

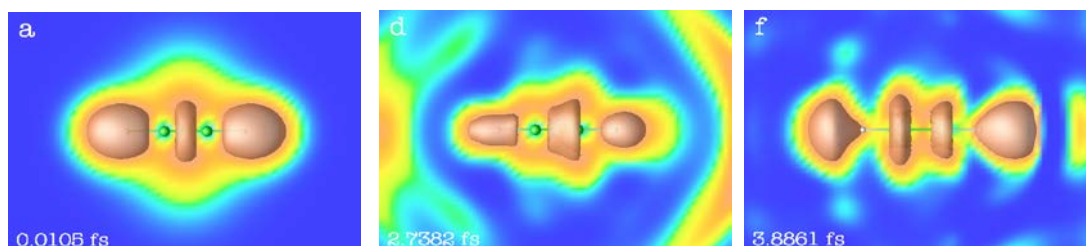


## ANALYSIS AND CONTROL OF ELECTRON DYNAMICS

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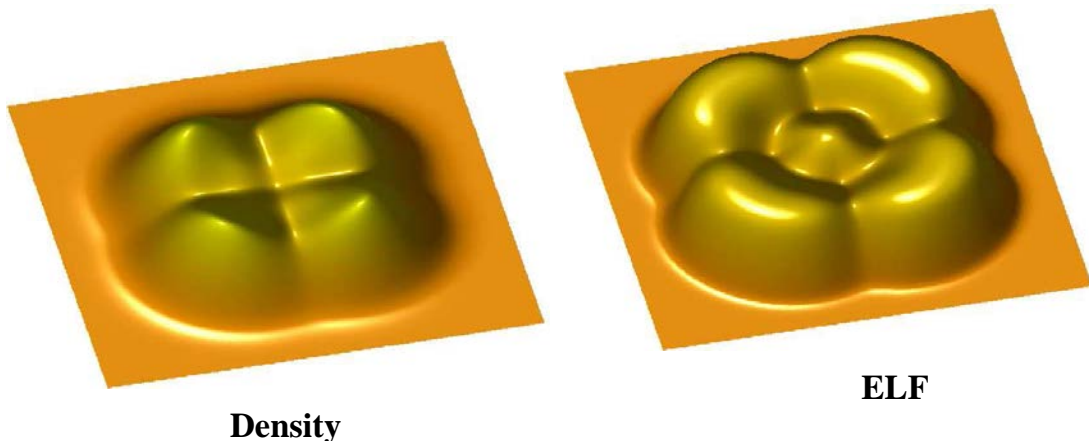
In the mid eighties, Runge and Gross developed the mathematical foundation of time-dependent density functional theory [1]. Traditional density functional theory exclusively deals with ground-state properties of atoms, molecules and solids. Our time-dependent generalization allows the ab-initio calculation of excited-state properties and thereby makes a whole new arena of phenomena accessible to a first-principles treatment. In the nineties, simultaneously with Marc Casida, we devised an explicit scheme of calculating molecular excitation energies [2,3,4] and oscillator strengths which, by now, has become a standard technique in quantum chemistry. Hundreds of groups worldwide use this method to calculate molecular excitation spectra.

Time-dependent density functional theory (TDDFT), however, is not restricted to weak probes of molecules or solids (which yield the excitation spectra). Non-linear optical properties as well as interactions of strong laser pulses with matter can be treated as well. In the past years, we have successfully described strong-field phenomena, such as the generation of high harmonics. We have developed a theoretical tool, the so-called **time-dependent electron localization function (TDELf)**, which allows the time-resolved observation of the laser-induced formation or breaking of chemical bonds, thus providing a visual understanding of the dynamics of excited electrons [5, 6,7]. Questions like: "How, and how fast, does an electron travel from one state to another?" have been successfully answered with this approach. As an example, the figure below shows snapshots of a laser-induced  $\pi$ - $\pi^*$  transition in acetylene.



The torus-like structure between the carbon atoms in the first picture shows the triple bond, while the two tori in the last picture clearly represent an antibonding state. It is clear from the plots that the transition is completed after about 3.9 fs. Information of this type may soon become experimentally available with atto-second pump-probe spectroscopy.

