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# Pump-Probe Noise Spectroscopy of Molecular Junctions

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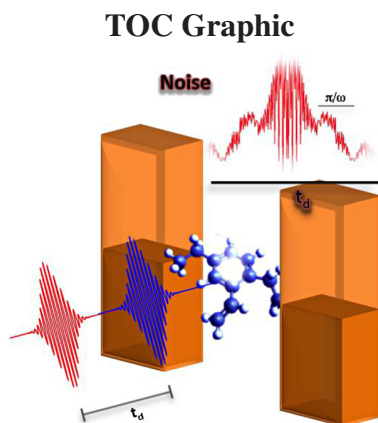
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## Abstract

Slow response of electronic components in junctions limits direct applicability of pump-probe type spectroscopy in assessing the intra-molecular dynamics. Recently the possibility of getting information on sub-pico-second timescale from *dc* current measurements was proposed. We revisit the idea of picosecond resolution by pump-probe spectroscopy from *dc* measurements, and show that any intra-molecular dynamics not directly related to charge transfer in the current direction is missed by current measurements. We propose a pump-probe *dc* shot noise spectroscopy as a suitable alternative. Numerical examples of time-dependent and average responses of junctions are presented for generic models.



Pump-probe spectroscopy data from *dc* shot-noise measurements in molecular junctions.

Development of experimental techniques at nanoscale lead to significant progress in the field of molecular electronics.<sup>1-3</sup> Today experimental research in the field studies charge<sup>4,5</sup> and spin<sup>6-8</sup> fluxes in molecular wires, noise<sup>9,10</sup> and optical<sup>11-13</sup> spectroscopies, spin manipulation<sup>14,15</sup> and tip induced chemistry,<sup>16,17</sup> molecular imaging<sup>18,19</sup> and nanocars,<sup>20,21</sup> heating<sup>22-25</sup> and thermoelectric nanodevices.<sup>26-30</sup> While originally most of experiments were focused on steady-state response of molecular junctions,<sup>31-33</sup> lately time-dependent and transient characteristics started to attract attention.<sup>34-39</sup> Correspondingly, theoretical research followed with development of tools for characterization of time-dependent processes in junctions.<sup>40-49</sup>

Dynamics of a system related to conformational change (switching, thermal fluctuations, telegraph noise, current induced chemistry) happens at timescale of milliseconds,<sup>34,39,50</sup> which easily

can be measured in experiments. Intra-molecular electronic dynamics has characteristic timescales of picoseconds. Two-dimensional optical spectroscopy<sup>51-53</sup> in terahertz regime may be a promising tool for study of the transients, but its application to molecular junctions is hard due to plasmonic excitations in the contacts. At the same time detection of the transients in picosecond range by direct time-resolved transport measurements is not possible since standard ultrafast electronic components are operating in the gigahertz regime and thus for intra-molecular dynamics are too slow. We note that recently fast voltage pulses were realized and an optical read-out technique was utilized to determine time-dependent electronically-generated electrostatic potentials within STM junctions.<sup>54</sup> These measurements enable access to transient processes on the nano-second time scale. However, transients on the sub-picosecond timescale, characterizing electronic and nuclear dynamics in molecules, were not yet reached experimentally.

In Ref. 55 two of us proposed utilizing Laser Pulse Pair Sequencies (LPPS) combined with *dc* current measurements as a reliable source of information on intra-molecular dynamics in the pico-second range. Using a second order time-dependent perturbation theory for the molecule-leads coupling it was shown that *dc* current recorded as a function of the time delay between laser pulses contains information on the intra-molecular dynamics timescale. In particular, it was shown that the dependence of the steady-state current on the delay time reveals the periods of molecular dynamics on the sup-pico-second timescale. The reason for such dependence is the same as in the usual pulse-probe experiments, where the probing pulse provides information on intra-molecular correlations within the coherence time of the system. In junctions coherence affects photocurrent, which results in an interference pattern similar to that observed in steady-state which path measurements in molecular junctions.<sup>56,57</sup> The method was expected to provide a new probe into the complexity of non-equilibrium transport in molecular junctions.

Here we revisit the modeling of Ref. 55. Utilizing the non-equilibrium Green function technique, we show that while information on dynamics related to charge transfer in the direction of the current indeed can be obtained from the measurements proposed in Ref. 55, that scheme misses intra-molecular dynamics due to electron transfer into molecular states not participating in the for-

mation of the current directly. As a suitable alternative we propose measurement of time-averaged noise. Such measurement will provide information on intra-molecular dynamics missed by the *dc* current measurements. The NEGF approach utilized below is preferable to second order perturbation theory when system-bath correlations are important in definition of transport characteristics of a junction. This is the case when molecular resonances are close to Fermi energy of a contact, when degeneracy between eigenstates of the system is present, or in time-dependent noise calculations where the steady-state full counting statistics is not applicable.

