Methodological Advances in State-Specific Multireference Coupled Cluster Theory

Wesley D. Allen, Francesco A. Evangelista, and Andrew C. Simmonett
Center for Computational Chemistry and Department of Chemistry, University of Georgia, Athens, Georgia 30602 USA

State-specific and rigorously size-extensive Mukherjee multireference coupled cluster theory (Mk-MRCC) has been developed into a powerful method for chemical research in several recent studies.[1-3] The first production-level program (PSIMRCC) for Mk-MRCCSD has been coded into the freely available PSI3 package.[4] This breakthrough was aided by the derivation of closed-form expressions for the terms coupling different references in the amplitude equations.[2] Moreover, a hierarchy of Mk-MRCCSDT-*n* (*n* = 1a, 1b, 2, 3) methods for the iterative inclusion of connected triple excitations has been formulated and implemented for the first time.[3] The effectiveness of our Mk-MRCC methods is established by extensive computations on benchmark problems, including F_2, C_2, O_2, O_3, NH, NF, CH_2, SiH_2, and H_2CO. For F_2, at the complete basis set (CBS) limit, Mk-MRCCSD applied with a (2,2) active space and localized orbitals gives (r_e, D_e, ω_e) = (1.4134 Å, 38.5 kcal mol^{-1}, 915 cm^{-1}), in exceptional agreement with the spectroscopic values of (1.4119 Å, 38.3 kcal mol^{-1}, 917 cm^{-1}). Similarly, for CH_2 and O_2, CBS Mk-MRCCSD predicts singlet-triplet splittings [ΔE(S-T)] within 0.2 kcal mol^{-1} of experiment.

In chemical applications of Mk-MRCCSD theory, outstanding results have been obtained for the optimum geometric structures, vibrational frequencies, and adiabatic excitation energies of *ortho*-, *meta*-, and *para*-benzyne. Our CBS Mk-MRCCSD extrapolations yield ΔE(S-T) = 38.9, 20.8, and 4.7 kcal mol^{-1}, respectively, for these three diradicals, as compared to the corresponding experimental values of 37.5, 21.0, and 3.8 kcal mol^{-1}. For antiaromatic systems, Mk-MRCCSD/cc-pVTZ theory provides the first reliable automerization barriers of cyclobutadiene (D_{4h}–D_{2h}, 9.2 kcal mol^{-1}), perfluorocyclobutadiene (D_{4h}–D_{2h}, 14.5 kcal mol^{-1}), and cyclooctatetraene (D_{8h}–D_{4h}, 7.0 kcal mol^{-1}). In the C_8H_8 case, the Mk-MRCCSD/cc-pVTZ singlet-triplet splitting is 12.8 kcal mol^{-1}, within 0.7 kcal mol^{-1} of experiment. Finally, we report Mk-MRCC predictions of UV/Vis spectra of novel carbenes that have led to the first isolation and identification of these species in matrix isolation experiments. Notably, application of a four-reference Mk-MRCCSD/aug-cc-pVTZ wave function reveals that the S_1 open-shell singlet state of the elusive hydroxymethylene species has a twisted (C_1) geometric structure with a torsion angle of 108.4° and excitation energy T_0 = 56.8 kcal mol^{-1}, corresponding precisely to the onset of electronic absorptions observed near 510 nm.

---

1 F. A. Evangelista, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **125**, 154113: 1-16 (2006).
2 F. A. Evangelista, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **127**, 024102: 1-17 (2007).
3 F. A. Evangelista, A. C. Simmonett, W. D. Allen, H. F. Schaefer, and J. Gauss, *J. Chem. Phys*. **128**, 124104: 1-13 (2008).
4 T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny, and W. D. Allen, *J. Comput. Chem.* **28**, 1610-1616 (2007).