Suppressing the current through molecular wires: comparison of two mechanisms

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Abstract. The electron tunneling through a molecular junction weakly coupled to two leads is studied in the presence of a time-dependent external field. For this purpose, the wire is modeled in a tight-binding approach and a master equation approach is employed. Two different ways of suppressing the current through the wire are compared: coherent destruction of tunneling (CDT) and a laser field obtained by optimal control theory. The CDT localizes the electrons at the individual sites and it is effective if the amplitude of a high-frequency laser field fulfills a certain amplitude criterion. As the name of the phenomenon indicates, it is a coherent effect. In the alternative approach, the optimal control theory, a target current flow pattern is defined and the corresponding laser field is calculated. It is shown that the two mechanisms are influenced differently by introducing dephasing effects into the system. Furthermore, the currents flowing in, through and out of the wire are investigated in more detail to understand the physical processes behind the suppression of the net current.

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1. Introduction

An understanding of the fundamental limits for transferring light to electrical energy is required if one wants to be able to control electronic circuits optically. Especially for single-molecule junctions, the quantum mechanical nature of electrons becomes important and it may be possible to observe novel effects when they interact with light [1]. On the experimental side, it is rather complicated to focus the laser light onto a molecular junction with a width below the diffraction limit of the light. Nevertheless, the developments in tip-enhanced near-field scanning optical microscopy [2], for example, look very promising. Coupling of a laser field to an adsorbed molecule on a surface with the help of scanning tunneling microscopy [3] is another possible implementation and several experiments in this general direction have been performed recently (e.g. [4]–[8]).

On the theoretical side, one class of approaches allows the calculation of the current response to an ac-driving field. Especially in the strong-field limit, most of these theories are based on the Floquet formalism which is a theory that can be applied to any periodically driven system [9, 10]. In some of these investigations (especially concerning quantum dots) the spin of the electrons plays an important role [11]–[13]. In other investigations the effect of short laser pulses on the current through a molecular junction has been determined [1], in recent publications even optimal laser control theory was employed [14, 15]. In similar studies ring currents through ring-like molecules were calculated and controlled [16]–[18]. Although these investigations lack the coupling to the leads, the coupling of the molecule to a laser field and the calculation of a current make those approaches interesting for the present context.

A different class of studies is concerned with light-induced currents [19]–[23]. In contrast to the aforementioned considerations, the main focus of these investigations is to create a current in situations in which otherwise no current would flow. Some of these studies are actually concerned with improving the molecule–field interaction part of the Hamiltonian to get a better description of real physical systems (see for example [24]). Different scenarios of controlling the tunneling in molecular wires and quantum dots have been proposed based on different mechanisms [9, 11], [25]–[28]. Already a simple two-level system can significantly be altered...
in its dynamics by using a periodic driving such as a cw laser field. Two renowned phenomena are dynamical localization of, for example, ultracold atoms in magneto-optical traps [29] and coherent destruction of tunneling (CDT) for a particle in a bistable system which was first investigated by Grossmann et al [30]–[32].

The aim of this contribution is to analyze two different approaches to switch the current through molecular wires in detail: the phenomenon of CDT and optimal control theory. In the case of a periodically driven multi-site quantum model, CDT implies that the particles become localized at the individual sites by quenching the tunneling between the sites. This phenomenon can be explained using Floquet theory in the case of a periodic laser field in which the quasi-energies of the time-dependent Floquet states become degenerate [33]–[35]. The phenomenon occurs for certain amplitudes of the laser field at fixed frequencies for which the effective coupling between the sites becomes zero. Although CDT was first detected for two-level systems it was also shown to work for more complicated systems such as models for molecular wires [9, 27], [36]–[38] and even in combination with short laser pulses to switch the current [39, 40]. The effect of noise on CDT has, for example, been studied using random periodic δ-function ‘kicks’ in a driven double-well system [41].

