Cluster-in-Molecule Local Correlation Approach for Periodic Systems

Yuqi Wang, Zhigang Ni, Wei Li,* and Shuhua Li*

School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry of MOE, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing 210023, People's Republic of China

Email: mg1724082@smail.nju.edu.cn, shuhua@nju.edu.cn

Abstract

The cluster-in-molecule (CIM) local correlation approach for periodic systems with periodic boundary condition is developed, which allows electron-correlation calculations of various crystals computationally tractable. In this approach, the correlation energy per unit cell of a periodic system can be evaluated as the summation of the correlation contributions from electroncorrelation calculations on a series of finite-sized clusters. Each cluster is defined to contain a subset of localized Wannier functions (WFs) (for the occupied space) and projected atomic orbitals (for the virtual space), which can be derived from a periodic Hartree−Fock calculation. Electron-correlation calculations on clusters at second-order Møller−Plesset perturbation theory (MP2) or coupled cluster singles and doubles (CCSD) can be performed with well-established molecular quantum chemistry packages.