Separation of electron correlation energy based on the FNDMC energy with the node from the Hartree-Fock Slater determinant

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Distinguishing between dynamic and non-dynamic electron correlation energy is a fundamental concept in quantum chemistry. It can be challenging to make a clear distinction between the two types of correlation energy or to determine their actual contributions in specific cases using wave-function theory (WFT). This is because both single-reference and multi-reference WFT methods cover both types of correlation energy to some extent. Fixed-node diffusion quantum Monte Carlo (FNDQMC) accurately covers dynamic cor- relations, but it is limited in overall accuracy by the node of the trial wave function. We propose a method for separating electron correlation energy into dynamic and non-dynamic components by using FNDQMC and a restricted Hartree-Fock Slater determinant to fix the node. This approach provides an unambiguous and useful procedure for separating electron correlation energy, as demonstrated on multiple systems, including the He atom, bond breaking of H_2, BH, HF, and the H_2-H_2 system.

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