Enhanced quantum Monte Carlo optimization and Jastrow-pfaffian wave functions

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The treatment of electron correlation in systems exhibiting strong interactions between valence electrons remains one of the major unsolved problems in quantum chemistry. In this regime, the typical hierarchy of corrections to an independent particle wave function fails qualitatively, rendering the usual approaches of perturbation theory, coupled cluster theory, and Kohn-Sham density functional theory unreliable. While multi-reference methods such as complete active space self-consistent field theory and the density matrix renormalization group have made substantial progress in this regime, neither of these approaches is feasible when a two or three dimensional system contains a large number of strongly interacting electrons. Examples of such systems can be found in iron-sulfur and other multi-metal protein cores, the superconducting cuprates, actinide and lanthanide materials, and highly conjugated molecules involved in the light harvesting process.

We demonstrate progress in the development of many-body Jastrow-pfaffian wave functions, an alternative class of strongly correlated wave function closely related to the Jastrow-Slater form used ubiquitously in quantum Monte Carlo. This ansatz combines a many-body Jastrow factor capable of encoding strong, short ranged correlations with a pfaffian pairing function capable of capturing electron delocalization. We discuss recent advances in variational optimization techniques that allow us to work with much more flexible Jastrow factors and pairing functions than was previously possible. We demonstrate that this enhanced flexibility allows for an accurate description of electronic correlation in a number of challenging proof-of-principal examples exhibiting strong electron interactions: the two dimensional Hubbard model at all hopping-to-repulsion ratios, the simultaneous all-bond dissociation of a small hydrogen cluster, and the singlet-triplet excitation in free base porphin.