Coherent destruction of the current through molecular wires using short laser pulses

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Received zzz, revised zzz, accepted zzz
Published online zzz

PACS 73.63.Nm, 03.65.Yz, 33.80.-b

A molecular wire coupled to two electron reservoirs is investigated within a tight-binding approach including spin and Coulomb interaction. Under the assumption of weak coupling to the electron reservoirs a quantum master equation can be derived for the electron transport through the wire. Motivated by the phenomenon of coherent destruction of tunneling for monochromatic laser fields, the influence of Gaussian laser pulses on the transport through the wires is studied. For situations in which the maximum amplitude of the electric field fulfills the conditions for the destructive quantum effect the average current through the system can be suppressed even for a wire consisting of only one site. Turning on the electron correlation does not destroy the suppression of the current by the laser.

1 Introduction  Electronic transport through molecular wire has been studied intensively theoretically as well as numerically in recent years [1, 2]. A molecular wires consists of a molecule which is coupled to two leads acting as electron source and drain. Depending on the bias voltage applied across the wire there will be a charge flow through the wire which might consist of a single molecule only. Most electron transport experiments are described by the scattering approach put forward by Landauer [3, 4]. Another class of theories of quantum transport utilizes the non-equilibrium Green’s function approach [5]. This formalism has the advantage of being formally exact within the lead-wire coupling but the dependence of Green’s functions on two time arguments makes it rather difficult to calculate the quantities involved. If one treats the lead-wire coupling perturbatively one can derive quantum master equations for the electron dynamics in the wire and the current through the wire which can be treated in the standard fashion for master equations [6–9]. This kind of quantum master equations is usually used to study the dynamics of a system coupled to a thermal bath [10, 11]. Often these theories are based on a second-order perturbation theory in the system-bath coupling and sometimes together with the neglect of memory effects (Markov approximation). In the present contribution we will use this formalism for the coupling of the wire to fermionic reservoirs [9, 12]. We make use of the spectral decomposition of the spectral density \( J(\omega) \) first introduced by Meier and Tannor [13]. Initially this formalism was applied within the time-nonlocal approach based on the Nakajima-Zwanzig equation. Afterwards the same methods was used for master equations based on a time-local formalism [14, 15]. For molecular wires these two versions of quantum master equations have been compared recently [12].

In addition to the coupling to fermionic reservoirs, the relevant system, i.e. the wire, is coupled to a laser field. First experimental [16] and theoretical [6, 9] studies in this direction have been performed. On the theoretical side most of these studies are based on a perturbative treatment in the environmental coupling

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corresponding lead by the spectral density function with a time-dependent external electric field.

time to a thermal bath. The coupling of the sites to each other is described by the hopping element $\Delta$ and to the

corresponding lead by the spectral density function $J_R(\omega)$. The on-site energies $E_n$ of the wire can be manipulated

with a time-dependent external electric field $E(t)$.

this allows for an easy inclusion of time-dependent laser fields. For time-periodic laser fields the Floquet

formalism can be employed [6] while for arbitrary time-dependent laser fields the present authors derived

a formalism which treats the laser-wire interaction exactly [9]. This approach employs the above described

spectral decomposition of the spectral density.

In previous publications [9, 17, 18] it was shown that the current through the molecular wire can be

suppressed using the phenomenon of coherent destruction of tunneling (CDT). This effect was first studied

by Grossmann et al. [19, 20] showing that the tunneling dynamics in a periodically driven quantum system

can be quenched. At a fixed frequency of the laser the CDT occurs for certain amplitudes of the laser

field. In the case of periodic laser fields the CDT can be studied using the Floquet theory [17, 18]. In

a recent study [21] we showed that the CDT can also be observed for rather short laser pulses. In the

case of a cw-laser field one has to average the current over one period of the carrier frequency to see

the complete suppression of the current. For short laser pulses the current is to be averaged over several

periods. In Ref. [21] three periods were employed for this purpose, here we take five periods. In the current

contribution we want to extend the previous study by including spin to be able to study on-site electron

correlation. Furthermore we study the effects of the laser pulse on a system with one site only. Throughout

the paper $\hbar$ and the Boltzmann constant $k_B$ are set to unity.

2 Hamiltonian and master equation To study the effects mentioned in the introduction we use a

system consisting of two parts: the relevant system $H_S(t)$, mimicking the wire, and the reservoirs $H_R$

modeling the leads. Thus the total Hamiltonian is given by $H(t) = H_S(t) + H_R + H_{SR}$ with the wire-lead

coupling $H_{SR}$. The wire consists of $N$ sites coupled to each other by a hopping element $\Delta$ (see Fig. 1).

