Linear-Scaling Electron-Correlation Theory for Two-Component Relativistic Hamiltonian

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In order to perform practical relativistic electron correlation calculations, the linear-scaling divide-and-conquer (DC)-based electron-correlation theories such as the second-order Møller–Plesset (MP2) [1] and coupled cluster theories with single and double excitations (CCSD) [2,3] as well as the Hartree-Fock (HF) [4,5] and have been combined with the local unitary transformation (LUT) scheme [6,7] at the infinite-order Douglas-Kroll-Hess (IODKH) level [8,9], which is based on the locality of relativistic effects. Numerical applications in hydrogen halide molecules, $(HX)_n$ (X = F, Cl, Br, and I) clarified that the present methods, namely DC-HF, MP2, and CCSD with the LUT-IODKH Hamiltonian, reproduce the results obtained using conventional methods with small computational costs. The combination of both LUT and DAC techniques could be the first approach that achieves overall linear-scaling with a small prefactor for relativistic electron correlation calculations (see Fig. 1) [10].

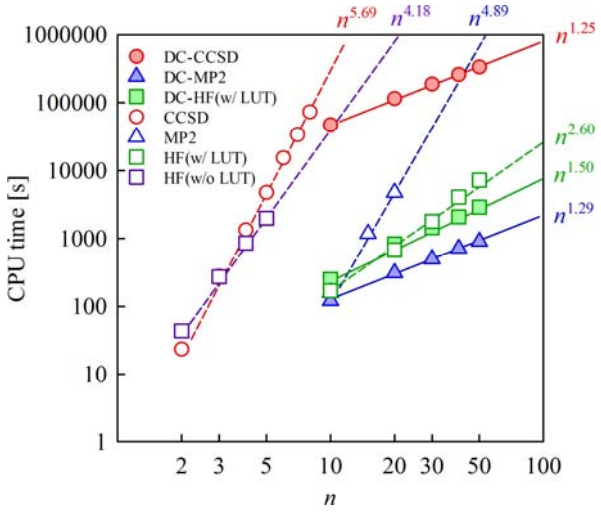

FIG. 1. System-size dependence of step CPU time in $(HF)n$ (n = 2, 3, …, 50) as calculated using conventional and DAC-based HF, MP2, and CCSD methods using IODKH/IODKH Hamiltonians with (w/) and without (w/o) LUT scheme. A single core of a Hexa Core Xeon/3.33 GHz processor was used.

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