Another formalism to switch the current through molecular wires is optimal control theory. It is usually applied to study the laser pulse control of molecular dynamics. This kind of control problem was studied in detail for simple chemical reactions in the gas phase as well as in the liquid phase, experimentally [42] as well as theoretically [43]. First approaches to coherent control of molecular dynamics were based on intuitive schemes like the Brumer–Shapiro procedure in the frequency domain [44] or the pump–dump scheme in the time domain [45]. The control algorithms by Judson and Rabitz [46] as well as the Krotov algorithm [47] give complete freedom to the laser pulses to be shaped. Recently, this optimal control formalism was extended to handle also target states distributed in time [48]–[50]. In our previous paper [15], we generalized the control formalism to situations with time-dependent targets in open quantum systems and applied it to molecular wires. After selecting a target, one utilizes the optimal control theory to optimize the time-dependent control field. Under the influence of this field, indeed a current which is similar to the predefined current pattern is obtained. In this paper, we will use such an electric field to suppress the current. This vanishing current is similar to the CDT scenario.

A comparison between the suppression of the current through a molecular wire based on CDT and based on optimal control theory is done below. To do so, we first introduce the model Hamiltonian in the next section. In section 3, different (partial) currents are defined in order to be able to discuss the current suppression in more detail. Thereafter in section 4, CDT and optimal control theory are applied in numerical case studies. The paper ends with some conclusions. Throughout the paper ̄h is set to unity.

2. Theoretical model

2.1. System Hamiltonian

The system under consideration consists of a tight-binding Hamiltonian with \(N\) sites describing the wire coupled to two fermionic reservoirs modeling the leads (see figure 1). In the numerical studies below, we restrict ourselves to wires with two sites. Furthermore, the molecular-wire part is coupled to a phonon bath introducing dephasing and energy relaxation processes.
Figure 1. Schematic picture of a spinless two-site molecular wire coupled to two fermionic reservoirs and a phonon bath. \(E(t)\) denotes an external laser field whereas \(E_{F,1}\) and \(E_{F,r}\) are the left and right Fermi levels. The coupling of the left lead and the right lead with the wire is described by \(J_L(E)\) and \(J_R(E)\), respectively. \(\Delta\) denotes the coupling between the two sites of the wire.

The total Hamiltonian for this scenario is given by \(H(t) = H_S(t) + H_R + H_P + H_{SR} + H_{SP}\). The relevant system, i.e. the wire, is given by \(H_S(t)\), the fermionic reservoirs by \(H_R\) and the system–reservoir coupling by \(H_{SR}\). In addition, one has the phonon bath Hamiltonian \(H_P\) and the system–bath coupling \(H_{SP}\). Denoting the creation (annihilation) operator by \(c_n^\dagger\) (\(c_n\)) the tight-binding description of the electrons in the molecular wire reads

\[
H_S(t) = \sum_n \varepsilon_n c_n^\dagger c_n - \Delta \sum_n (c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}) - \mu E(t).
\]

The first term describes the on-site energies \(\varepsilon_n\) and the second term the nearest-neighbor hopping. The third term gives the coupling between the wire and the laser field \(E(t)\). Here we assume for the dipole operator [9]

\[
\mu = e \sum_n x_n = e \sum_n \frac{2n - N - 1}{2} c_n^\dagger c_n,
\]

where \(c_n^\dagger c_n\) is the electron number operator.

As mentioned above there are two different types of environments. On one hand, the wire is coupled to two electronic leads that are modeled by two independent reservoirs of uncorrelated electrons in thermal equilibrium. The coupling of the left electronic lead with the first site of the wire is given by

\[
H_{SR} = \sum_{x=1}^2 K_x \Phi_x = \sum_q \left( V_q c_1^\dagger c_q + V_q^* c_q^\dagger c_1 \right)
\]

with \(\Phi_1 = \sum_q V_q c_q\), \(\Phi_2 = \sum_q V_q^* c_q^\dagger\), \(K_1 = c_1^\dagger\), \(K_2 = c_1\), and a wire–lead coupling strength \(V_q\) for each reservoir mode. A similar expression holds for the coupling to the right lead.

