A novel approach to strong correlation: Geminal wavefunctions with Doubles and Singles-like excitations

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The state-of-the-art quantum chemistry methods are built from one-electron functions, and orbitals, which are capable of capturing a large fraction of the missing electron correlation. Among these methods, the standard single-reference CC method delivers remarkable accuracy, particularly for weakly correlated systems, with reasonable polynomial scaling. However, it fails when addressing systems where strong correlation effects play a crucial role in the description of systems. These systems, referred to as strongly correlated systems, have a large number of quasi-degenerate states, leading to electron-electron interaction energy energies surpassing the energy gaps between orbitals. The study of such systems poses computational challenges, primarily due to including a large number of Slater determinants, representing electronic configurations, in the calculations. 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 introduced as a promising approach to study and generalize popular wavefunction forms like CI, CC, and geminal-product wavefunctions. We have implemented this framework in Fanpy, an open-source Python package for quickly developing and testing multideterminant wavefunctions and related ab initio methods in electronic structure theory. Its highly modular structure offers two greatest virtues, first is the "sandbox-like" ability to handle any wavefunction ansatz and their combinations; and the second is the ease in transition from the formal "pen and paper" conception of a method to its complete implementation.

Strongly correlated systems exhibit electronic distributions that are dominated by more than one determinant. Given the limited computational power, one has to use multireference methods or geminal-based approaches. Geminals, which are two electron functions, prove more effective at modeling strong electron correlation effects but come at the cost of increased complexity and substantially high computational cost compared to independent particle models. This challenge gave the idea of combining CC and geminal methods, resulting in a new family of geminal wavefunctions inspired by CC. This novel approach aims to leverage the advantages of both methods.

Here, we will present our studies on novel geminal-based methods and their applications to model systems. We will emphasize on approaches that incorporate variants of singles-like excitations in geminal wavefunctions, such as Antisymmetrized Product of 1-reference orbital Geminals (AP1roG), Antisymmetrized Product of Geminals (APG), and Antisymmetrized Products of Geminals with disjoint orbitals sets (APsetG). A key advantage of the proposed methods is that they do not require orbital optimization, while recovering a large fraction of the electron correlation, making them promising tools to study strongly correlated systems.