Applications of FNDMC based separation of electron correlation energy

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Separation of dynamic and non-dynamic electron correlation energy is a useful concept in quantum chemistry. However, it may be difficult to make unambiguous distinction between these, or, evaluate their actual contributions in specific scenarios. Most often, non-dynamic correlation energy is obtained by taking the difference between the full-valence complete active space self-consistent field (CASSCF) calculation and HF reference. As we will show, CASSCF naturally includes some a priori unknown portion of dynamic correlation energy, making the separation somewhat unpredictable. Fixed-node diffusion quantum Monte Carlo (FNDQMC) method covers dynamic correlations exactly, and, its accuracy is limited by the node of the supplied trial wave function. Here we show that a combination of WFT and FNDQMC method using Hartree-Fock Slater determinant to fix the node within FNDQMC, enables an unambiguous and useful procedure for separation of electron correlation energy into dynamic and non-dynamic contributions. Moreover, such separation allows for quantifying the amount of dynamic correlation contained in CASSCF correlation energy. This is illustrated on multiple systems including bond breaking of HF, BH and CO molecules, and parametric H4 system. The proposed separation procedure provides useful insights for our understanding of electron correlation effects in complex systems.

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