Quantum Transport

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The ultimate goal of molecular electronics is the design of electronic devices where the basic units, such as transistors, are single molecules. On the theoretical side, the generic task is to calculate the current-voltage (IV) characteristics of systems consisting of a single molecule sandwiched between two semi-infinite metallic leads.

In our group we follow two different approaches to describe the transport properties of single molecules. On one hand we consider the so-called "standard approach" which can deal with molecular junctions once a steady-state current is achieved. On the other hand, to be able to study the transient behavior after switching, AC bias, as well as electron pumps, we have developed a novel methodology that allows the study of time-dependent effects in the transport properties of molecular devices.

Steady-state approach to molecular optical switches

To study steady-state transport, a combination of density functional theory (DFT) with Green's function techniques has been developed and widely used by several groups [1] and can now be considered the standard ab-initio technique to calculate the current-voltage (IV) characteristics of single molecules sandwiched between two "semi-infinite" metallic leads.

The basic idea is to divide the system in 3 different regions. The left and right semi-infinite leads are represented in terms of the corresponding Kohn-Sham Green's functions, G_L and G_R. The central part of the system is described by a Kohn-Sham equation where, in addition to the ordinary Kohn-Sham potential, the coupling to the leads is incorporated by the non-Hermitian self-energy operators

$$\Sigma_L = H_{CL}\, G_L\, H_{LC}\ , \quad \Sigma_R = H_{CR}\, G_R\, H_{RC}, \tag{1}$$

where H_{CL}, H_{LC}, H_{CR}, H_{RC} are the blocks of the Kohn-Sham-Hamiltonian matrix connecting the central region with the left/right leads.

Using this method the Transmission Function of the whole system can be calculated as

$$T\,(E) = trace(\Gamma_L\, G\,(E)\ \Gamma_R\, G(E)^{\dagger}) \tag{2}$$

where $\Gamma_{L/R} = i\left(\Sigma_{L/R} - \Sigma^{\dagger}_{L/R}\right)$ are the non-Hermitian parts of the self-energies and G is the Green function of the complete (Kohn-Sham) system. Once the transmission function is known, the IV characteristics follows from the Landauer formula:

$$I(V) = \frac{2e}{h}\int \mathrm{d}E\, T\,(E,V)[f(E,\mu_+) - f(E,\mu_-)\ ] \tag{3}$$

Using this methodology we have recently studied the electronic and transport properties of Chrysazine type molecules [2]. According to our calculations the isolated Chrysazine presents 3 geometrical isomers related to the orientation of the hydrogen atom at the H-O-phenyl lateral rings of the molecule (structures on the left panel in Fig. 2). From the Transmission Function of the extended molecule (Fig. 1) and their corresponding IV characteristics (Fig. 2 middle and right panel), it was shown that this system can be used as a molecular optical switch. In other words, comparing the current shown in the middle and right panels of Fig. 2 (corresponding to an asymmetric or symmetric connection to the leads of the Chrysazine molecule) we observe that there is a difference in the transport properties of this system, which is correlated to the differences in the molecular orbitals and transmission function shown in Fig. 1. The different geometrical isomers show as well a different electron-transport behavior upon applying a voltage to the system.

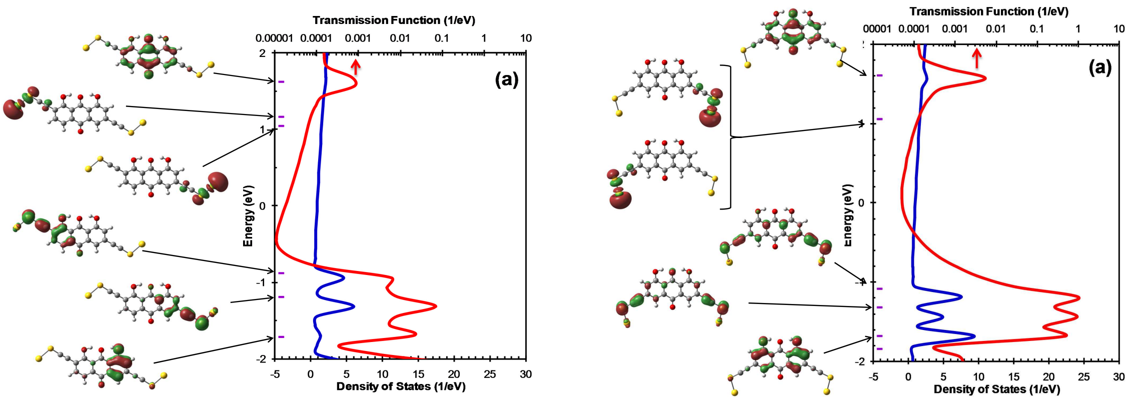

FIG. 1: Transmission function (red) and density of states (blue) together with the corresponding frontier molecular orbitals for the isomer (a) of the asymmetric (left) and symmetric (right) structures. (Structures on the upper part of the left panel of Fig. 2)

The analysis of the orbital distribution of the different isomers confirms that the transport occurs through a bias window rather than through a single channel (see orbitals in Fig. 1). In addition, the IV characteristics of the symmetrically connected Chrysazine (structures on the right of left panel in Fig. 2) shows that within a bias voltage range from 3.5 to 4.2 V, the IV of structures (b) and (c) are similar while the current through structure (a) in the same bias window is twice as large (see right panel in Fig. 2). This suggest that if the device is operated within this bias window one could produce an optical rotation of the hydrogen to isomerize the molecule, for example, from structure (a) to (b), according to the results shown in Fig. 2 this optical rotation will produce a jump in the current, which indicates the possibility of using the Chrysazine-type molecules as optical switches.

