

Piecewise interaction picture density matrix quantum Monte Carlo for electrons with finite temperature

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We present our recent development, piecewise interaction picture density matrix quantum Monte Carlo (PIP-DMQMC) [J. Chem. Phys. 156, 184107 (2022)], for calculating the N-body density matrix of an ensemble of interacting electrons. In density matrix quantum Monte Carlo (DMQMC), it is advantageous to start the simulation with an approximate density matrix at a finite temperature, as this reduces the error made from propagating from the identity matrix. However, this has the drawback that more simulation time is spent preparing to sample the density matrix at a given temperature. I will show our recent work where we realized that a piecewise propagator could be used to propagate beyond the end of the simulation and capture more data at other temperatures. This is further advantageous because the sign problem can be effectively managed in the density matrix by considering rows and columns separately [J. Chem. Theor. Comput. 17, 10, 6036 (2021)]. We will also present data from our most recent development, the calculation of specific heat capacities and entropies, from Gaussian process regression models of the internal energy. Applications will be shown on a variety of systems including diatomic dissociation curves.