The paper is organized as follows. After introducing a model of a molecular junction, we discuss the theoretical method for performing time-dependent simulations of current and noise characteristics. Simple generic models are employed to present numerical results illustrating our findings. Our presentation is finalized with conclusions and future research directions.

We consider a model of a junction with a molecule  $M$  coupled to two contacts  $L$  and  $R$  and driven by an external laser field  $\vec{E}(t)$ . The field is treated classically. The contacts are assumed to be reservoirs of free electrons, in general, each at its own equilibrium. We note that realistic *ab initio* simulation should also include plasmon excitations in the contacts, so that the local field driving the molecule due to the external field, as well as the plasmon and molecular responses (see e.g. Ref. 45 for such consideration). The model we consider here assumes that  $\vec{E}(t)$  is the actual local field experienced by the molecule, regardless of how this particular field was formed. The simplification is commonly used when the molecular response is at the focus of interest (see e.g. Ref.<sup>58</sup>). The Hamiltonian of the model is

$$\hat{H}(t) = \hat{H}_M(t) + \sum_{K=L,R} \left( \hat{H}_K + \hat{V}_K \right) \quad (1)$$

where  $\hat{H}_M(t)$  and  $\hat{H}_K$  ( $K = L, R$ ) are molecular and contacts Hamiltonians, respectively.  $\hat{V}_K$  is the

coupling between the molecule and the contact  $K$ . Explicit expressions are

$$\hat{H}_M(t) = \sum_{m_1, m_2} \left( H_{m_1 m_2}^M - \left( \vec{\mu}_{m_1 m_2} \cdot \vec{E}(t) \right) \right) \hat{d}_{m_1}^\dagger \hat{d}_{m_2} \quad (2)$$

$$\hat{H}_K = \sum_{k \in K} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k \quad (3)$$

$$\hat{V}_K = \sum_{m, k} \left( V_{mk} \hat{d}_m^\dagger \hat{c}_k + H.c. \right) \quad (4)$$

Here  $\hat{d}_m^\dagger$  ( $\hat{d}_m$ ) and  $\hat{c}_k^\dagger$  ( $\hat{c}_k$ ) are creation (annihilation) operators for electron in molecular level  $m$  and state  $k$  of the contacts, respectively.  $H_{m_1 m_2}^M$  and  $\vec{\mu}_{m_1 m_2}$  are matrix elements of the molecular Hamiltonian operator  $\hat{H}^M$  (in the absence of driving) and the molecular dipole moment operator  $\hat{\vec{\mu}}$  in a selected single-electron basis (e.g. molecular or Kohn-Sham orbitals). Note that although here we consider a quadratic Hamiltonian (as commonly used in *ab initio* (TD)DFT simulations), the approach can be extended also to take into account interactions in the molecule explicitly (for example, following Refs.<sup>41,49</sup>). However, the present level of consideration already allows to illustrate the proposed approach.

In treating the model (1)-(4) we follow Refs.<sup>43,45,46</sup> Within the wide band approximation (WBA)<sup>59</sup> one can write equations-of-motion

$$i \frac{\partial}{\partial t} \mathbf{G}^r(t, E) = \mathbf{I} - \left( E \mathbf{I} - \mathbf{H}^M + \vec{\mu} \vec{E}(t) + \frac{i}{2} \Gamma \right) \mathbf{G}^r(t, E) \quad (5)$$

$$-i \frac{\partial}{\partial t'} \mathbf{G}^r(E, t') = \mathbf{I} - \mathbf{G}^r(E, t') \left( E \mathbf{I} - \mathbf{H}^M + \vec{\mu} \vec{E}(t') + \frac{i}{2} \Gamma \right) \quad (6)$$

$$i \frac{d}{dt} \mathbf{G}^<(t, t) = \left[ \mathbf{H}^M - \vec{\mu} \vec{E}(t); \mathbf{G}^<(t, t) \right] - \frac{i}{2} \{ \Gamma; \mathbf{G}^<(t, t) \} \\ + i \sum_{K=L,R} \int \frac{dE}{2\pi} f_K(E) \left( \Gamma^K \mathbf{G}^a(E, t) - \mathbf{G}^r(t, E) \Gamma^K \right) \quad (7)$$

for retarded, Eqs. (5) and (6), and lesser, Eq.(7), projections of the single-particle Green function. Here  $G^r(t, E) \equiv \int dt' e^{iE(t-t')} G^r(t, t')$  and  $G^r(E, t') \equiv \int dt e^{iE(t-t')} G^r(t, t')$  are the right and left Fourier transforms of the retarded Green function  $G^r(t, t')$ , respectively,  $f_K(E)$  is the Fermi distribution in the contact  $K$ , and  $\Gamma = \sum_{K=L,R} \Gamma^K$  is the electron escape rate matrix due to coupling

to the contacts, where  $[\Gamma^K]_{m_1 m_2} \equiv 2\pi \sum_{k \in K} V_{m_1 k} V_{k m_2} \delta(E - \varepsilon_k)$  is energy-independent within the WBA.

