Block correlated coupled cluster theory and its applications

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In this talk, I will present the general formulation of block correlated coupled cluster (BCCC) theory with a complete active-space self-consistent-field (CASSCF) reference function [1,2]. This theory provides an alternative approach for describing molecular electronic structures with strong multireference character. In this approach, a multireference block is defined to incorporate nondynamic correlation, and all other blocks involve just a single spin orbital. The cluster operator is introduced to take dynamic correlation into account. The truncation of the cluster operator up to the four-block correlation level leads to the CAS-BCCC4 scheme. The CAS-BCCC4 method computationally scales as the traditional single-reference CCSD, and is applicable for medium-sized molecules. The CAS-BCCC4 method has been efficiently implemented and applied to investigate the potential energy surfaces for bond breaking processes in a number of molecules (such as F_2, H_2O, N_2), spectroscopic constants in some diatomic molecules, activation barriers for several reactions, singlet-triplet gaps in some diradicals, and low-lying excitation energies in some small molecules [2-6]. A comparison of our results with those from full configuration interaction and other theoretical methods shows that the present approach can provide more accurate descriptions for all systems under study than widely used CASPT2 or MR-CISD methods.

References:

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