Resonating CASSCF and Resonating coupled-cluster approaches for ion-radical systems

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Ion-radical systems exhibit one of most complicated electronic structures since the radical and the hole coexist. So, for this class of systems, weak points of theories we examine are exposed. During the past decades, many theoretical researchers in the DFT community studied this problem, clarifying several important issues. First, the so-called one-electron self-interaction error (SIE), which is well analyzed by Perdew and Zunger (PZ)[1], causes the severe failure in describing the dissociating profile of this type of species [2]. Second, the PZ type of self-interaction correction (SIC) does not completely resolve the problem [3]. Third, the most essential point is whether the condition suggested by Perdew-Parr-Levy-Balduz (PPLB) [4] is satisfied or not [5]. We pointed out that even the CASSCF (and CASSCF-DFT) treatments with sufficiently wide active-spaces lead to spatially broken-symmetry (BS) solutions for ion-radical species consisting of equivalent sites and that the resonating CI (Res-CI) treatment using BS-Hartree-Fock (HF) solutions satisfies the PPLB condition [6]. In the refs [6], we suggested to employ "broken-symmetry" solutions obtained from CASSCF or coupled-cluster (CC) calculations as basis for Res-CI. In this work, we develop these kinds of "post-HF based" Res-CI. We apply this new type of methods for ion-radical species, and examine the effects of (i) electron correlation effects and (ii) the asymmetry degree on the localization of the hole.

Reference

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