The creation and annihilation operators of electrons at site $n$ with spin $\sigma$ are denoted by $c_{n\sigma}^\dagger$ and $c_{n\sigma}$,

respectively, so that the tight-binding description of the molecular wire reads

$$H_S(t) = \sum_{n,\sigma} E_n c_{n\sigma}^\dagger c_{n\sigma} - \Delta \sum_{n,\sigma} (c_{n\sigma}^\dagger c_{n+1,\sigma} + c_{n+1,\sigma}^\dagger c_{n\sigma}) + U \sum_n c_{n\uparrow}^\dagger c_{n\uparrow} c_{n\downarrow}^\dagger c_{n\downarrow} - \mu E(t). \quad (1)$$

In the first term we assumed the on-site energies $E_n$ to be spin-independent. The second term describes

the nearest-neighbor hopping of electrons with the same spin and the third term the on-site electron interaction

within the wire. The laser-wire interaction is given by the last term and for the dipole operator we assume

[6]

$$\mu = e \sum_n x_n = e \sum_{n,\sigma} \frac{2n - N - 1}{2} c_{n\sigma}^\dagger c_{n\sigma} \quad (2)$$

for wires with more than one site and a constant for a wire consisting of only one site.
The two electronic leads that are modeled by two independent reservoirs of uncorrelated electrons in thermal equilibrium. In the derivations below only the left lead will be considered but the formalism has to be applied to the right lead as well. Denoting the creation and annihilation operators of an electron in the reservoir modes $\omega_q$ with spin $\sigma$ by $c_{q\sigma}^\dagger$ and $c_{q\sigma}$, respectively, the coupling of the left lead to first site of the wire is given by

$$
H_{SR} = \sum_{\sigma,x=1,2} K_{x\sigma} \Phi_{x\sigma} = \sum_{q\sigma} (V_q c_{1\sigma}^\dagger c_{q\sigma} + V_q^* c_{q\sigma} c_{1\sigma})
$$

(3)

with $\Phi_{1\sigma} = \Phi_{2\sigma} = \sum_q V_q c_{q\sigma}$, $K_{1\sigma} = K_{2\sigma} = c_{1\sigma}^\dagger$, and a wire-lead coupling strength $V_q$.

As one is normally not interested in the dynamics within the leads but only within the wire, a quantum master equation (QME) based on a second-order perturbation theory in the wire-lead coupling has been developed for the reduced density matrix of the wire $\rho_S(t)$ [9]

$$
\frac{\partial \rho_S(t)}{\partial t} = -i\mathcal{L}_S(t)\rho_S(t) - \sum_{\sigma x x'} [K_{x\sigma}, \Lambda_{xx'\sigma}(t)]\rho_S(t) - \rho_S(t)\Lambda_{xx'\sigma}(t) \tag{4}
$$

with the corresponding auxiliary operators for the wire-lead coupling

$$
\Lambda_{xx'\sigma}(t) = \int_{t_0}^{t} dt' C_{xx'}(t-t')U_S(t,t')K_{x'\sigma}, \quad \Lambda_{xx'\sigma}(t) = \int_{t_0}^{t} dt' C_{xx'}(t-t')U_S(t,t')K_{x'\sigma} \tag{5}
$$

Here we employed the definitions $U_S(t,t') = T_+ \exp\{-i \int_t^{t'} d\tau \mathcal{L}_S(\tau)\}$ and assumed the reservoir correlation functions $C_{xx'}(t) = \text{tr}_R\{e^{iH_0 t} \Phi_{x} e^{-iH_0 t} \Phi_{x'} \rho_R\}$ with the reservoir density matrix $\rho_R$ to be spin-independent. Using this form has the advantages over the Redfield approach [22] that the memory terms are included and that the wire-laser coupling is treated exactly within the dipole approximation.

In the system-bath approach used the coupling to the fermionic reservoirs is described by a single quantity, namely the spectral density $J_R(\omega) = \sum_q \pi |V_q|^2 \delta(\omega - \omega_q)$. In principle this coupling can be different for the right and the left lead but we assume it to be equal for both cases. For a dense spectrum of reservoirs the sum becomes a smooth function. To be able to use the theorem of residues to determine the bath correlation functions, one approximates the spectral density by a numerical decomposition into Lorentzian functions [9, 13]

$$
J_R(\omega) = \sum_{k=1}^{m} \frac{p_k}{4\Omega_k (\omega - \Omega_k)^2 + \Gamma_k^2}, \tag{6}
$$

with real fitting parameters $p_k$, $\Omega_k$ and $\Gamma_k$. Furthermore one uses the fact that $J_R(\omega) \approx 0$ for $\omega \leq 0$ which is fulfilled for a wide range of parameters $\Omega_k$ and $\Gamma_k$. With the roots of $n_F$ and $\Phi$, the application of the theorem of residues results in

