Molecular properties from density matrix response

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Although DFT has been very successful, it also meets with important problems. The dissociation of electron pair bonds, and their weakening towards transition states, are problematic cases for (approximate) DFT. In the calculation of response properties with TDDFT, there are grave errors when one tries to construct excited state potential energy surfaces: upon stretching of bonds the excitation energy becomes totally wrong [1], the TDDFT method fails to describe doubly excited character [2,3], and it fails for charge transfer transitions.

All these problems stem from the difficulty that functionals working with the local density and its derivatives have in recognizing the correlation of electrons along a lengthening bond. A remedy can be found in one particle reduced density matrix (1RDM) functional (or natural orbital (NO) functional) theory.

We will first briefly discuss why NO functionals can and do lead to much better representation of ground state energy curves than DFT in either LDA or GGA variants.

Next we will demonstrate that that are significant advantages in using the response of the 1RDM rather than that of the electron density. The latter response is used in TDDFT, the former leads to TDDMFT [4]. We will show that in principle all the problems of TDDFT highlighted above can be solved in TDDMFT [5,6].

References:

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