Quantum Monte Carlo study of the thermochemistry of small hydrocarbons*

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A theoretical study is reported on the thermochemical properties of 20 small hydrocarbons based on the diffusion Monte Carlo (DMC) variant of the quantum Monte Carlo method. The 20 hydrocarbons include both radicals and closed-shell molecular systems containing 1 to 4 carbons centers that appear in combustion reactions. Using DMC trial functions constructed from Hartree-Fock (HF) and multi-configurational self-consistent field (MCSCF) wave functions, we have computed the atomization energies, heats of formation and bond dissociation energies for these systems. The DMC thermochemical results are compared to experimental data as well as complete basis set extrapolations for Moller-Plesset second-order perturbation theory, coupled-cluster singles-doubles (CCSD) with perturbative triples (CCSD(T)), and B3LYP methods to gauge the accuracy of the DMC method.

The amount of non-dynamical correlation energy, or single-reference character in CCSD, was determined by examining the T1 diagnostic test of CCSD calculations.[1] This diagnostic test has been demonstrated to be a better quantifier of multi-reference character than the leading coefficient in a multi-configurational wave function. The results of the T1 diagnostic are correlated with DMC atomization energies in order to provide a measure of the quality of HF trial wave functions. The idea is to gauge the accuracy a priori of a DMC calculation that uses a HF trial function from the T1 diagnostic. In cases where DMC atomization energies from HF trial functions are poor, multi-determinant trial functions will be used to improve the results.

[1]T. J. Lee and P. R. Taylor, *Int. J. Quant. Chem. Symp.* **23**, 199 (1989).

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