

Screened Hybrid DFT and CAS-DFT study of ion-radical systems

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Theoretical description of the ionic radical state is one of important issues in relation to charge-transfer reactions. This ionic radical electronic structure is known as a troublesome case for applications of DFT [1,2]. For instance, a spurious low-lying surface appears at long-internuclear distances of He dimer cation for DFT computational results.

Essentially, the self-interaction error due to approximated exchange term in DFT is the main cause of this phenomena. These effects are inspected using both usual DFT and self-interaction corrected (SIC) DFT by Cremer and his coworkers [2].

We examine some DFT methods for ion-radical systems such as He_2^+ , ethylene dimer cation, etc. In particular, the results of screened hybrid DFTs based on Coulomb-division scheme [3] are investigated for some types of Coulomb-divisions. Further, we applied iterative version of CASCI/CASSCF-DFT [4,5] for ion radical systems. The results are discussed in relation to the importance of short-and-long range parts of exchange term, nonlinear structure of fundamental equations, and orbital-and-geometry relaxation effects.

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