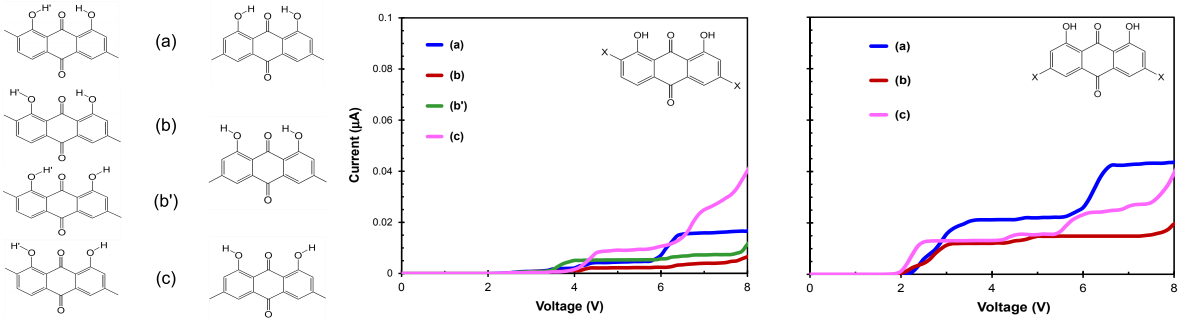

FIG. 2: Left panel: Structures corresponding to the asymmetric (left) and symmetric (right) connection of the Chrysazine molecule to the metallic leads. Middle and right panels: CurrentVoltage characteristics for the extended structures (a), (b), (b′) and (c) for the asymmetric (middle) and symmetric (right) connection

Time-dependent phenomena in quantum transport

The second approach pursued in our group focuses on time-dependent phenomena. The Landauer-plus-DFT approach, by construction, inherits the main assumption of the Landauer formalism that for a system driven out of equilibrium by a dc bias, a steady current will eventually be achieved. In other words, the dynamical formation of a steady state does not follow from the formalism but rather constitutes an assumption.

We find several situations in which the steady state assumption is not valid. The first example is a correlated single-level quantum dot (QD) weakly coupled to the leads, i.e. a typical case where one would expect to observe the Coulomb blockade(CB) phenomenon [3]. In essence, CB is due to an electrostatic barrier induced by the electrons in the device which prevents further electrons from tunneling in, unless the bias is sufficiently increased to supply the necessary charging energy of the device. To describe CB in nanoscale transport it is particularly important to ensure the charge quantization of the device. To guarantee this in a DFT calculation, the exchange-correlation (XC) potential must exhibit the so-called “derivative discontinuity”, i.e., the XC potential jumps by a constant when the number of electrons on the QD passes through an integer. We use a novel XC functional featuring the proper derivative discontinuity and find that the assumption that the system evolves towards a steady state is not generally justified. Instead, the discontinuity of the potential leads to self-sustained oscillations induced by electron correlations, with history dependent frequency and amplitude.