On the other hand, the wire is coupled to a phonon bath. The free phonon bath Hamiltonian is given by \(H_P = \sum_q \omega_q d_q^\dagger d_q\). Here \(d_q^\dagger\) and \(d_q\) denote the creation and annihilation operators of a phonon in bath mode \(q\) with energy \(\omega_q\). The occupation distribution of the phonon bath can be obtained within the Bose statistics as \(\langle b_q^\dagger b_q^\dagger \rangle = n_B(\omega_q)\delta_{qq'}\) where \(n_B\) is the Bose function.
coupling of the phonon bath to the molecule is assumed to be linear in the phonon degrees-of-freedom and local in the site basis of the wire, i.e.

\[ H_{SP} = \sum_n M_n \Phi, \]  

(4)

defining \( \Phi = \sum_q \gamma_q (b_q + b_q^\dagger) \), \( M_n = c_n^\dagger c_n \) and the wire–phonon coupling strength \( \gamma_q \).

2.2. Quantum master equation (QME)

As one is usually not interested in the dynamics within the leads but only within the wire, a QME based on a second-order perturbation theory in the wire–lead coupling and wire–phonon coupling has been developed for the reduced density matrix of the wire \( \rho_S(t) \) [27]

\[ \frac{\partial \rho_S(t)}{\partial t} = -i \mathcal{L}_S(t) \rho_S(t) - \sum_{x,x'} [K_x, \Lambda_{xx'}(t) \rho_S(t) - \rho_S(t) \hat{\Lambda}_{xx'}(t)] \]

\[ - \sum_n [M_n, \Theta_n(t) \rho_S(t) - \rho_S(t) \hat{\Theta}_n(t)] \]

(5)

with the Liouville operator \( \mathcal{L}_S(t) \) applying \( H_S \), i.e. \( \mathcal{L}_S(\tau) = [H_S(\tau), \cdot] \), the auxiliary operators for the wire–lead coupling

\[ \Lambda_{xx'}(t) = \int_{t_0}^t dt' C_{xx'}(t - t') U_S(t, t') K_{x'x}, \]

(6)

\[ \hat{\Lambda}_{xx'}(t) = \int_{t_0}^t dt' C^*_{x'x}(t - t') U_S(t, t') K_x \]

(7)

and the auxiliary operators for the wire–phonon coupling

\[ \Theta_n(t) = \int_{t_0}^t dt' C(t - t') U_S(t, t') M_n, \]

(8)

\[ \hat{\Theta}_n(t) = \int_{t_0}^t dt' C^*(t - t') U_S(t, t') M_n. \]

(9)

Here, \( U_S(t, t') = T_+ \exp\{-i \int_{t_0}^t d\tau \mathcal{L}_S(\tau)\} \) is the time evolution operator and \( T_+ \) the time-ordering operator. The correlation functions for the reservoirs are denoted by \( C_{xx'}(t) = \text{tr}_R \{ e^{iH_S t} \Phi_x e^{-iH_S t} \Phi_{x'} \rho_R \} \) and for the thermal bath by \( C(t) = \text{tr}_P \{ e^{iH_P t} \Phi e^{-iH_P t} \Phi \rho_P \} \), where \( \rho_R \) denotes the spin-independent equilibrium density matrix of the reservoirs and \( \rho_P \) the equilibrium density matrix of the phonon bath.