We also have applied the concept of the ELF to 2D systems. The figure below on the right-hand side shows the ELF of a 12-electron quantum dot with four minima.



One can clearly identify a region of enhanced electron localization in the center, i.e., a feature similar to a chemical bond. Like for chemical bonds, the localization is visible only in the ELF, not in the plot of the density on lefthand side.

Most recently our work on time-dependent effects has focused on the study of **time-dependent transport phenomena**. Using our TDDFT approach to quantum transport [8], we calculate the electronic current through a single molecule attached to (semi-infinite) metallic leads. We have studied a variety of time-dependent effects (see also the section on quantum transport), such as electron pumping [9]. An electron pump is a device which, without any static bias, generates a (macroscopic) net current upon application of a time-dependent field. An example is given in the figure below which shows (a) a schematic picture of the experiment and (b) the corresponding AFM picture of a carbon nanotube on a piezo-electric surface. When a sound wave is generated on the surface, a running electric wave along the nanotube is produced by the piezo-electric effect. This leads to a measurable net current through the nanotube.

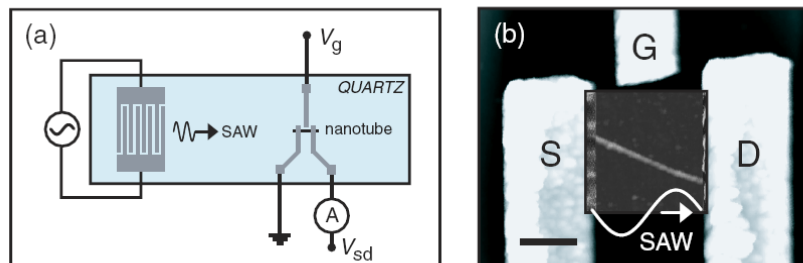
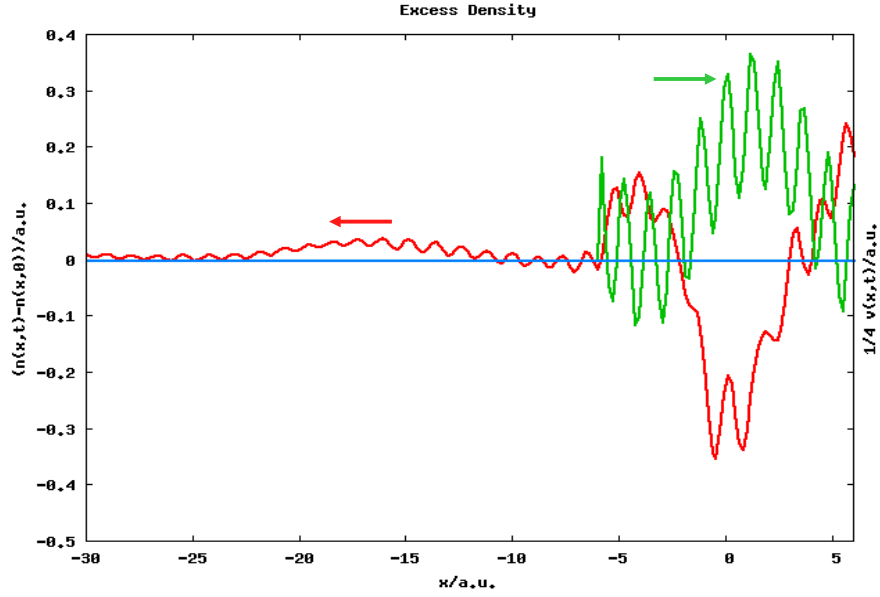
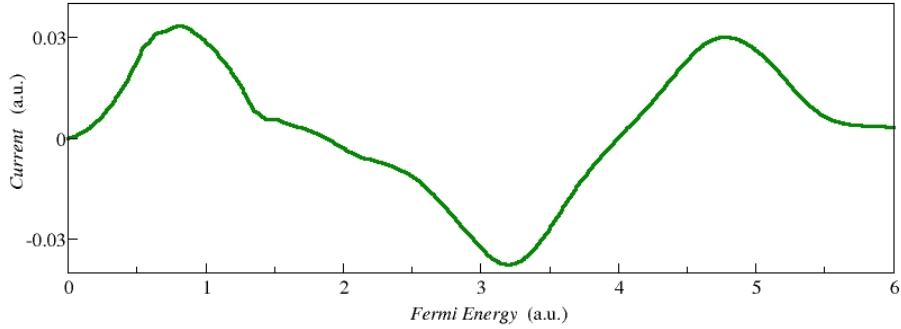


