# Nonlinear Optics from real-time TDDFT

## First-Principles Description of Nonlinear Optical Properties of Light-Absorbing Materials

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## In Short

- Ab initio study of nonlinear optical properties of light-absorbing materials by real-time timedependent density-functional theory: Focus on hybrid inorganic/organic interfaces
- Sub-ps charge-transfer dynamics at hybrid interfaces excited by laser pulses
- Assessment of the role of electron-vibrational coupling in driving the dynamics excitation processes

Among the materials for the next generation of optoelectronic devices, inorganic-organic interfaces are of particular importance. Combining inorganic semiconductors, conjugated organic molecules, and metal nanostructures into hybrid materials will lead to novel features that can potentially give rise to a new class of devices. To achieve this goal in its entire complexity, a thorough characterization of the intrinsic electronic and optical properties of these systems is essential. First-principles theory represents the most effective formalism in this context. Densityfunctional theory (DFT) and its time-dependent extension (TDDFT) are among the most popular and powerful approaches for these purposes.

We have been applying these methods to investigate the nonlinear optical (NLO) properties of macrocyclic carbon-conjugated molecules such as the freebase phthalocyanine ( $H_2$ -Pc), the porphine, and the  $C_{60}$  fullerene. We have focused on the description of optical limiting, a third-order optical nonlinearity consisting in the attenuation of the light transmitted through the material upon increasing intensity of the incident beam. We have provided the first ab initio description of this phenomenon adopting on a nonperturbative approach based on real-time TDDFT (RT-TDDFT). The good agreement with experimental results for the prototypical case of H<sub>2</sub>-Pc demonstrates the success of the proposed scheme 1. More recently, we have further improved the description of optical limiting by including the contributions from triplet excitation channels. To this end, we have derived an analytic expression for the corresponding absorption coefficient in the nonlinear regime, which we have subsequently used to post-process the results from RT-TDDFT calculations. A publication reporting these results is currently in preparation 2.

We have applied RT-TDDFT to investigate transient absorption spectroscopy (TAS) in carbonconjugated molecules such as ethylene, benzene and thiophene. In Fig. 1 the results of the simulations performed on ethylene are shown. The frequency of the laser pulse is set in resonance with the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied one (LUMO), which in case of the ethylene molecule is at 7.8 eV. The duration of the pulse is set to 17 fs and the TAS is computed by probing the systems every 2 fs, starting from t = 0 fs when the laser pulse is initially turned on. In all the spectra shown in Fig. 1 a pre-peak appears around 2 eV short after the turning on of the laser. The value of this time delay depends on the laser intensity: the weaker the external perturbation, the longer the appearance of the pre-peak is delayed. This emerging maximum, which is associated to excited-state absorption (see also 3), persists almost steadily during the whole duration of the simulation, also after the laser is turned off. The dynamics of the pumped peak at about 7.8 eV is also strongly influenced by the laser intensity. When the most intense pulse is applied, alternating maxima and minima recall the dynamics associated to Rabi oscillations. The analysis of these results is the subject of a publication in preparation 4.

With the knowledge acquired so far, in the continuation of the project we will investigate the ultrafast charge-carrier dynamics of a hybrid interface formed by the 2,3,5,6-tetrafluoro-7,7,8,8tetracyanoquinodimethane (F4TCNQ) molecule phvsisorbed on a hydrogenated Si(111) surface 5. The peculiarity of this material is the large amount of charge transfer: The strong electron acceptor F4TCNQ adsorbed on the H-Si(111) surface acts as an effective *p*-dopant such that the resulting hybrid interface has partially occupied states in the gap region (see Fig. 2a). Starting from the structures proposed in Ref. 5, we have characterized the electronic structure and the (linear) optical absorption of this system using RT-TDDFT. The absorption spectrum of the hybrid interface is characterized by two peaks in the visible region which do not appear in the spectrum of the bare Si surface, plotted for comparison. This characteristic suggests the hybrid nature of these features, labeled HE1 and HE2 in Fig. 2b. Both peaks are due to transitions between occupied surface states and the partially unoccupied hybrid LUMO (Fig. 2c). As next step, we will study the TAS and the charge-carrier dynamics at the F4TCNQ:H-Si(111) interface upon the excitation



Figure 1: Transient absorption spectra of ethylene (right panel) adopting three increasing pulse intensities. The shape of the adopted laser pulse is depicted on top of each heat map. Its frequency is set in resonance with the transition from the highest occupied to the lowest unoccupied state at 7.8 eV.



**Figure 2:** a) a) Density of states (DOS) of the hybrid interface F4TCNQ:H-Si(111): Atom-resolved contributions are indicated by solid and dotted colored lines while the total DOS is represented by the gray shaded area. The vertical line indicates the Fermi energy. b) Optical absorption spectrum computed from RT-TDDFT using a weak kick: the result obtained for the hybrid interface is compared to the one computed for the isolated Si surface. b) Dominant orbital contributions to the excitation HE1, which corresponds to a transition between an occupied hybrid orbital and the partially unoccupied LUMO (blue arrows in the PDOS).

with a laser pulse in resonance with the frequency of HE1 and HE2 at 2.2 and 2.9 eV, respectively. With this study we will determine how the intensity of the applied laser pulse impacts the amount of charge transfer and its dynamics at the interface. Moreover, we will assess the role of electron-vibrational coupling in driving the excitation process and the charge-transfer dynamics. The ultimate goal of this analysis is to shed light on the physical mechanisms that drive the charge transfer in these materials in the sub-ps time window.

Calculations will be carried out with OCTOPUS 6, an open-source code that offers an efficient parallel implementation of RT-TDDFT for supercomputing architectures. This package also includes the Ehrenfest scheme for coupled electron-nuclear dynamics, which is adopted to investigate the effects of electron-vibrational coupling in the ultrafast charge transfer.

#### WWW

https://www.physik.hu-berlin.de/en/eos

## **More Information**

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#### **Project Partners**

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