

Virtues and shortcomings of the Exact Exchange Approximation within Time-Dependent Density Functional Theory - applications to atoms and the electron gas.

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Abstract

The performance of the time-dependent Hartree-Fock approximation (TDHF) or, as it is sometimes called, the RPA with exchange has been investigated in many systems. The optical absorption spectra of atoms and small molecules have been calculated close to the continuum edge and are usually superior to those of the RPA. Small discrete excitation energies are similar to those of the RPA and not very impressive. Neither are static polarizabilities and van-der-Waals coefficients although these usually improve on the RPA results. Total energies are much superior to those of the RPA but difficult to calculate for larger finite or extended systems.

Over the past decades Time-Dependent Density-Functional Theory (TDDFT) has emerged as a computationally simpler tool for obtaining particle conserving excitation energies of both finite and infinite systems. The computational advantages increase with the size of the systems. Most calculations within TDDFT have made use of the so called adiabatic approximations in which the beyond-RPA effects are treated in an unrealistic, frequency independent way. In a series of papers from the group in Lund we have investigated the properties of the simplest but fully frequency dependent approximation beyond the so called ALDA (the adiabatic local-density approximation). The approximation is obtained by using the Hartree-Fock approximation to the electronic self-energy in a variety of methods like starting from the so called linearized Sham-Schlüter equation or using the full variational approach to many-body perturbation theory. The resulting approximation is here referred to as the exact exchange approximation (EXXA). The variational approach for deriving the EXXA paves the way for approximations involving very sophisticated correlation effects but some of the inherent limitations of this approach will also be emphasized.

We have found that the EXXA rather accurately reproduces the results of the TDHF approximation for static properties, small excitation energies and spectra close to the absorption edge - but at a considerably lower computational cost.

Unfortunately, the spectra predicted by the EXXA become senseless at higher excitation energies due to the existence of poles in the upper half plane of the resulting optical response function. We have traced this failure of the EXXA to zero eigenvalues of the non-interacting Kohn-Sham density response function combined with the use of the so called Klein functional in the derivation of the EXXA.

We discuss possible ways out of this dilemma and we also present a related approach which has proven capable of producing very accurate exchange-correlation potentials which form a necessary ingredient for the calculation of the density response function within TDDFT.

