-Fock (hHF) theory[3], which proves identical to conventional HF where real-valued solutions exist, and produces smoothly varying analytic continuations of these into the complex plane when solutions would conventionally coalesce. These hHF solutions are a smooth and continuous basis for NOCI calculations, and provide a compact representation of multireference wavefunctions[4], upon which foundation perturbation theory methods may be used to give good correlation energies[5].

This talk will showcase some examples of multiple Hartree–Fock solutions and their holomorphic extensions and their use in creating smooth potential energy surfaces for diatomics and transition metal complexes.

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