Noncovalent Interactions: Quantum Monte Carlo Approaches CCSD(T) to 0.1 kcal/mol

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An accurate description of noncovalent molecular interaction energies is one of the most challenging tasks in computational quantum chemistry. Typically, nonempirical CCSD(T)/CBS values have been used as a benchmark reference. The practical use of the CCSD(T) is however fairly limited due to the rapid growth of its computational cost ($O(N^7)$) with the number of considered basis functions N. Here we show, that the fixed-node diffusion Monte Carlo (FN-DMC) method with a more favourable scaling ($O(M^3)$), with the number of electrons M, is capable of reaching the CCSD(T)/CBS within subchemical accuracy (< 0.1 kcal/mol) on a testing set of six small noncovalent complexes. These include dimers of ammonia, water, hydrogen fluoride, methane, ethene and ethene/ethyne complex. In larger complexes, where we test the identified protocol, i.e. benzene/water, benzene/methane, and the T-shape benzene dimer, FN-DMC provides interaction energies that agree within 0.25 kcal/mol with the best available CCSD(T)/CBS estimates. The demonstrated predictive power in conjunction with the favourable scaling of the FN-DMC thus provides new opportunities for studies of the vast and important class of medium/large noncovalent complexes.