For an arbitrary driving  $\vec{E}(t)$  we solve system (5)-(7) utilizing the fourth order Runge-Kutta scheme. The results are used to calculate current,  $I_K(t) \equiv \langle \hat{I}_K(t) \rangle$ , and noise,  $S_{KK}(t_1, t_2) \equiv \frac{1}{2} \langle \{ \hat{I}_K(t_1) \hat{I}_K(t_2) \} \rangle$  at the molecule-contact interface  $K$ , where  $\hat{I}_K(t) \equiv i \sum_{m,k} \left( V_{mk} \hat{d}_m^\dagger(t) \hat{c}_k(t) - V_{km} \hat{c}_k^\dagger(t) \hat{d}_m(t) \right)$  is the current operator.

As discussed in the introduction direct measurement of molecular response at pico-second timescales is not feasible, and only averaged (*dc*) components of current,  $I_K^{dc}$ , and noise,  $S_{KK}^{dc}$ , can be recorded. Explicit expression for signals averaged over a time period from  $t_i$  to  $t_f$  are

$$I_K^{dc} \equiv \frac{1}{t_{fi}} \int_{t_i}^{t_f} dt I_K(t) = -\frac{1}{t_{fi}} \text{Im} \int_{t_i}^{t_f} dt \text{Tr} \left[ \Gamma^K \left( \mathbf{G}^<(t, t) + \int \frac{dE}{2\pi} f_K(E) \mathbf{G}^r(t, E) \right) \right] \quad (8)$$

$$\begin{aligned} S_{KK}^{dc} &\equiv \frac{1}{t_{fi}} \int_{t_i}^{t_f} dt_1 \int_{t_i}^{t_f} dt_2 S_{KK}(t_1, t_2) \\ &= \frac{4}{t_{fi}} \text{Re} \int_{t_i}^{t_f} dt \int \frac{dE}{2\pi} \text{Tr} \left[ -iG^r(t, E) \left( \Sigma_K^<(E) G^r(E, t) [1 - \rho(t)] - \Sigma_K^>(E) G^r(E, t) \rho(t) \right) \Gamma^K \right. \\ &\quad \left. + G^r(E, t) \left( [1 - \rho(t)] \Sigma_K^<(E) - \rho(t) \Sigma_K^>(E) \right) + G^r(E, t) \rho(t) \Gamma^K [1 - \rho(t)] G^a(t, E) \Gamma^K \right] \\ &+ \frac{4}{t_{fi}} \text{Re} \int_{t_i}^{t_f} dt_1 \int_{t_i}^{t_f} dt_2 \int \frac{dE_1}{2\pi} \int \frac{dE_2}{2\pi} e^{i(E_1 - E_2)(t_1 - t_2)} \\ &\quad \text{Tr} \left[ iG^r(t_1, E_2) \left( \Sigma_K^<(E_2) [1 - \rho(t_2)] - \Sigma_K^>(E_2) \rho(t_2) \right) G^a(t_2, E_1) \Gamma^K \right. \\ &\quad \left. - G^r(t_1, E_2) \Sigma_K^<(E_2) G^r(t_2, E_1) \Sigma_K^>(E_1) - G^r(E_1, t_1) \rho(t_1) \Gamma^K G^r(E_2, t_2) [1 - \rho(t_2)] \Gamma^K \right] \end{aligned} \quad (9)$$

Here  $t_{fi} \equiv t_f - t_i$ ,  $\rho(t) \equiv -iG^<(t, t)$ ,  $\text{Tr}[\dots]$  is trace over molecular subspace, and  $\Sigma_K^<(E) = i\Gamma^K f_K(E)$  and  $\Sigma_K^>(E) = -i\Gamma^K [1 - f_K(E)]$  are the lesser and greater projections of self-energy due to coupling to contact  $K$ . Note in deriving (9) we followed Ref. <sup>49</sup> and utilized the generalized Kadanoff-Baym ansatz. <sup>60</sup>

Following Ref. <sup>55</sup> the external driving is a laser pulse pair sequence (see Fig. 1), so that  $t_{fi}$  in