2.3. Reservoir coupling

The properties of the coupling to the left and right fermionic reservoirs are described by the spectral densities \( J_L(\omega) \) and \( J_R(\omega) \), respectively, so that one can choose different spectral densities for the couplings to the left and to the right lead. In the following only the coupling to the left lead is described in detail for simplicity. Therefore, we will only use \( J_L(\omega) \) in the
following. One should be aware of the fact that the respective Fermi energies of the leads enter into the coupling terms and thus the coupling is in general different even if the same form and strength of the spectral density is chosen. For a dense spectrum, $J_L(\omega)$ is a smooth function and one can approximate it by a numerical decomposition into few Lorentzian functions [27]

$$J_L(\omega) = \sum_{k=1}^{N_k} \frac{p_k}{4\Omega_k(\omega - \Omega_k)^2 + \Gamma_k^2}$$

(10)

with real fitting parameters $p_k$, $\Omega_k$ and $\Gamma_k$. Using the theorem of residues and denoting the Fermi function as $n_F$ yields [27]

$$C_{12}(t) = \sum_{k=1}^{N_k} \frac{p_k}{4\Omega_k} \left(n_F(-\Omega_k^+ + E_F)e^{-\gamma_k t} - \frac{2i}{\beta} \sum_{k=1}^{N_k} J_L(v_k)e^{-iv_k t} \right) \equiv \sum_{k=1}^{N_k+N_R} a_{12}^k e^{\gamma_k^* t},$$

(11)

$$C_{21}(t) = \sum_{k=1}^{N_k} \frac{p_k}{4\Omega_k} \left(n_F(\Omega_k^- - E_F)e^{\gamma_k t} - \frac{2i}{\beta} \sum_{k=1}^{N_k} J_L(v_k)e^{iv_k t} \right) \equiv \sum_{k=1}^{N_k+N_R} a_{21}^k e^{\gamma_k^* t}$$

(12)

with the abbreviation $\Omega_k^\pm = \Omega_k \pm i\Gamma_k$ and the Matsubara frequencies $v_k = \frac{2\pi k + \pi}{\beta} + E_F$. The infinite sums over $v_k$ can be truncated at a finite value depending on the temperature $T$ and the spectral width of $J_L(\omega)$. With these forms of $C_{12}$ and $C_{21}$ one can obtain a set of differential equations for the set of auxiliary density operators $\Lambda_{s_{x'}}(t)$ and $\hat{\Lambda}_{s_{x'}}(t)$ [27]

$$\frac{\partial}{\partial t} \Lambda_{s_{x'}}(t) = a_{s_{x'}} \Lambda_{s_{x'}}(t) + \gamma_{s_{x'}}^* \Lambda_{s_{x'}}^*(t),$$

(13)

$$\frac{\partial}{\partial t} \hat{\Lambda}_{s_{x'}}(t) = (a_{s_{x'}})^* K_{s_{x'}} - i[H_s(t), \hat{\Lambda}_{s_{x'}}(t)] + (\gamma_{s_{x'}})^* \hat{\Lambda}_{s_{x'}}^*(t),$$

(14)

which yield $\Lambda_{s_{x'}}(t) = \sum_{k=1}^{N_k+N_R} \Lambda_{s_{x'}}^k(t)$ and $\hat{\Lambda}_{s_{x'}}(t) = \sum_{k=1}^{N_k+N_R} \hat{\Lambda}_{s_{x'}}^k(t)$.

2.4. Phonon–bath coupling

Again the only quantity needed to describe the coupling to the phonon bath is the spectral density function $J_P(\omega)$. It contains information on the frequencies of the bath modes and their coupling to the system [51]. Several forms of the spectral density are used in the literature either based on model assumptions or based on the analysis of numerical calculations. Meier and Tannor [52] used a numerical decomposition of the spectral density which is not restricted to any special form of spectral density

$$J_P(\omega) = \sum_{k=1}^{N_P} \frac{\hat{p}_k}{\frac{\omega}{(\omega + \hat{\Omega}_k)^2 + \hat{\Gamma}_k^2}}$$

$$= \sum_{k=1}^{N_P} \frac{\hat{p}_k}{\frac{1}{(\omega + \hat{\Omega}_k)^2 + \hat{\Gamma}_k^2} - \frac{1}{(\omega + \hat{\Omega}_k)^2 + \hat{\Gamma}_k^2}}$$

