Methodological Advances in State-Specific Multireference Coupled Cluster Theory

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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.[1-4] The first production-level program (PSIMRCC) for Mk-MRCCSD has been coded into the freely available PSI3 package. 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] Finally, a new second-order multireference perturbation theory (Mk-MRPT2) has been developed as a companion to Mk-MRCC methods, particularly for computations with very large one-particle basis sets used in multireference focal point extrapolations to *ab initio* limits or applications to expansive chemical systems.[4]

The effectiveness of our Mk-MRCC methods is established by extensive computations on benchmark problems, including F_2, C_2, O_2, O_3, and CH_2. 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. In particular, Mk-MRCCSD/cc-pVTZ theory averts unphysical vibrational frequencies arising from orbital instabilities, a pitfall that has plagued single-reference correlation methods. For *meta*-benzyne, the problem of erroneous bicyclic minima is solved by both Mk-MRCCSD and Mk-MRPT2 theory, and the efficiency of the latter method is demonstrated by cc-pV5Z computations involving 766 basis functions. For cyclic polyenes, Mk-MRCCSD/cc-pVTZ provides reliable automerization barriers for 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.

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