$$
C_{12}(t) = \sum_{k=1}^{m} \frac{p_k}{4\Omega_k \Gamma_k} \left(n_F(-\Omega_k^- + E_F)e^{-i\Omega_k^- t} - \frac{2i}{\beta} \sum_{k=1}^{m'} J_R(\nu_k^+) e^{-i\nu_k^+ t} \right) = \sum_{k=1}^{m+m'} a_{12}^k e^{\gamma_{12}^k t} \tag{7}
$$

$$
C_{21}(t) = \sum_{k=1}^{m} \frac{p_k}{4\Omega_k \Gamma_k} \left(n_F(\Omega_k^+ - E_F)e^{i\Omega_k^+ t} - \frac{2i}{\beta} \sum_{k=1}^{m'} J_R(\nu_k^-) e^{i\nu_k^- t} \right) = \sum_{k=1}^{m+m'} a_{21}^k e^{\gamma_{21}^k t} \tag{8}
$$

with the abbreviations $\Omega_k^\pm = \Omega_k + i\Gamma_k$ and $\Omega_k^- = \Omega_k - i\Gamma_k$ and the Matsubara frequencies $\nu_k = \frac{2\pi k}{\beta} + E_F$. Rigorously, the sum over the Matsubara frequencies would be infinite but it can be truncated at a finite $m'$ depending on the temperature of the system $T$ and the spectral width of $J_R(\omega)$. The pure exponential
With the chosen energy settings, a time unit in the system corresponds to 0.66 fs. Using Eq. (11) the current unit can be extracted to be

\[ I_c = \text{amplitude} \]

The condition was originally developed for cw laser fields but as already shown earlier in the case of spinless electrons [21] is also important for short laser pulses. In the case of no electron correlation as shown in

\[ \text{Fig. 2} \quad \text{The scenario of CDT for a Gaussian laser field for a system with one site and without electron interaction. The top panel shows the laser field, the middle one the current through the wire, and the lowest panel the averaged current.} \]

dependence of the correlation function on time allows one to derive a set of differential equations for the auxiliary density operators

\[
\frac{\partial}{\partial t} \Lambda_{xx'\sigma}^k(t) = a_{xx'} K_{xx'\sigma}^k \rho_S(t) - i[H_S(t), \Lambda_{xx'\sigma}^k(t)] + \gamma_{xx'} \Lambda_{xx'\sigma}^k(t), \tag{9}
\]

\[
\frac{\partial}{\partial t} \Lambda_{xx'\sigma}^k(t) = (a_{xx'}^*)^\dagger \rho_S(t) K_{xx'\sigma}^k - i[H_S(t), \Lambda_{xx'\sigma}^k(t)] + (\gamma_{xx'}) \Lambda_{xx'\sigma}^k(t), \tag{10}
\]

with \( \Lambda_{xx'\sigma}^k(t) = \sum_{k=1}^{m+m'} \Lambda_{xx'\sigma}^k(t) \) and \( \Lambda_{xx'\sigma}^k(t) = \sum_{k=1}^{m+m'} \Lambda_{xx'\sigma}^k(t) \).

Using the electron number operator of the left lead with the summation performed over the reservoir degrees of freedom \( N_l = \sum_{q\sigma} c_{q\sigma}^\dagger c_{q\sigma} \) one can now derive an expression for the current [9]

\[
I_l(t) = e \frac{d}{dt} \text{tr} \{ N_l \rho_S(t) \} = -ie \text{tr} \{ [N_l, H(t)] \rho_S(t) \} = 2e \text{Re} \left( \text{tr}_S \left\{ c_{1\sigma}^\dagger \Lambda_{12\sigma}(t) - c_{1\sigma}^\dagger \Lambda_{12\sigma}(t) \right\} \right). \tag{11}
\]

3 Results In this section results are shown for a wire consisting either of one or two sites. The parameters for both cases are the same. The energy scale used is the tight-binding hopping parameter \( \Delta \) which is set to 0.1 eV. For the case of one site this is of course an artificial parameter since it does not play a role in this particular system. Nevertheless we use this energy scale since it is used in other work as well. The temperature is set to \( T = 0.25\Delta \approx 290 \) K. For simplicity a simple spectral density is used which consists only of one Lorentzian in Eq. (6). The parameters are chosen to be \( p_1 = 50 \) eV, \( \Gamma_1 = 50 \) eV, and \( \Omega_1 = 5 \) eV which results in a maximum coupling strength between wire and leads of 0.1 \( \Delta \). For these parameters the condition \( J_R(\omega) \approx 0 \) for \( \omega \leq 0 \) is nicely fulfilled. The site energies are \( E_1 = E_2 = 50 \) eV and therefore located at the maximum of the coupling to the leads. The Fermi energies are set to \( E_{F,1} = 50.2 \) eV \( E_{F,1} = 49.8 \) eV leading to a bias voltage of 0.4 eV. The laser pulse used in all calculations has a Gaussian shape \( E(t) = A \exp \left( -\frac{(t - T)^2}{2(\sigma^2)} \right) \sin(\omega_\ell t) \) with \( \sigma = 100 \) fs, \( T = 400 \) fs and a maximum amplitude of \( A = 2.405 \) eV. This amplitude corresponds to a full CDT [9, 17]. The carrier frequency is set to 1 eV. With the chosen energy settings, a time unit in the system corresponds to 0.66 fs. Using Eq. (11) the current unit can be extracted to be \( I_0 = 2.43 \times 10^{-4} \) A.

