

***A TDDFT perspective on nonlinear electronic processes: optics,  
photoemission and resonant tunneling***

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In this talk we will review the recent advances within density-functional based schemes to describe spectroscopic properties of complex systems with special emphasis to modelling new time and spatially resolved electron spectroscopies (including transient pump-probe techniques). Pros and cons of present functionals will be highlighted and provide insight in how

to overcome those limitations by merging concepts from many-body perturbation theory and time-dependent density functional theory. We show that the exact exchange-correlation potential of time-dependent density-functional theory displays dynamical step structures that have a spatially non-local and time non-local dependence on the density [1,2]. Using onedimensional

two-electron model systems, we illustrate these steps for a range of nonequilibrium dynamical situations relevant for modeling of photo-chemical/physical processes:

field-free evolution of a non-stationary state, resonant local excitation, resonant complete charge-transfer, and evolution under an arbitrary field. Lack of these steps in usual

approximations yield inaccurate dynamics, for example predicting faster dynamics and

incomplete charge transfer. Furthermore, as an electron transfers between closed-shell

molecular fragments at large separation, the exact correlation potential of time-dependent density functional theory gradually develops a step and peak structure in the bonding region.

This structure has a density-dependence that is non-local both in space and time, and even the exact ground-state exchange-correlation functional fails to capture it. In the complementary case of charge-transfer between open-shell fragments, an initial step and peak vanish as the charge-transfer state is reached. As illustration of the techniques we will focus on the efficient conversion of light into electricity ("artificial photosynthesis") . We will illustrate it by means of

extensive simulations of the dynamics of a photoexcited supramolecular carotene-porphyrinfullerene

triad, which is a prototypical artificial reaction center, by means of high time-resolution femtosecond spectroscopy and first-principles quantum-dynamical simulations [3]. We look at the primary charge transfer process in this supramolecular triad and provide compelling evidence that the driving mechanism of the photoinduced current generation cycle is a correlated wavelike motion of electrons and nuclei on the timescale of few tens of femtoseconds. We highlight the fundamental role of the interface between chromophore and charge acceptor in triggering the coherent wavelike electron-hole splitting.

*[1] Fundamentals of Time-Resolved Charge-Transfer in Time-Dependent Density Functional Theory*

*Johanna I. Fuks, Peter Elliott, Angel Rubio, Neepa T. Maitra*

*Journal Of Physical Chemistry Letters 4, 735 - 739 (2013)*

*[2] Universal Dynamical Steps in the Exact Time-Dependent Exchange-Correlation Potential*

*Peter Elliott, Johanna I. Fuks, Angel Rubio, Neepa T. Maitra*

*Physical Review Letters 109, 266404 (2012)*

*[3] Quantum coherence controls the charge separation in a prototypical artificial light harvesting system*

*C. A. Rozzi, S. M. Falke, N. Spallanzani, A. Rubio, E. Molinari, D. Brida, M. Maiuri, G. Cerullo, H.*

*Schramm, J. Christoffers, C. Lienau*

*Nature Communications 4, 1602 (2013)*