

Advances in Multireference Coupled Cluster Theory

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A state-specific and rigorously size-extensive multireference coupled cluster theory (Mk-MRCC) and a companion second-order perturbation theory (Mk-MRPT2) have been developed into powerful and practical tools for chemical research. The effectiveness of our Mk-MRCC methods is established by extensive computations on benchmark systems, including the low-lying electronic states of O₂, CH₂, HCF, and H₂CO, the dissociation of F₂, and the problematic ozone molecule. In chemical applications of Mk-MRCC theory, outstanding results have been obtained for the optimum geometric structures, vibrational frequencies, and electronic excitation energies of the organic diradicals *ortho*-, *meta*-, and *para*-benzyne, as well as the cyclic polyenes cyclobutadiene and cyclooctatetraene. A rigorous Mk-MRCC torsional surface has been generated for the classic problem of the stereomutation of cyclopropane. The seemingly simple organic molecule cyclobutanetetraone (C₄O₄) is demonstrated by Mk-MRCC theory to actually have a triplet rather than a closed-shell singlet ground state! Finally, joint theoretical and experimental work is presented on novel hydroxycarbenes (RCOH; R = H, CH₃, and phenyl) that has led to the first isolation and identification of these species. These hydroxycarbenes show rapid tunneling ($t_{1/2} \approx 2$ hrs) at 11 K through prodigious energy barriers of almost 30 kcal mol⁻¹, a remarkable phenomenon confirmed by our high-accuracy computations of barrier penetration integrals.