Abstract

The multireference Brillouin-Wigner coupled clusters method with connected triple excitations has been developed and implemented in the ACES II program. This method provides an accurate description of both the static and dynamic correlation, and is thus suitable for chemical systems with quasidegeneracies, e.g. in cases of bond breaking, studies of larger sections of potential energy surface, and systems with multi-determinantal character like diradicals.

The connected triples were included in both iterative and noniterative way. The iterative approach is more rigorous and conceptually straightforward, but computationally more demanding than the noniterative one.

The iterative inclusion of connected triples was done in two successive steps. First, in the MR BWCCSDTα method, all terms except for the disconnected and unlinked ones in the T_3 equation have been included. Second, the missing terms were included to obtain the MR BWCCSDT method.

The noniterative inclusion of connected triples was based on triples correction to matrix elements of the effective Hamiltonian, which yield the total energy by diagonalization. In the MR BWCCSD(T_d) method only the diagonal elements of effective Hamiltonian are corrected, wheres in MR BWCCSD(T) method correction is performed for all the elements. In all cases, the triples correction is done after the size-extensivity correction.

In order to assess the performance of the newly developed methods, following four systems were studied: low lying electronic states of the oxygen molecule, C_{2v} insertion pathway of Be to H_2, singlet-triplet gaps of methylene and silylene, and the automerization barrier of cyclobutadiene.