Size-Extensive Wave Functions for Quantum Monte Carlo: A Linear Scaling Generalized Valence Bond Approach

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We present a new class of multideterminantal Jastrow-Slater wave functions constructed with localized orbitals to describe complex potential energy surfaces of molecular systems in quantum Monte Carlo (QMC). We elaborate a coupling scheme between electron pairs, which exploits the local nature of the orbitals and progressively includes new classes of excitations, yielding a sequence of wave functions of increasing complexity. The resulting wave functions are compact, scale linearly with the size of the system, can correlate all valence electrons, and are size extensive. We assess the performance of our wave functions in QMC calculations of the homolytic fragmentation of N-N, N-O, C-O, and C-N bonds, very common in molecules of biological interest. We find excellent agreement with experiments and, even with the simplest forms of our wave functions, we satisfy chemical accuracy and obtain dissociation energies superior to the CCSD(T) results computed with the large cc-pV5Z basis set. We will also present preliminary results on the performance of our QMC wave functions for the estimate of barriers heights of reactions.

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