Fig. 3 In Fig. 2 the current and the averaged current are shown together with the laser field. The amplitude \( A = 2.405 \) eV of the laser field is chosen such that the CDT condition is fulfilled. The CDT condition was originally developed for cw laser fields but as already shown earlier in the case of spinless electrons [21] is also important for short laser pulses. In the case of no electron correlation as shown in
Fig. 3 For a wire with only one site the population dynamics (left panel) and the averaged current (right panel) is shown for different values of electron interaction $U$. In the graph displaying the populations the upper four curves correspond to the population of the spin up orbital which is identical to the population of the spin down orbital. The lower four curves show the probability of a double occupancy of the site.

Fig. 2 no big difference can be seen compared to the case of spinless electrons. For very short times one can see the loading of the initially empty wire sites, then an equilibration before the laser pulse sets in. At the maximum of the laser field the average current is completely suppressed. Interestingly Fig. 2 shows a wire consisting only of one site and a constant dipole moment. So the laser suppresses the transport between the site and the leads which are directly coupled to it. Earlier studies always used wires of at least two sites and in those studies it was not clear if the laser blocks the current between the sites of the wire or between the wire and the leads. The present study clearly shows that the CDT also works to suppress the current between the wire and the leads.

Fig. 3 shows the occupation probabilities and average current for different values of the electron interaction $U$. Shown are the probabilities of finding a spin-up electron $tr(c_1^{\dagger}c_1\rho_S)$ which is equal to that of finding a spin-down electron. In addition the probability of a doubly occupied site displayed. While increasing the electron interaction $U/\Delta$ from 0 to 5 the probability for a doubly occupied site decreased as expected. The probability to find a spin-up or -down electron on the site decreases at the same time since this contains also the probability for double occupancy. Interestingly enough, the laser pulse allows for a doubly occupied site to an amount which is also seen without electron correlation. So during the maximum of the laser pulse the double occupancy is the same irrespective of electron interaction. Therefor the energy barrier created by electron interaction is, in a sense, overcome by the energy of the laser pulse. So it is not astonishingly that the current through the wire is the same during the maximum of the laser pulse. But since at that moment in time the CDT condition is fulfilled, the current is zero independent of electron correlation. The equilibrium current without laser pulse is smaller in the case of electron interaction since the energy of the doubly occupied state is moved above the Fermi level due to correlation. So this level can not participate in the current when the laser is off.

The case of a wire with two sites is shown in Fig. 4. Again the occupation probabilities of the different orbitals are shown. This time the dipole operator is given by Eq. (2) and so the population on the two sites is different. Also in this case the probability of doubly occupied sites decreases with electron interaction but can be increased or decreased by the laser pulse which only shifts the site energies. The current suppression through the phenomenon of CDT looks very similar to that of a one-site wire or that of spinless electrons [21].

4 Conclusions In the present contribution we extended our earlier work [21] by including spin to be able to treat on-site interaction and by investigating the case of a wire with only one site. Again it could be shown that the phenomenon of CDT exists in models of molecular wires also for short laser pulses and not
only for monochromatic laser fields. The amplitude condition as for cw-laser fields plays an important role but has to be investigated further. As shown earlier [21] longer pulses suppress the current more effectively so it might be possible to find a better modified CDT condition for short Gaussian laser pulses or to find more effective pulse forms. The on-site interaction between the electrons does not effect the effect of current suppression which can be understood, at least partially, by looking at the occupation probabilities and the effect of the laser pulse on them.

The employed model of a molecular wire is of course rather simplistic. Higher excited states should be taken into account and also dephasing effects. The dephasing effects can be studied by coupling the wire to an additional thermal bath in the same spirit than the coupling to the electron reservoirs. This will be done in the future to investigate how quickly the coherent effect of CDT gets washed out. For cw-laser fields that has been studied within the Floquet approach [18]. It is unclear in how far short laser pulses might work better than cw-laser fields because they do contain a range of amplitudes and so some of the amplitudes might still fulfill a modified CDT criterion under the influence of a thermal bath.

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