

Time-dependent density functional theory for core excited states

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Time-dependent density functional theory (TDDFT) is one of the most popular methods to calculate low-lying excited states because of its reasonable accuracy with low-computational cost. However, TDDFT fails to describe core and Rydberg excitations with high accuracy [1,2]. Based on our assessment [1] and analysis [2], we have proposed two different kinds of new exchange-correlation functionals for core and Rydberg excitations: pure [3] and hybrid functionals [4-6]: The hybrid functional, core-valence B3LYP (CV-B3LYP) [4], is designed to reproduce the behaviors of the BHHLYP and B3LYP functionals for core and valence regions separately. The newly developed functional, core-valence-Rydberg B3LYP (CVR-B3LYP) [5], is constructed so as to accurately describe the excitations from core and occupied valence orbitals not only to unoccupied valence orbitals (C→V and V→V excitations) but also to Rydberg orbitals (C→R and V→R excitations). Based on the arbitrariness of virtual orbitals, CVR-B3LYP overcomes the disadvantages of CV-B3LYP by adopting the appropriate portions of HF exchange for unoccupied valence and Rydberg regions separately.

C→V, C→R, V→V, and V→R excitation energies of C₂H₂, C₂H₄, CH₂O, CO, and N₂ molecules were calculated with the use of the cc-pCVTZ. Single s and p Rydberg basis functions of Dunning-Hay were added for describing 3s and 3p orbitals. Rydberg orbitals were distinguished from the others by the second moments of the orbitals. While the results of CV-B3LYP have similar accuracy to those of CVR-B3LYP for C→V and V→V excitations, CV-B3LYP gives inaccurate results for C→R and V→R excitations. CVR-B3LYP provides accurate descriptions for not only (C→V, V→V) but also (C→R, V→R) excitations: The mean absolute errors (MAEs) of CVR-B3LYP are 0.3, 0.7, 0.3, and 0.3 eV for C→V, C→R, V→V, and V→R excitations, respectively. Thus, CVR-B3LYP is a powerful tool for describing all types of excitations with high accuracy.

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