

# Renormalized Coupled-Cluster Methods: Recent Developments and Applications to Radicals, Biradicals, and Bond Breaking

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In 1989, Pople and co-workers proposed the CCSD(T) approach. Over the years, the CCSD(T) method, which is based on a principle of adding the relatively inexpensive correction due to triply excited clusters to the CCSD (coupled-cluster singles and doubles) energy, has become a standard that often symbolizes the success of coupled-cluster theory in quantum chemistry. Unfortunately, like any other traditional single-reference method, CCSD(T) cannot be applied to biradicals, bond breaking, and other situations involving larger non-dynamical correlation effects. The development of practical single-reference procedures that could be applied to at least some of these situations with a 'black-box' effort similar to a conventional CCSD(T) calculation is an important goal of contemporary quantum chemistry. We will discuss some of our recent efforts toward the development of such procedures by focusing on the renormalized coupled-cluster methods.

The renormalized coupled-cluster methods, such as CR-CCSD(T), CR-CCSD(TQ),<sup>1</sup> and the recent rigorously size extensive formulation of CR-CCSD(T), termed CR-CC(2,3),<sup>2</sup> which are all derived from the asymmetric energy expressions that define the method of moments of coupled-cluster equations<sup>1,2</sup> and which are available in the GAMESS package,<sup>3</sup> represent a new generation of single-reference approaches that eliminate the failures of conventional coupled-cluster approximations, such as CCSD(T), whenever non-dynamical correlation effects become more significant. At the same time, the CR-CC(2,3) approach is as accurate as CCSD(T) for closed-shell molecules near the equilibrium geometries. We will show that the relatively inexpensive renormalized coupled-cluster methods provide an accurate and balanced description of reaction pathways involving bond breaking, radicals, and biradicals, singlet-triplet gaps in magnetic systems, and excited states dominated by one- and two-electron transitions, enabling one to address interesting mechanistic problems in organic and bioinorganic chemistries, and photochemistry.

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<sup>2</sup> P. Piecuch and M. Włoch, *J. Chem. Phys.* **123**, 224105 (2005); P. Piecuch, M. Włoch, J.R. Gour, and A. Kinal, *Chem. Phys. Lett.* **418**, 467 (2006); M. Włoch, J.R. Gour, and P. Piecuch, *J. Phys. Chem. A* **111**, 11359 (2007).

<sup>3</sup> M.W. Schmidt et al., *J. Comput. Chem.* **14**, 1347 (1993); M.S.Gordon and M.W.Schmidt, in *Theory and Applications of Computational Chemistry: The First Forty Years*, edited by C.E.Dykstra, G.Frenking, K.S.Kim, and G.E.Scuseria (Elsevier, Amsterdam, 2005), p. 1167.