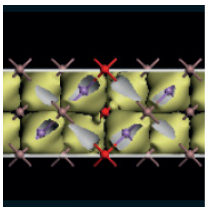

Time-resolved carrier transfer at molecular junction interface

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Recent theoretical and experimental advances in elec- tronic transport through molecular wires and junctions have generated interest for handling time-dependent regimes [1]. Molecular electronic devices are indeed a promising alternative to standard electronic switches due to their fast response on the pico-second time scale. Recently, wave function (WF) approach emerges as an alternative to Green's function formalism for the dynam- ical simulation of systems far from equilibrium without additional computational effort, at least within mean- field approximations [3]. In this work, the approach is used for the study of a molecular junction subjected to ultra-short excitation pulses. Numerical analysis enables us to correlate the time-dependent photocurrent to the underlying intramolecular dynamics.

Wave function approach is a technique based on the Keldysh formalism, in which one constructs wave functions instead of Green's functions. We use a tight-binding Hamiltonian $(t) = \Sigma_{i,j} H_{i,j}(t) c_i^{\dagger} C_j$. The model describes a two level donor-acceptor molecular junction (D-A) in contact with two leads as represented Fig. 1. We assume that the system is unperturbed in its far past ($t < 0$). So that the problem is separated into a stationary part and a field-induced deviation throughout the hamiltonian and wave function partitions. Further detail could be found in [3].

In the case of a single ultrafast femtosecond pulse (1P), analysis of the dynamics of the intramolecular orbital populations (not shown) reveals that the pulse induces a HOMO-LUMO transition at the donor, followed by intramolecular tunneling oscillations between the donor and acceptor LUMO states. The electron decay is oscillating between the two leads, resulting in a left- to-right transient photocurrent within the relaxation time.

We show that an interplay between the pulse intensity and the molecular-metal coupling results in rearrangements of non-equilibrium molecular population between high- and low-conducting channels. This may lead to either enhancement or suppression of the 1P-photocurrent (see Fig.2,3). We notice from our investigation that the system shows up two characteristic frequencies: the field-induced frequency and an internal frequency which corresponds to the tunneling oscillation between the D- A LUMO states. In the weak *tunnel coupling regime*

$(\Gamma \ll A_1)$, carrier life time $\tau_v \sim h/\Gamma$ is long enough, so that even after the pulse is turned off, current is still flowing through the junction. The oscillation frequency of the photocurrent reveals internal tunnelling oscillations between the D-A LUMO states (Fig. 2) [4]. In contrast, in the *strong tunnel coupling regime* $(\Gamma \gg A1)$, carriers have a short life time so that almost no current flows after the pulse off. During the pulse, the photocurrent follows the field amplitude with on top field-induced oscillations, as shown Fig. 3.

In the case of *two pulses* (2P), the second pulse occurs while the system has not reached a stationary configuration. Two limit cases are intuitive. For a delay between the two pulses $\tau \ll \delta$ (δ pulse width), the 2P-photocurrent signal is the same as the 1P-photocurrent generated by a single pulse of amplitude $A_1 + A_2$ (see Fig. 4). In contrast, when $\tau \gg \delta, \tau_v$ (relaxation time), the 2P-photocurrent is the result of the two independent 1P-responses.

In between, as the case shown Fig. 5, we investigate the direct photocurrent (integrated current) as a function of delay τ, which confirms and generalizes the previous analysis (Fig.6).

Thanks to the accuracy of ultrafast spectroscopy with photocurrent detection scheme, this work open avenues toward the possibility of controlling or analyzing the internal quantum properties of nanodevices with pump- probe photocurrent spectroscopy [2].