(15)
with arbitrary real parameters $\hat{\rho}_k$, $\hat{\Theta}_k$ and $\hat{\Gamma}_k$. For the present studies the spectral density is taken in the Ohmic form with exponential cutoff

$$J_p(\omega) = \xi \omega \exp(-\omega/\omega_c).$$

(16)

In this case three terms ($N_p = 3$) in equation (15) were needed for an accurate fit [52]. Using equation (15) and the theorem of residues it is convenient to calculate the bath correlation function

$$C(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} J_p(\omega) \frac{e^{i\omega t}}{e^{\beta\omega} - 1},$$

(17)

which, as a consequence from equation (15), can be expressed as a sum of exponentials [52]–[54] and therefore allows for further analytical treatment

$$C(t) = \frac{2i}{\beta} \sum_{k=1}^{N_p} J_p(i\hat{\nu}_k) e^{-\hat{\nu}_k t} + \sum_{k=1}^{N_p} \frac{\hat{p}_k}{4\Omega_k \hat{\Gamma}_k} \left\{ e^{i\hat{\Omega}_k^+ t} n_B(\hat{\Omega}_k^+) + e^{-i\hat{\Omega}_k^- t} (n_B(\hat{\Omega}_k^-) + 1) \right\}$$

$$= \sum_{k=1}^{N_p+N_p'} a^k e^{\nu_k t},$$

(18)

using $\hat{\Omega}_k^+ = \hat{\Theta}_k + i\hat{\Gamma}_k$, $\hat{\Omega}_k^- = \hat{\Theta}_k - i\hat{\Gamma}_k$, the Bose–Einstein distribution $n_B(\omega) = \exp(\beta\omega) - 1)^{-1}$ and the Matsubara frequencies $\hat{\nu}_k = 2\pi k / \beta$. The auxiliary operators $\Theta_n^k$ and $\hat{\Theta}_n^k$ can be determined via

$$\frac{\partial}{\partial t} \Theta_n^k(t) = a^k M_n - i[H_S(t), \Theta_n^k(t)] + \gamma^k \Theta_n^k(t),$$

(19)

$$\frac{\partial}{\partial t} \hat{\Theta}_n^k(t) = (a^k)^* M_n - i[H_S(t), \hat{\Theta}_n^k(t)] + (\gamma^k)^* \hat{\Theta}_n^k(t),$$

(20)

which yield $\Theta_n(t) = \sum_{k=1}^{N_p+N_p'} \Theta_n^k(t)$ and $\hat{\Theta}_n(t) = \sum_{k=1}^{N_p+N_p'} \hat{\Theta}_n^k(t)$.

The obtained coupled differential equations (5), (13), (14), (19) and (20) can be integrated numerically applying, for example the Runge–Kutta scheme.

3. Current operator

Using the electron number operator of the left lead with the summation performed over the reservoir degrees-of-freedom $N_l = \sum_{\omega} b_{\omega}^\dagger b_{\omega}$, the expression for the current from the left lead to the wire is given by [27]

$$I_1(t) = e \frac{d}{dt} \text{tr} \left\{ N_l \rho_S(t) \right\}$$

$$= -ie \text{tr} \left\{ [N_l, H(t)] \rho_S(t) \right\} = \text{tr} \left\{ \Lambda(t) \rho_S(t) \right\}.$$  \hspace{0.5cm} (21)

Here $e$ denotes the elementary charge ($e > 0$). The current operator introduced above can be expressed as

$$\Lambda(t) \rho_S(t) = e \left[ \Lambda_{12}(t) \rho_S(t) c_1^\dagger - c_1^\dagger \rho_S(t) \Lambda_{12}(t) + c_1 \rho_S(t) \Lambda_{21}(t) + \Lambda_{21}(t) \rho_S(t) c_1 \right].$$

(22)

The above equation describes the current $I_1(t)$ between the left lead and the molecule. A similar expression holds for $I_2(t)$ from the right lead into the molecule. In a steady state and after

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averaging over one period of the driving field, $I_I$ and $I_r$ have the same magnitude but opposite signs and therefore a total transient current through the molecular junction can be defined as

$$I_I(t) = (I_I(t) - I_r(t))/2.$$ The time-dependent average current $I_I(t)$ will be determined below by averaging $I(t)$ over five periods of the fast oscillating carrier field.