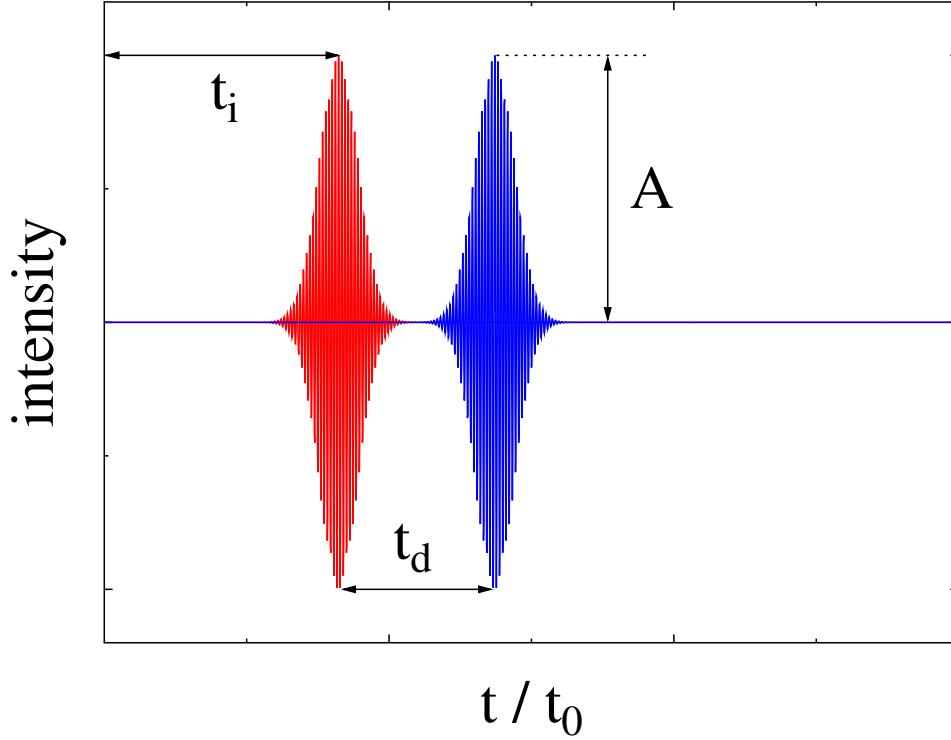


Figure 1: (Color online) Sketch of a laser pulse pair of the LPPS.

Eqs. (8) and (9) is the pulse pair repetition period. The driving force is

$$-\vec{\mu} \vec{E}(t) = A \left( \cos [\Omega(t - t_i)] e^{-(t-t_i)^2/2\tau^2} + \cos [\Omega(t - t_d - t_i)] e^{(t-t_d-t_i)^2/2\tau^2} \right) \quad (10)$$

where  $A$  is the amplitude and  $\Omega$  is the frequency of the driving field,  $t_i$  is initial delay time,  $\tau$  is a pulse width, and  $t_d$  is the delay time between the pair.

As was discussed in Ref. 55 this type of a junction pump-probe experiment allows to get information on intra-molecular dynamics from *dc* measurements. We note that intra-molecular dynamics survives only when the system is in an underdamped regime. That is, the characteristic time for the dynamics is smaller than the characteristic relaxation time of the system. In junctions with molecules chemisorbed on contacts the latter is characterized by the inverse of the electron escape rate,  $\Gamma$ . Since  $\Gamma$  has to be small (relative to intra-molecular interactions), simulations based on perturbative treatment of the molecule-leads coupling to second order (as is the case in Ref.<sup>55</sup>) are justified. However, there are cases in which going beyond second order seems plausible: 1. Situation



