

Excitation energies with time-dependent density *matrix* functional theory

Evert Jan Baerends, Klaas J. H. Giesbertz, Oleg V. Gritsenko, Katarzyna Pernal
*Section Theoretical Chemistry, Faculty of Exact Sciences,
Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam,
The Netherlands*

Time-dependent density functional theory in its current adiabatic implementations exhibits three striking failures: a) totally wrong behavior of the excited state surface along a bond-breaking coordinate;¹ b) lack of doubly excited configurations, affecting again excited state surfaces; c) much too low charge transfer excitation energies. We address these problems with time-dependent density *matrix* theory (TDDMFT).^{2,3} First, a brief introduction into density matrix functional theory will be given, reviewing the current state-of-the-art of functional development in an application to E vs R curves for bond dissociation of A-H bonds of the first row 10-electron hydrides.⁴ For two-electron systems the exact exchange-correlation functional is known in DMFT, hence exact response equations can be formulated. This affords a study of the performance of TDDMFT in the TDDFT failure cases mentioned (which are all strikingly exhibited by prototype two-electron systems such as dissociating H_2 and HeH^+). At the same time, adiabatic approximations, which will eventually be necessary, can be tested without being obscured by approximations in the functional. We find:^{5,6} a) In the fully non-adiabatic (ω -dependent, exact) formulation of linear response TDDMFT, it can be shown that LR-TDDMFT is able to provide exact excitation energies; in particular the first order (linear response) formulation does not prohibit the correct representation of doubly excited states; b) Within previously formulated simple adiabatic approximations³ the bonding-to-antibonding excited state surface as well as charge transfer excitations are described without problems, but not the double excitations; c) An adiabatic approximation is formulated in which also the double excitations are fully accounted for.

1. K. J. H. Giesbertz, E. J. Baerends, Chem. Phys. Lett. **461** (2008) 338
2. K. Pernal, O. V. Gritsenko, E. J. Baerends, Phys. Rev. A **75**, 012506 (2007)
3. K. Pernal, K. J. H. Giesbertz, O. Gritsenko, E. J. Baerends, J. Chem. Phys. **127**, 21401 (2007)
4. D. Rohr, K. Pernal, O. Gritsenko, E. J. Baerends, J. Chem. Phys. **129** (2008) 164105
5. K. J. H. Giesbertz, E. J. Baerends, O. V. Gritsenko, Phys. Rev. Lett. **101** (2008) 033004
6. K. J. H. Giesbertz, K. Pernal, O. V. Gritsenko, E. J. Baerends, J. Chem. Phys. **130** (2009) 114104