Orbital Rotations in 1-Reference Geminal Coupled Cluster

Pratiksha Balasaheb Gaikwad, Taewon D. Kim, Ramón Alain Miranda-Quintana

Quantum Theory Project, Department of Chemistry, University of Florida, Gainesville. FL

In Quantum Chemistry, computationally tractable standard approximation methods are available for weakly correlated systems. Whereas the study of strongly correlated systems is often computationally expensive because of the inclusion of many electronic configurations which increase with the system size. But strong correlation is significant in common occurrences in chemical reactions such as bond stretching or breaking and in complicated electronic structures often observed for rare-earth elements, lanthanides and iron-sulfur proteins, etc. Because of the combinatorial scaling of the number of parameters with the number of electrons and orbitals, there are no truly black-box methods available to study these systems. Recently, the Flexible Ansatz for N-body Configuration Interaction (FANCI) framework was proposed to study and generalize popular wavefunction structures like Configuration Interaction, Coupled-Cluster, and geminal-product wavefunctions [Computational and Theoretical Chemistry 1202 (2021), p. 113187]. The Python library – Fanpy – has been developed based on the FANCI framework to implement and study new wavefunctions. Here, we will present some of these newly developed geminal wavefunction methods on benchmarking 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.