

DEVELOPMENT AND FIRST TESTS FOR AN ADDITIVE LONG RANGE CORRECTED XC-FUNCTIONAL

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Time dependent density functional theory (TDDFT) has become a powerful and widely used tool for the description of excited states of large molecules with up to several hundreds of atoms and is often considered the method of choice due to its low computational cost. While the theoretical treatment of low lying optically allowed locally excited electronic states is usually in good agreement with experimental data, the description of 'dark' states on the other hand is problematic: Doubly and higher excited states are not included at all in the TDDFT framework and the energy of charge transfer (CT) states is usually drastically underestimated by up to several eV due to the so called 'self interaction error'. Furthermore, CT states do not exhibit the correct $1/R$ behavior when looking at the potential energy curves of a dimer along an intermolecular separation coordinate R .

It has been shown that the $1/R$ behavior of CT states may be regained by using coulomb attenuated functionals, but the energy of CT states is still drastically underestimated. The ansatz for our new xc-functional is to correct the excitation energy of every transition according to the amount of charge transfer character of the given transition. Local excitations should not be shifted while CT excitations should be shifted upwards in energy. The 'amount' of charge transfer character for a given transition may be estimated by the orbital overlap of the molecular orbitals involved in the specific transition. The lower the orbital overlap, the higher the charge transfer character of the transition. The energy of the lowest charge transfer excitation of a dimer at infinite distance is given to zeroth order by the difference between electron affinity (EA) and ionization potential (IP), thus it is possible to estimate and correct for the self interaction error if EA and IP are known.

Since this energy correction is an additive functional it may in principle be added to every existing functional without the need of refitting the functional parameters.

Literature: