

An additive long-range potential to correct for the charge-transfer failure of time-dependent density functional theory

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Time-dependent density functional theory is one of the most widely used methods for the calculation of excited states of large molecules. However, it exhibits substantial problems with charge-transfer (CT) excited states when conventional exchange-correlation functionals are employed. Here, we introduce an additive long-range potential that can, in principle, be directly employed with any existing local, GGA or hybrid-functional, without re-fitting of the original functionals. The additive potential consists of two parts: (1) long-range Hartree-Fock is included by means of a switching function. Instead of using one error-function as is usually employed we utilize a linear combination of two error-functions that allows us to switch on non-local Hartree-Fock exchange at larger electron-electron distances than zero. The inclusion of Hartree-Fock exchange at long-range recovers the correct $1/R$ -asymptote along charge separation coordinates.(2) The quality of excitation energies of CT states strongly depends on the extend of charge transfer, i.e. on the spatial overlap of the electron donating and accepting orbitals. Therefore we calculate the spatial overlap and use it as a measure of how large the excitation energies of CT states need to be shifted to higher energies. Both corrections have been implemented together into a development version of the Q-Chem programme package. First examples of its successful application are presented.