Local Correlation Calculations Using Cluster-In-Molecule Standard and Renormalized Coupled-Cluster Methods

Wei Li,[a] Jeffrey R. Gour,[a] and Piotr Piecuch[a,b]
[a]*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA*
[b]*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA*

A linear scaling local correlation approach, termed 'cluster-in-molecule' and abbreviated as CIM (Ref. 1) is extended to the coupled-cluster (CC) theory with singles and doubles (CCSD) and CC methods with singles, doubles, and non-iterative triples, including CCSD(T) and the completely renormalized CR-CC(2,3) approach.[2] As in the original CIM work that dealt with the second-order many-body perturbation theory and CC doubles (CCD) approach, the main idea of the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods is the realization of the fact that the total correlation energy of a large system can be obtained as a sum of contributions from the occupied orthonormal localized molecular orbitals and their respective occupied and unoccupied orbital domains. Unlike the earlier implementations of the CIM-CCD approach,[1] which utilized pilot CCD codes with the explicit nested loop structure, the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods developed in this work are characterized by the high computational efficiency in both the CIM and CC parts, enabling the calculations for much larger systems than previously possible. This is achieved by combining the natural linear scaling of the CIM ansatz with the fully vectorized CC codes that rely on the use of diagram factorization and recursively generated intermediates. By comparing the results of the canonical and CIM-CC calculations for normal alkanes and water clusters, it is demonstrated that the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) approaches recover the corresponding canonical CC correlation energies to within 0.1-0.4 % or so, while offering the linear scaling of the computer costs with the system size and savings in the computer effort by orders of magnitude. By examining the dissociation of dodecane into $C_{11}H_{23}$ and CH_3 and several lowest-energy structures of the $(H_2O)_n$ clusters with n=10-20, it is shown that the CIM-CC methods accurately reproduce the relative energetics of the corresponding canonical CC calculations.

[1] S. Li, J. Ma, and Y. Jiang, *J. Comp. Chem.* **23**, 237 (2002); S. Li, J. Shen, W. Li, and Y. Jiang, *J. Chem. Phys.* **125**, 074109 (2006).
[2] 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).