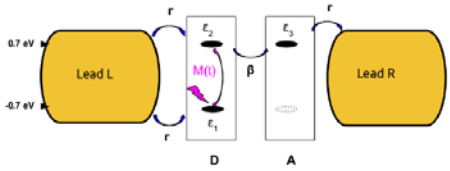

Fig. 1. Donor-acceptor (D-A) molecular junction. $M(t)$ est $A_1 \cos(\omega_0 t)\exp(-t^2/2\delta^2)+A_2\cos(\omega_0(t-\tau))\exp(-(t-\tau)^2/2\delta^2)$. $A_{1,2}$, δ and τ are respectively the pulse amplitude, width and delay.

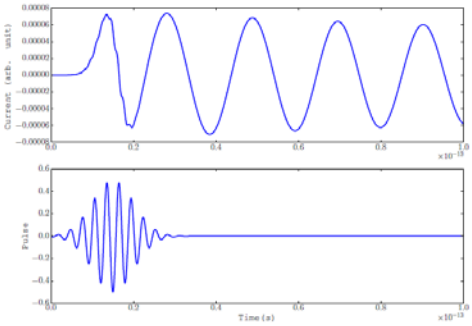

Fig. 2. Weak tunnel coupling $A_1 = 0.5 > \Gamma = 0.02, \beta = 0.1$. D-A photocurrent for single pulse, shows long relaxation time.

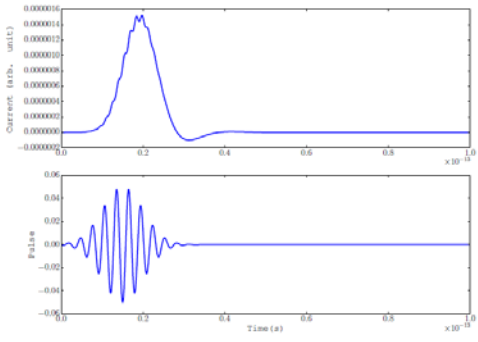

Fig. 3. Strong tunnel coupling $A_1 = 0.05 < \Gamma = \beta = 0.1$. D-A photocurrent for single pulse.

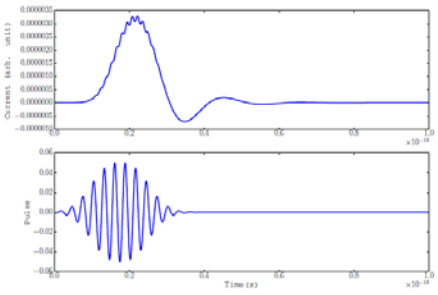

Fig. 4. D-A photourrent for double pulse shows a single pulse response. $A_1 = A_2 = 0.05 < \Gamma = 0.06, \beta = 0.1, \tau = 5fs$.

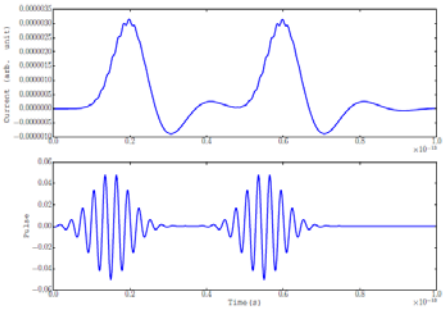

Fig. 5. D-A photocurrent for double pulse shows two independent single pulse response. $A_1 = A_2 = 0.05 < \Gamma = 0.06, \beta = 0.1, \tau = 40fs$.

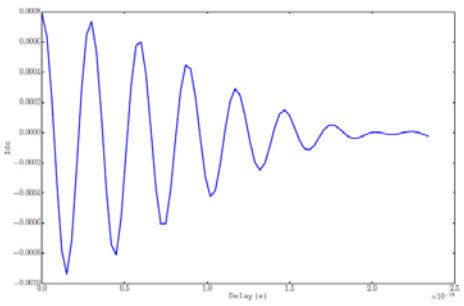

Fig. 6. I_{dc} the difference in the direct 2P-photocurrent and 2 times the direct 1P-photocurrent. $A_1 = A_2 = 0.5 > \Gamma = \beta = 0.1$. I_{dc} tend to zero as $\tau \gg \delta, \tau_v$, transcient component is suppressed.

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