In the following, we want to analyze the currents further and therefore split the currents into their components. One can rewrite the current operator between the left lead and the wire as

$$I_{I, I} = I_+ I_ -$$

which describe the tunneling of an electron from the left lead to the wire and the opposite process, respectively. Introducing the currents

$$I_+ (t) = \text{tr} \{ I_+ \rho_S(t) \}$$

and

$$I_- (t) = \text{tr} \{ I_- \rho_S(t) \},$$

one gets $I_I = I_+ - I_-$ as shown in figure 2.

Furthermore, the current between the individual sites in the molecular wire can be determined. Within the tight-binding model of the wire the operator for the current between two sites is given by

$$I_{i, i+1} = ie \Delta \left( c_i^\dagger c_{i+1} - c_{i+1}^\dagger c_i \right).$$

Using this operator the value of the current between two sites of the wire can be determined as

$$I_{i, i+1} = \text{tr} \{ I_{i, i+1} \rho_S(t) \} = ie \Delta \text{tr} \left\{ (c_i^\dagger c_{i+1} - c_{i+1}^\dagger c_i) \rho_S \right\}. $$

In the steady state regime and without external fields the current $I_{i, i+1}$ shall have the same absolute value as the current between lead and wire $I_I$. 

**Figure 2.** Scheme of the current between left reservoir and left-most site of the wire. $I_+$ and $I_-$ denote the current from the left lead into the wire and the opposite process, respectively. $I_I = I_+ - I_-$ describes the net current.
4. Numerical simulation

After describing the system and the QMEs, we now want to describe the numerical results of influencing the system by an external field. A wire consisting of two sites is chosen with equal site energies denoted as \( \epsilon_0 \). Since we use a bias voltage symmetric with respect to this energy, the Fermi energies are given as \( E_{F,L} = \epsilon_0 + V_b/2 \) and \( E_{F,R} = \epsilon_0 - V_b/2 \). For the coupling between wire and leads a simple spectral density with only one Lorentzian \((m = 1)\) was chosen. With \( \Omega_1 = \epsilon_0 \) the maximum of the coupling is located at \( \epsilon_0 \). Using \( \Gamma_1 = 5\omega \) the coupling between the leads and the system is close to the wide-band limit. Choosing \( p_1 = 0.04\omega \Omega_1 \Gamma_1^2 \) we obtain a maximum coupling strength of \( 0.01\omega \) which is smaller than the thermal energy \( k_B T = 0.025\omega \). The intersite coupling \( \Delta \) is \( 0.01\omega \) and therefore much smaller than the external field energy \( \omega \). So the results below are all within the high-frequency limit concerning the laser field. As discussed above, for the coupling to the phonon bath an Ohmic spectral density with exponential cutoff as given in equation (16) with \( \omega_c = 0.05\omega \) is used. The carrier frequency \( \omega \) is set to 1 eV. With those energy settings, a time unit in the system corresponds to 0.66 fs.

4.1. CDT

First, we describe the results for the phenomenon of CDT. CDT works with monochromatic laser fields [35] as well as with laser pulses [39] to control the current through molecular wires. It was shown that within the high-frequency limit of a monochromatic laser field the condition necessary for CDT is that the ratio of laser amplitude \( A \) and laser frequency \( \omega \) has to be a root of the zeroth-order Bessel function \( J_0(A/\omega) \). So the phenomenon can be observed, e.g. for amplitudes equaling \( 2.405\omega \) or \( 5.502\omega \). The effect can be modeled by replacing the intersite coupling \( \Delta \) by an effective coupling \( \Delta_{\text{eff}} = \Delta J_0(A/\omega) \) [9]. As shown previously, CDT also works to suppress the current in a single-site molecular junction, i.e. also the current between the leads and the site can be effectively reduced [40]. This already poses the question if in a molecular junction with two sites, only the current between the sites or, at the same time, between the sites and between sites and leads are suppressed.