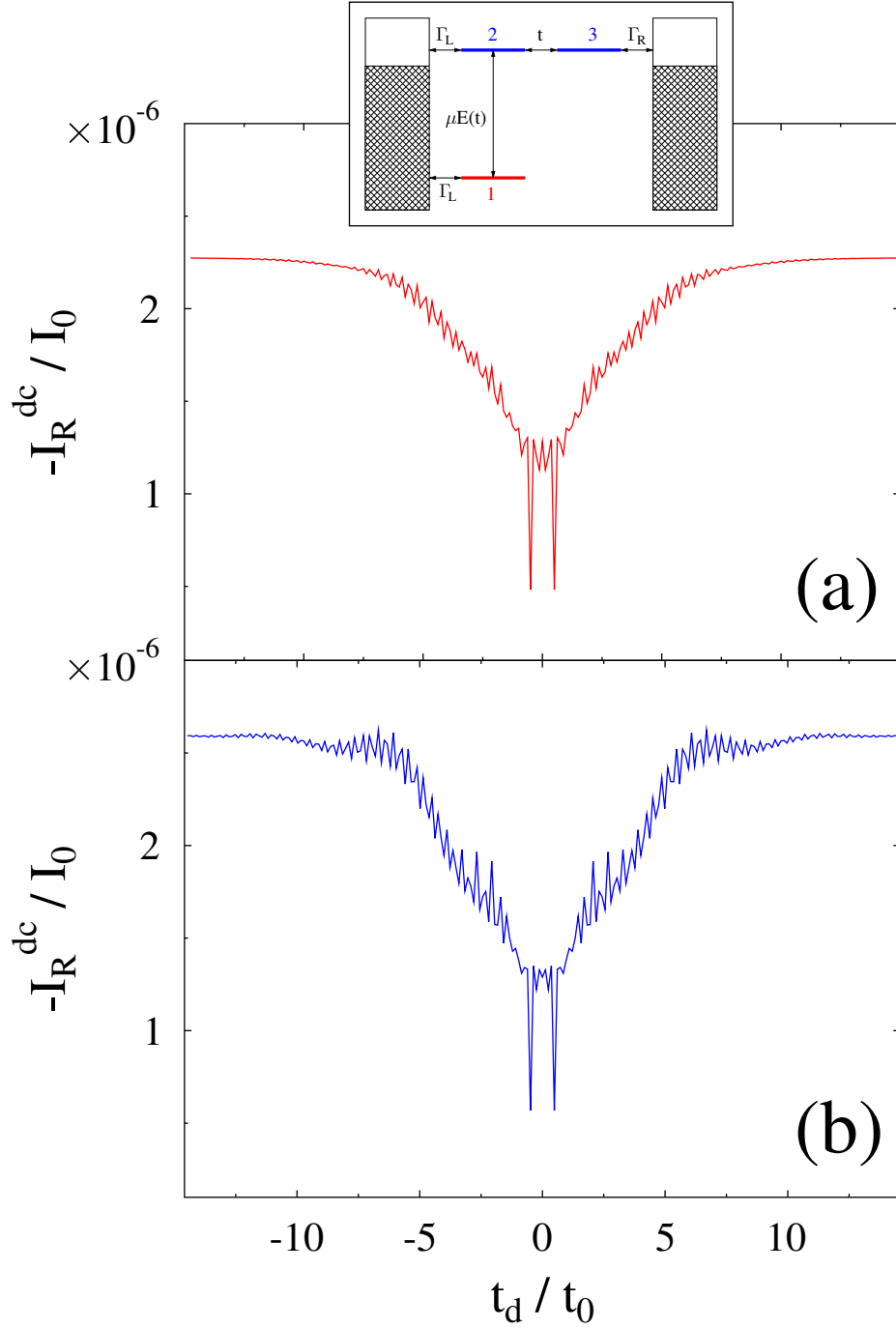


Figure 2: (Color online) Average current, Eq. (8), at the right molecule-contact interface as function of the LPPS delay time  $t_d$ . Shown are result of calculations with the (a) Redfield quantum master equation invoking the wide band approximation and (b) non-equilibrium Green functions technique. Inset introduces the model of a molecular bi-chromophoric junction. See text for parameters.

where the chemical potential is at resonance with the molecular level; 2. Presence of degeneracy between eigenstates of the system; and 3. Noise simulation of a driven time-dependent transport. Indeed, at resonance or when degeneracy is present the perturbative treatment of the coupling to the leads may break down<sup>61</sup> especially when  $\Gamma \gg k_B T$ .<sup>62</sup> Also, noise simulations of a time-dependent process, where the steady-state full counting statistics is not applicable, requires either accounting for higher order terms in the perturbative treatment, or employing Green function techniques.

We start with an illustration of NEGF calculations of field induced dynamics and transport when the molecule has a level resonant with the Fermi energy. Figure 2 shows *dc* current calculated for the model considered in Ref.<sup>55</sup> (see inset) when the LUMOs are gated to be close to Fermi energy in the contacts. Here and below we utilize the wide band limit and use  $\Gamma$  as the unit of energy and  $t_0 \equiv \hbar/\Gamma$  as unit of time. Current and noise, Eqs. (8) and (9), will be presented in units of  $I_0 \equiv e/t_0$  and  $S_0 \equiv e^2/t_0$ , respectively. This way our analysis becomes scalable, and thus easily comparable to different experimental setups as long as characteristic electron escape rate is defined. Fermi energy in the contacts is taken as the origin,  $E_F = 0$ . The parameters of the calculation are  $k_B T = 0.03$ ,  $\varepsilon_1 = -31.25$ ,  $\varepsilon_2 = \varepsilon_3 = t = 0.625$ ,  $A = 3.125$ ,  $\Omega = \varepsilon_2 - \varepsilon_1$ ,  $t_i = 14.5$ ,  $\tau = 1.2$ , and  $t_{fi} = 4.9 \cdot 10^5$ . For example, for a reasonable estimate of the electron escape rate  $\Gamma \sim 0.1$  eV<sup>63</sup> the parameters of the calculation are  $T \approx 100$  K,  $\varepsilon_1 \approx -3$  eV,  $\varepsilon_2 = \varepsilon_3 = t \approx 0.06$  eV,  $A \approx 0.3$  eV,  $\Omega \approx 3$  eV,  $\tau \approx 6$  fs, and  $t_{fi} \approx 2$  ns. All these parameters are within a realistic range. Indeed, for molecules with dipole moment of  $\sim 10$  D<sup>64</sup> and local fields  $\sim 10^8 - 10^9$  V/m<sup>65,66</sup> the estimated molecular coupling to the driving force is  $10^{-3} - 10^{-1}$  eV.

