Description of Difficult Singlet/Triplet Splitting Problems with Coupled Cluster Theory

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Coupled-cluster (CC) theory is widely accepted as the most accurate and generally applicable approach in quantum chemistry. CC calculations are usually performed with single Slater-determinant references, e.g. canonical Hartree-Fock (HF) wavefunctions. On one hand, this is an attractive feature because typical CC calculations are simple to set up and there is no ambiguous user input required. On the other hand, there is some concern that CC results may be unreliable if the reference determinant provides a poor description of the system of interest. In this context, the prime suspects are systems that display static correlation effects, i.e. where the HF ground state has a relatively low weight in the full CI expansion. However, in many cases the reported "failures" of CC can be attributed to an unfortunate choice of reference determinant, rather than intrinsic shortcomings of CC itself. This is mainly connected to well known effects like spin-contamination, wavefunction instability and symmetry-breaking.

In this talk, a particularly difficult singlet/triplet splitting problem in two phenyldinitrene molecules is investigated, where single-reference CCSD(T) calculations were reported to give poor results. The reason for this is analyzed by using different reference determinants (e.g. restricted open-shell, RO, and symmetry-broken UHF) for CCSD(T), as well as performing higher level CCSDT calculations. We find that CCSD(T) does give qualitatively correct results for this problem, if the proper reference state is obtained. Quantitative accuracy can be obtained by using symmetry-broken reference determinants, at the expense of large spin-contamination.

Alternatively, doubly-electron attached equation-of-motion (DEA-EOM) approaches are a powerful tool for handling such systems. They are operationally single-determinant methods (i.e. simple to set up), while adequately taking the multi-reference nature of these molecules into account. Both the DEA-EOM and the similarity transformed DEA-STEOM-CCSD methods are found to be highly accurate. Our results indicate that CC is a powerful tool for describing systems with both static and dynamic correlation, although there are some pitfalls, mainly associated with the choice of the reference determinant.