Ground and Excited-state QMC Energies:
The Importance of Wave Function Optimization

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We present an efficient method to optimize Jastrow-Slater wave functions for both ground and excited states. The approach is within the framework of the so-called energy fluctuation potential method [1] which minimizes the energy in an iterative fashion based on Monte Carlo sampling and a fitting of the local energy fluctuations. The orbitals are here optimized together with the configuration interaction coefficients through the use of additional single excitations to a set of external orbitals. An improved set of orbitals is then obtained from the natural orbitals of this enlarged expansion [2]. For excited states, the approach is extended to treat state-averaging for the optimization of multiple states of the same symmetry [2].

The performance of our approach is illustrated with the lowest states of several organic molecules, where a careful construction of the wave function and the reoptimization of its determinantal part are often required to obtain accurate excitation energies within fixed-node diffusion Monte Carlo [2,3]. For instance, for a molecule as simple as ethene, optimizing the starting trial wave function corrects the initial diffusion Monte Carlo excitation energies by as much as 0.5-0.6 eV, yielding results in excellent agreement with experiments [2].