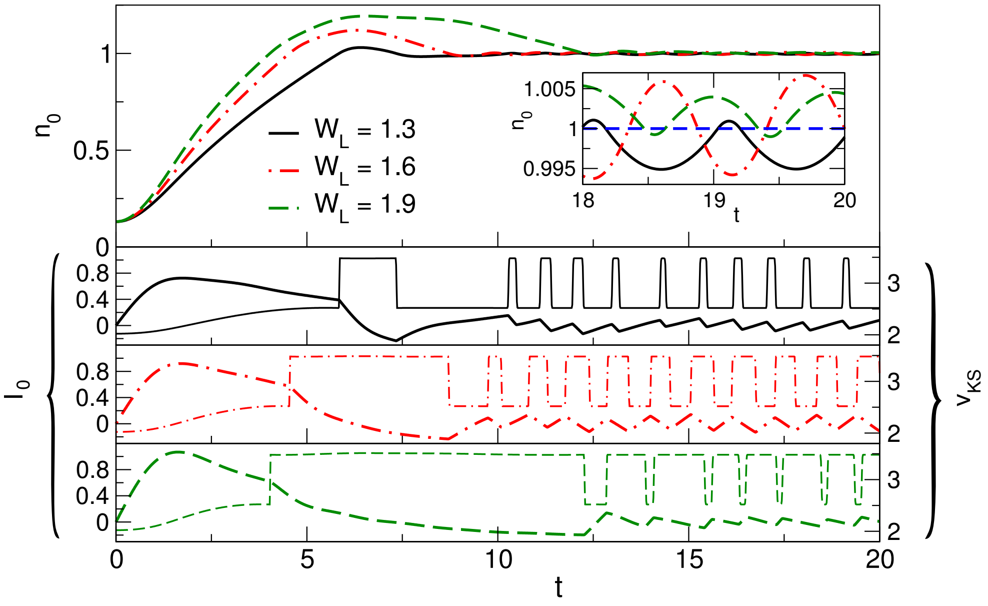

FIG. 3: Time evolution of the density, current and KS potential for three different biases. In all panels, solid, chain and dashed line refer to $W_L = 1.3$, 1.6, 1.9, respectively. Top panel: densities at the QD. The inset shows the density at the end of the propagation period. Middle three panels: current through the QD (thick lines) and KS potential (thin lines). Bottom panel: current five sites away from the QD.

By following the time-dependent density on the QD (the upper-most panel of Fig. 3), one sees upon applying the bias, the charge density is constantly accumulating on the dot until it reaches an integer value (n=1), at which the Kohn-Sham potential jumps up. This prevents more electrons from tunneling in and causes some of the charge to flow back into the leads. As the charge density of the dot decreases, it hits the integer value again, therefore the potential jumps back down, and the process repeats. The oscillations are also present in the current (middle three panels of Fig. 3), but this time with a much larger amplitude relative to its average value. Note that away from the QD, the oscillations in the current (and in the density) die out (bottom panel). Oscillations are clearly visible also in the Kohn-Sham potential (middle three panels). Due to the fairly large jump in the XC potential and the small amplitude of the oscillations of the density at the dot, the KS potential is a train of almost rectangular pulses.

The dynamical picture of CB, manifesting itself as a periodic sequence of charging and discharging of the QD, is a direct consequence of electronic correlations, so one might think that for strictly non-interacting electrons the steady-state assumption is always valid. However, it can be shown analytically that after switching on a dc bias, the current first shows some transient oscillations and then converges to the steady state value predicted by the Landauer formula only if the Hamiltonian of the junction has a smooth density of states. On the other hand, if the long time limit of the Hamiltonian supports at least two bound states, the system does not evolve to a steady state, and instead, persistent, non-decaying, localized current oscillations are observed which can be much larger than the steady part of the current [4].

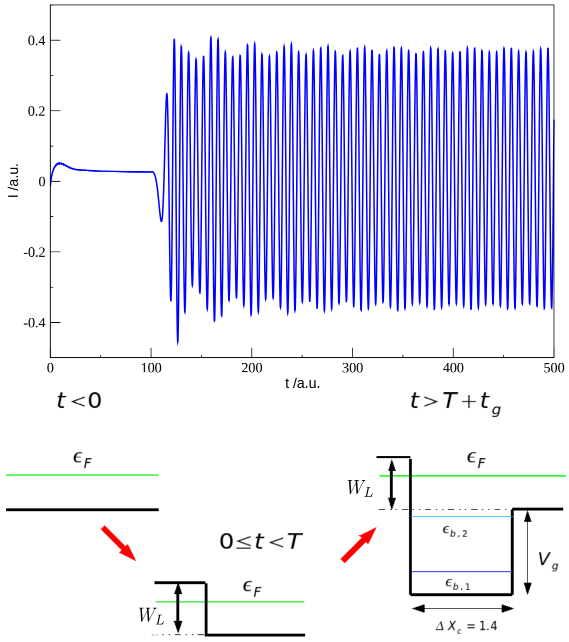

FIG. 4: Upper pannel: Time evolution of the current at $x = 0(W_L = 0.15)$. At $T = 100$ a.u., a gate potential is turned on ($V_g = 1.3$ a.u. and $t_g = 20$ a.u.) which creates two bound states, resulting in large oscillations of the current. Lower panel: schematic representation of the system and its time evolution.

In the upper panel of Fig. 4 the TD current in the center of the device region is plotted (the system and its time evolution is shown schematically in the lower panel of Fig. 4) . The development of a steady-state current for $T < 100$ a.u. can clearly be recognized. After the bound states are created ($t > T + t_g$) the current starts to oscillate as expected.

The amplitude of the current oscillation is of the order of 0.35 a.u., i.e., *more than an order magnitude larger than the initial steady-state current*. The amplitude of these oscillations depends on the entire history of the applied potential and the initial state. The oscillation frequencies are given by the eigenenergy differences of the bound states.

Clearly, in the real world, phonon scattering will lead to damping of the oscillations described above. However, phonon scattering occurs on the time scale of pico-seconds while the electronic oscillations have oscillation periods of femto-seconds or less. Hence, if the ultimate goal of molecular electronics is to achieve switching times on the electronic time scale, the oscillations predicted here will be very relevant.

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