

Predicting excitation energies from short-range density functionals combined with the long-range strongly orthogonal geminal theory

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Predicting excitation energies from time-dependent density functional theory (TDDFT) can be performed at relatively low computational cost and often leads to satisfactory results, in particular for low-lying single excitations. However, some excitations (i.g. double excitations) remain beyond the reach of conventional approaches to TDDFT based on the adiabatic approximation.

Recently, we have proposed a formalism based on the Rowe's equation of motion that employs reduced density matrices obtained from the antisymmetrized product of strongly orthogonal geminals (APSG) model [1]. It leads to obtaining accurate excitation energies of molecules when static correlation effects are of importance. Unfortunately, close to equilibrium geometries of the investigated molecules the accuracy of the excitation energies is often only comparable or even inferior to that of the TDHF method [2].

We show that applying the principle of action and the linear response theory for the APSG functional leads to equations of the similar structure as the structure of equations obtained from the equations of motion. It opens an avenue to combining the TD-DFT and APSG approaches by range-separating of the electron-electron interaction and restricting density functionals to short-range and the APSG to long-range regimes, similarly to what has been proposed in the context of density matrix functionals [3] and MC-SCF [4]. Illustrative calculations of potential energy curves of excited states confirm that the short-range-TDDF – long-range-APSG approach leads to significant improvement over TDDFT.

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[4] Fromager, E., Knecht, S., Jensen, H.J.Aa., *J. Chem. Phys.*, 138:084101, 2013.