From Density Functional Theory to Density Matrix Functional Theory

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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], and 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 [3]. The exact position of the other nucleus, and the onset of strong correlation effects, are however manifest in orbital information: the shape and energy for occupied and virtual Kohn-Sham orbitals, and the occupation numbers for the natural orbitals. We will discuss how orbital dependent functionals can be used to describe the strong correlation in the indicated cases, both in the DFT context (with virtual orbital dependent functionals [4]) and in density matrix functional theory [5,6,7].

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