

Quantum Monte Carlo Algebraic Diagrammatic Construction: QMCADC

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We reformulate the second order algebraic diagrammatic construction (ADC) schemes for the polarization propagator within projection quantum Monte Carlo (PQMC), which brings them from a serial nature to a massively parallel one. This new stochastic route, namely quantum Monte Carlo algebraic diagrammatic construction (QMCADC), relaxes the memory requirements in a twofold way. First, the scarcity of wave functions is exploited through random walks, allowing to store only a portion of configurations rather than the entire space. Second, the memory load is distributed across computing nodes, enabling to leverage modern rapidly developing HPC distributed computing resources. We demonstrate that QMCADC is a stochastic solution to the ADC Hermitian eigenvalue problem by studying various closed-shell molecular systems. It is shown that QMC wave functions sampled stochastically converge to exact ADC wave functions, and deterministic ADC excitation energies are reproduced by QMCADC within a marginal and controllable error and with significantly lighter memory requirements per computing node. ADC schemes including various variants based on the polarization propagator and the electron propagator constitute a class of high-level quantum chemistry techniques and play an important role in accurate and reliable descriptions of behaviors of a certain class of molecules, and therefore QMC formulation of the second order ADC schemes for the polarization propagator is a significant forward step in the pathway towards designing electronic structure algorithms well suited for modern supercomputer clusters and feasible to investigate large systems.

Keywords: quantum monte carlo, adc, algebraic diagrammatic construction