The intramolecular dynamics related to Rabi oscillations between the two LUMO levels shows itself as oscillating features in the average current plotted as function of the pulse pair delay time (see Ref.<sup>55</sup> for details). Interestingly, the features of the internal dynamics are pronounced in the NEGF calculation and are absent in a Markovian quantum master equation calculation invoking the wide band approximation. We note that the fast alternations of the current in Figs. 2 comes directly from the molecule-field interaction, and do not reflect the intra-molecular dynamics. Specifically, the field-induced Rabi oscillations between the HOMO and LUMO of the driven chromophore are

set by the pulse intensity (which implies that their frequency is chirped within the pulse duration). The molecular response to the second pulse depends on these orbital occupations, which leads to the fast alternations observed in the dc current vs the delay time. Other interesting features in the current are the sharp downward peaks obtained when the two pulses nearly overlap in time. These reflect unique destructive interference between the two pulses, where the pulse envelopes are similar in magnitude at all times, but the underlying optical cycles are displaced by a half cycle. We emphasize that these fast alternations of the signal do not obscure the relevant information. Intra-molecular dynamics results from interference caused by coherence in the molecule, and is revealed as a slower signal variation seen in Fig. 2b. This is the signal which is expected to be detectable in the experiment.

We note that the model of molecular chromophores considered in Ref.<sup>55</sup> and shown in the inset of Fig. 2 introduces intra-molecular dynamics which is directly related to charge transfer between the contacts. Thus, it is quite reasonable to expect that fingerprints of the dynamics will be visible in the averaged current. We now turn to a different model representing a molecule with strong charge transfer transition<sup>67</sup> with its LUMO (level 2) coupled by electron transfer matrix element to a state (level 3) not directly attached to contacts (see inset of Fig. 3). The model is often used to illustrate effects of destructive interference on transport properties of junctions (see e.g. Ref.<sup>68</sup>). Clearly, also here inter-LUMO coupling induces Rabi oscillations between the two levels. However, contrary to the chromophores model the electron hopping does not contribute directly to the optically-induced current through the junction. Still, intra-molecular dynamics due to the Rabi oscillation is pronounced in both transient LUMO population (solid line in Fig. 3a) and current at the right molecule-contact interface (solid line in Fig. 3b) - note the oscillations at  $t \sim 11t_0$ . Here the parameters are  $k_B T = 0.045$ ,  $\epsilon_1 = -25$ ,  $\epsilon_2 = \epsilon_3 = 25$ ,  $t = 1$ ,  $A = 5$ ,  $\Omega = \epsilon_2 - \epsilon_1$ ,  $t_i = 9.1$ ,  $\tau = 0.75$ ,  $t_d = 6$ , and  $t_{fi} = 3 \cdot 10^5$ . Similar to the discussion of the parameters utilized for simulations presented in Fig. 2 one can check that for electron escape rate  $\Gamma \sim 0.01$  eV the parameters are within a realistic range. The calculations are performed within the NEGF.

As discussed above transients are not measurable at the timescale of intra-molecular dynamics,

