Adiabatic connection electron correlation from alternative ERPA channels: application to small molecules dissociation

G. Sanchez-Diaz, M. Richer, P. W. Ayers

Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario, Canada

sanchezg@mcmaster.ca

Strong electron correlation is among the largest outstanding problems in quantum chemistry. For several single and multireference wavefunctions, the electron correlation energy, defined as the energy difference between the exact and the approximate wavefunction models, can be derived from the linear response function based on an adiabatic connection formalism (AC). This method, pioneered by Pernal, relies on the transition density matrix as key parameter which can be straightforwardly approximated from particle-hole extended random-phase approximation (ERPA) solutions. It offers an efficient way to add missing (dynamic) correlation energy to the reference ground state wavefunction model. We present new adiabatic connection formulations in terms of the alternative particle-particle and hole-hole channels of random phase approximation (RPA) and test their performance on the dissociation energies of a small set of molecules comparing against the AC particle-hole approach.