Incorporating Orbital Rotations in a Natural Way in 1-Reference Geminal Coupled Cluster Method

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Strong correlation is significant in common occurrences in chemical reactions such as bond stretching or breaking. But the study of such strongly correlated systems is often computationally expensive because of the inclusion of a large number of Slater determinants in the computation. There are no truly black-box methods available to treat these systems, because of the combinatorial scaling of the number of parameters with the number of electrons and orbitals. Recently, the Flexible Ansatz for N-body Configuration Interaction (FANCI) framework was proposed to study and generalize popular wavefunction structures like CI, Coupled-Cluster, and geminal-product wavefunctions. Here, we will present benchmark calculations of some of these new methods on challenging model systems, with particular emphasis on approaches that use singles (or singles-like) excitations variants of paired-Coupled Cluster Doubles (pCCD), Antisymmetrized Product of Geminals (APG), and Antisymmetrized Products of Geminals with disjoint orbitals sets (APsetG). A key advantage of our methods is that they do not require orbital optimization, while recovering a large fraction of the electron correlation.