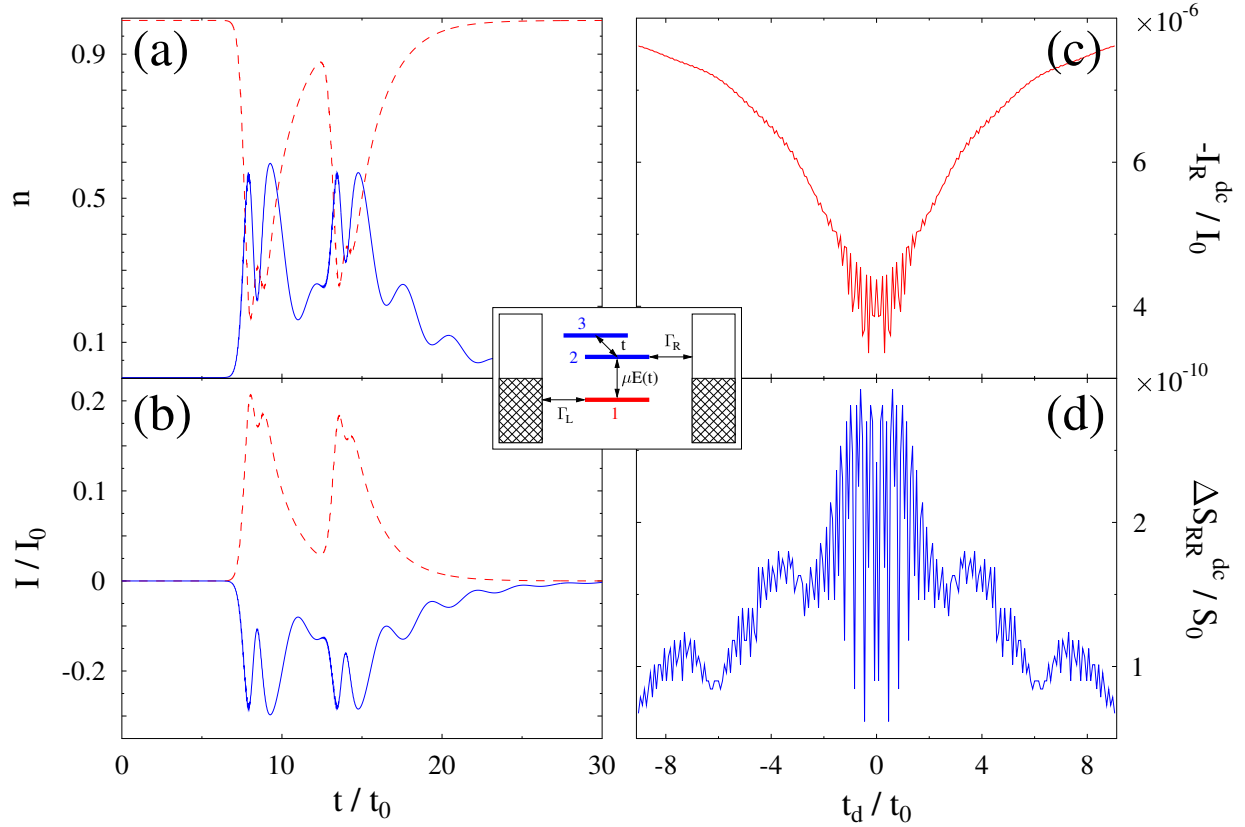


Figure 3: (Color online) Response of a junction incorporating a molecule with strong charge transfer transition (see inset) to LPPS driving. Shown are (a) transient populations of the HOMO (dashed line, red) and LUMO level 2 (solid line, blue) and (b) transient currents at the left (dashed line, red) and right (solid line, blue) molecule-contacts interfaces. Average transport characteristics of the junction are (c) average current, Eq. (8), and (d) shot noise  $\Delta S_{RR}^{dc}(t_d) \equiv S_{RR}^{dc}(t_d) - S_{RR}^{dc}(t_d \rightarrow \infty)$ , Eq. (9), at the right molecule-contact interface as functions of the pair pulse delay time,  $t_d$ . See text for parameters.

and average current does not capture the intra-molecular dynamics which is not directly related to charge-transfer in the current direction of the junction (see Fig. 3c). The next (second) cumulant of the full counting statistics is noise. Shot noise measurements in molecular junctions at steady state are an established field of research.<sup>9,10,69–71</sup> We propose to utilize *dc* measurements of shot noise for a driven time-dependent process, and utilize its average over pulse pair sequence, Eq. (9), to capture intra-molecular dynamics which is not directly related to the current formation. Figure 3d shows that such measurements will reveal the corresponding Rabi frequency even when the *dc* current misses it. Similar to our discussion of Fig. 2 also here the rich structure of the signal is caused by the overlap of the two pulses and is on the time scale of the field induced Rabi cycles between the chromophore orbitals. Also here, the information on intra-molecular dynamics is given by a slower variation of the noise signal.

While the possibility to measure the noise (even with much averaging) is a demanding experimental task, such measurements in molecular junctions at steady-state have been successfully done (see e.g. Refs. 9,10). Thus our proposal to extend the technique to account for time-averaged properties of a junction under external driving does seem to be reasonable. Indeed, for a reasonable estimate of  $\Gamma \sim 0.01$  eV for a molecule chemisorbed on the metal surface, unit of noise  $S_0 \approx 2 \times 10^{-5}$  A<sup>2</sup>/Hz. We note that measurements of excess noise of the order of  $10^{-26}$  A<sup>2</sup>/Hz were reported in the literature.<sup>9</sup>

Finally we demonstrate the ability of the pump-probe *dc* noise spectroscopy to account for circular currents in the system. Circular currents were discussed for molecular junctions containing benzene (and similar) molecules.<sup>72–75</sup> We consider a modification of the model discussed above, where the conducting LUMO (level 2) is coupled in a circular way to a set of levels (see inset of Fig. 4). We consider ferromagnetic contacts and assume spin-polarized current in the system dropping the spin index and using the same model (1)-(4) in our simulations. In the presence of magnetic field circular current will be induced in the set of LUMOs. Similarly to the previous consideration the average current will miss the corresponding dynamics (see Fig. 4c). At the same time *dc* noise measurements do allow to get the information (see Fig. 4d). The parameters of the

