Brueckner-based ΛCCSD(T) for Bond Breaking

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For molecules near equilibrium, coupled-cluster theory with singles, doubles, and perturbative triples [CCSD(T)] is considered the standard. As one stretches a bond, the accuracy of CCSD(T) degrades rapidly. Recent work (1) showed that by modifying the CCSD(T) to include the effect of Λ (the de-excitation operator from CC gradient theory) one can improve the bond-breaking. This method, called ΛCCSD(T), maintains the advantages of CCSD(T), in particular extensivity and $O(N^7)$ computational scaling, and is equally good near equilibrium. Instead of exhibiting large energetic turnovers for bond-breaking of singly-bonded molecules, ΛCCSD(T) has at most a small (few millihartree) error along the potential energy surface (PES). For more complicated bonding situations, e.g. N_2, ΛCCSD(T) is not quantitatively accurate across the PES, with errors of more than 20 millihartree.

In our work with ΛCCSD(T), we noticed that while RHF ΛCCSD(T) is better than RHF CCSD(T), UHF CCSD(T) and UHF ΛCCSD(T) are almost identical. If one were able to produce a stable spin-restricted CCSD solution that was adequate to longer bond distances, then ΛCCSD(T) could improve the solution past the spin-re-coupling region. Brueckner orbitals are more stable than HF orbitals and when one combines the use instability analysis of the Brueckner orbitals (2) with the ΛCCSD(T) energy functional the results improve. While the RB solution is stable, the improvement of ΛCCSD(T) is substantial. Because the RB solution becomes unstable at bond distances beyond the spin-re-coupling region, the improper behavior of UHF ΛCCSD(T) is irrelevant. We applied the combination of Brueckner orbitals and ΛCCSD(T) to a variety of bonding situations. For N_2 bond-breaking, the non-parallelity error is less than 10 millihartree out to twice the equilibrium bond length.

References

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