New Coupled Cluster, Geminals, and Seniority-Based Wavefunctions for Strongly Correlated Systems

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A precise understanding of the behavior of electrons in molecules and materials is needed to reliably predict their properties. Unfortunately, the complicated electronic structure of many promising compounds causes standard methods to fail catastrophically. Systems with this behavior are called strongly-correlated, and they are ubiquitous. Here we will discuss how a new framework: the *Flexible Ansatz for N-body Configuration Interaction* (FANCI), can help us to develop accurate and universally applicable wavefunction methods to treat strongly correlated fermions. In particular, our approach is inspired by the success of Coupled Cluster (CC) methods for weakly correlated systems, the versatility of quasiparticle (QP) wavefunctions to describe complex collective behavior, and the usefulness of the seniority quantum number. This motivated us to develop CC methods that can be formulated in terms of general QPs, as well as CC wavefunctions that are restricted to act in a given seniority sector. Our new wavefunctions have a uniform behavior over distinct electron correlation regimes, retaining the favorable properties of their parent CC variants, while avoiding the collapse of traditional CC in the strongly correlated regime. The "marriage" between CC and QP methods, while promising, has the key issue that one usually has to perform an expensive (and far from trivial) orbital optimization. Here we show how we can generalize the standard one-reference QP approaches in order to solve the orbital optimization problem not only in a truly black-box way, but also incorporating a large portion of the dynamic correlation often missing from simple geminal calculations.