Figure from: P.J. Leek, M.R. Buitelaar, V.I. Talyanskii, C.G. Smith, D. Anderson, G.A.C. Jones, J. Wei and D.H. Cobden, Phys. Rev. Lett. **95**, 256802 (2005)

A very interesting aspect, which can be explained by our ab-initio theory of quantum transport, is the fact that the current can have a direction opposite to the running wave. The figure below shows a snapshot of the excess density (in red), i.e. the time-dependent density minus the initial density, as it moves into the left lead whereas the time-dependent electric wave superimposed to the lattice potential of the carbon nano-tube (in green) moves to the right.

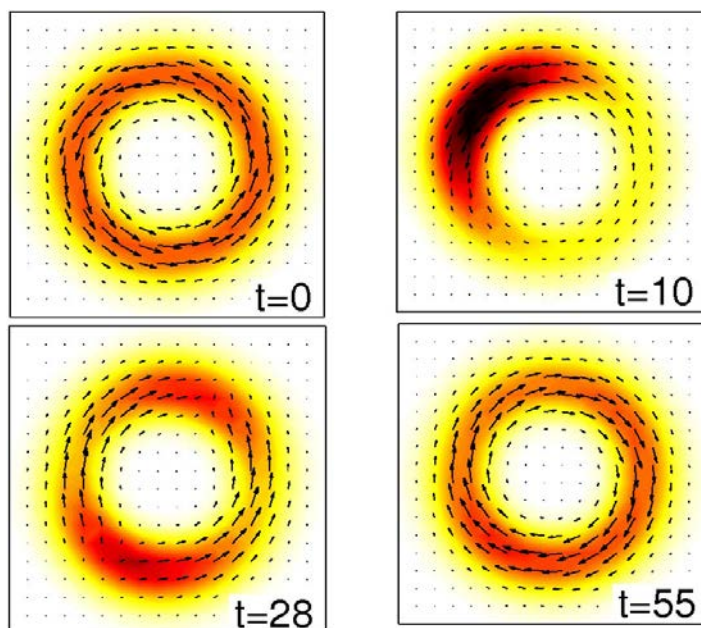


Depending on the frequency of the electric wave and on the Fermi energy of the leads, the current may go to the left (negative current) or to the right (positive current). The figure below shows the calculated time-averaged current [9] as a function of the Fermi energy (corresponding to different values of the gate voltage in the experiment).



The above calculation is a simple example of controlling the electronic dynamics with external parameters, i.e. the direction of the current is controlled by the value of the applied gate voltage.

This type of control can be taken to a much more sophisticated level by combining TDDFT with **quantum optimal-control theory** [10,11]. Here the goal is not to predict and/or analyze time-dependent processes resulting from a given driving field, but rather to determine the "best" laser pulse to achieve a given control target. Questions like: "Starting from a given initial state, by which laser pulse can one achieve maximal population of a given final state at the end of the pulse?" can be addressed in this way. The snapshots below show how the chirality of the current in a 2D quantum ring of 44 nm diameter can be switched by a suitably shaped laser pulse, calculated with our optimal control algorithm [12]. Arrows represent the current density, the color indicates the magnitude of the density, and the time scale is in effective atomic units. Interestingly, after about half of the pulse length ( $t=28$  a.u.), one finds the current density going in opposite directions on opposite sides of the ring, leading to a zero net current.



Using an analogous algorithm, we also have controlled the electron localization in a double quantum dot [13]. In a generalization of the control algorithms to quantum-classical systems we recently succeeded to selectively break molecular bonds by ultrashort laser pulses [14], formulating the control target in terms of classical nuclear degrees of freedom.

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