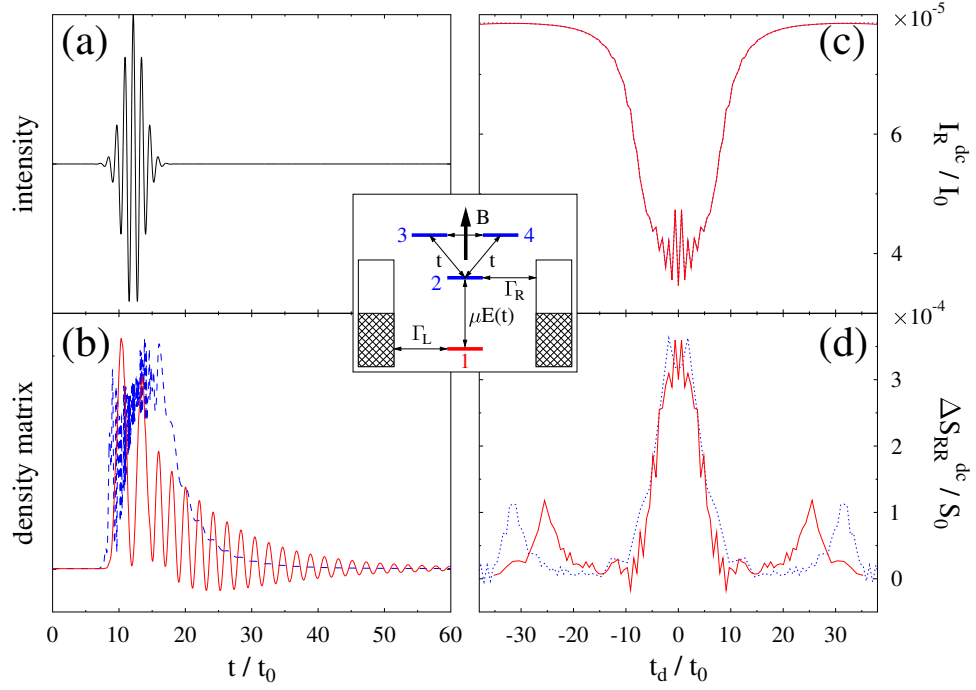


Figure 4: Response of a junction incorporating a ring structure in the presence of magnetic field  $B$  (see inset). Shown are (a) Single pulse and (b) transient response of the system - population of the LUMO level 2 (dashed line, blue) and coherence between levels 3 and 4 (solid line, red). Calculation is done for  $B = 5$  T. Also shown is average response to LPPS: (c)  $dc$  current, Eq. (8) and (d) average shot noise  $\Delta S_{RR}^{dc}(t_d) \equiv S_{RR}^{dc}(t_d) - S_{RR}^{dc}(t_d \rightarrow \infty)$ , Eq. (9), at the right molecule-contact interface (see inset) as functions of the pair pulse delay time,  $t_d$ . Average characteristics are presented for  $B = 5$  T (dotted line, blue) and  $B = 10$  T (solid line, red). See text for other parameters.

calculation are  $k_B T = 0.45$ ,  $\varepsilon_1 = -2.5$ ,  $\varepsilon_2 = \varepsilon_3 = \varepsilon_4 = 2.5$ ,  $t = 1$ ,  $A = 100$ ,  $\Omega = \varepsilon_2 - \varepsilon_1$ ,  $t_i = 6$ ,  $\tau = 1.5$ , and  $t_{fi} = 3 \cdot 10^4$ . The circular currents for two values of the magnetic field manifest themselves as peaks in the region  $t_d \sim 20$  or  $30t_0$ . The peak positions approximately correspond to the Larmor precession frequencies. The approximate character is to be expected, since our simple 3 LUMOs model is not a ring. It is interesting to note that contrary to previous results, where the data was confined to the central region, the peaks are satellites of the central peak. To understand the effect we note that the width of the central peak is defined by the relaxation time of the system,  $\sim 10/\Gamma$ , which is the timescale for a pump-probe experiment. In the case of the 3 LUMOs model (see inset of Fig. 4) levels 3 and 4 are detached from the leads, which results in long-living correlations within the system. Indeed, while most of the system excitation dies within the  $\sim 10/\Gamma$  relaxation time after the end of the pulse (compare panels a and b in Fig. 4), coherence between levels 3 and 4 (solid line Fig. 4b) survives much longer.

Summarizing, we discussed the possibility of obtaining data on the picosecond range from *dc* measurements of a molecular junction response to LPPS. Average current measurements, proposed by two of us in previous publication,<sup>55</sup> are shown to account only for intra-molecular dynamics directly related to charge transfer in the current direction in junctions. To allow access to information on other intra-molecular processes we proposed pump-probe noise spectroscopy as a suitable alternative. Similar to established noise measurements in molecular junctions at steady state, average shot-noise signal resulting from the junction response to LPPS contains richer information than the corresponding current data. In particular, we showed that Rabi oscillations within the molecule not in the direction of the current flow as well as circular currents in the system can be detected within the noise spectroscopy, but are missed by the current measurements. We employed the NEGF to calculate transient and average characteristics of molecular junctions simulated within simple generic models. The ability of this methodology to provide information on intra-molecular interactions is a goal for future theoretical research. We suggest that the (challenging) experimental verification of the proposed approach can be done by using a lock-in amplifier synchronized to the chopping frequency of the laser and coupled to the junction via a bias-tee and a power-detector

(a modified version of experimental setup presented in Ref.<sup>76</sup>). The measured signal in this case will be the difference between the frequency-dependent power with and without laser-excitation applied to the junction which is the excess noise power. Such a verification would bring a new powerful tool to characterize time-dependent and transient characteristics of molecular junctions.

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