Quantum Monte Carlo Algorithms for Diagrammatic Vibrational Structure Calculations

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Convergent hierarchies of theories for calculating many-body electronic or vibrational ground and excited-state wave functions, such as Møller-Plesset perturbation theory or coupled cluster theory, tend to rely on matrix-algebraic manipulations of large, high-dimensional arrays of two-electron integrals or anharmonic force constants, tasks which are intrinsically difficult to massively parallelize. On the other hand, existing quantum Monte Carlo (QMC) methods for anharmonic or vibrational wave functions tend to lack robust techniques for obtaining excited-state energies, especially for large systems. By exploiting analytical identities for matrix elements of position operators in a harmonic oscillator basis, we have developed stochastic implementations of the size-extensive vibrational self-consistent field (MC-XVSCF) and size-extensive vibrational Møller-Plesset second-order perturbation (MC-XVMP2) theories which do not require storing the potential energy surface (PES). The programmable equations of MC-XVSCF and MC-XVMP2 take the form of a small number of high-dimensional integrals evaluated using Metropolis Monte Carlo techniques. The associated integrands require independent evaluations of only the value, not the derivatives, of the PES at many points, a task which is trivial to parallelize. However, unlike existing vibrational QMC methods, MC-XVSCF and MC-XVMP2 can calculate anharmonic frequencies directly, rather than as a small difference between two noisy total energies, and do not require user-selected coordinates or nodal surfaces.