As the name indicates, CDT is a coherent phenomena and can be hindered by dissipative effects, i.e. with the addition of a phonon bath. This way the electrons can exchange energy with the environment and their states lose some of their coherence. So the electrons will be forced towards the site with lower site energy, similar to a spin-boson model. But since the phonon–bath coupling acts on the system only, no electrons will be forced into or out of the leads. In the figures described below, the current is reduced while increasing the damping strength. As shown in figure 3, for a monochromatic external field the current through the junction completely vanishes for certain amplitudes if no decoherence effects are present. When introducing a dissipative bath the effect of CDT gets washed out. Because of the perturbative treatment of the phonon–bath coupling only rather weak couplings can be utilized to demonstrate the effect for the temperatures used. The effect of CDT gets washed out at values of \( A/\omega \) which are equal to the roots of the Bessel function, i.e. the current increases while the current for ratios \( A/\omega \) between the roots of the Bessel function decreases with increasing damping. Similar results have been reported previously using the Floquet approach [35].

In a next step, we want to understand the effect in more detail. Therefore, we divide the current between the left lead and the wire into two parts as defined in equations (23) and (24). In the top panel of figure 4, the currents \( I_+ \) and \( I_- \) are shown whereas in the bottom panel the
Figure 3. Average current $\bar{I}$ as a function of laser amplitude $A$ for a monochromatic external field and different phonon–bath coupling parameters $\xi$.

Figure 4. Average value of the partial currents $I_+$ and $I_-$ between lead and wire and $I_{12}$ as function of the laser amplitude $A$. In the top panel, the upper two lines show the current $I_-$ and the lower two show $I_+$. Intersite current $I_{12}$ is displayed. For those amplitudes which fulfill the CDT condition one can observe in figure 4 that $I_+$ and $I_-$ have almost the same absolute value for the undamped case, i.e. $\xi = 0$. This means that the tunneling of an electron from the left lead into the wire and the opposite process have the same amplitude but opposite sign. So the net current $I_l = I_+ - I_-$ between left lead and wire vanishes. This is due to the special situation between the leads and the wire. Since the electrons are localized on the individual sites, there is no exchange between the sites and the intersite current $I_{12}$ is zero.
Figure 5. The average value of the net current $\bar{I}$ for different phonon–bath coupling parameters $\xi$ is shown in the upper panel. The bottom panel shows the shape of the laser field with a maximum amplitude $A = 2.405\omega$.

Adding dephasing effects to the system results in different absolute values of $I_+$ and $I_-$ and non-vanishing $I_{12}$ even for amplitudes fulfilling the CDT condition.

As shown previously by the current authors [39], it is also possible to make use of the phenomenon of CDT together with ultra-short laser pulses to suppress the current for short periods. As an example, in the bottom panel of figure 5, we show a laser pulse which follows a half-Gaussian form, a constant part, and, again, a half-Gaussian shape. In the same figure one can also see the resulting averaged current. Again the averaging is over a few cycles of the carrier frequency. The maximum amplitude of the laser amplitude fulfills the CDT condition, i.e. it equals $2.405\omega$ for about 200 fs. During this part of the pulse the averaged current is completely suppressed if no phonon bath is present. Cranking up the phonon–bath coupling constant $\xi$ from zero over $5\Delta$ and $10\Delta$ to $15\Delta$ one can observe that the suppression is not complete anymore, i.e. already at $\xi = 5\Delta$ the current is nonzero at all times. Some additional oscillatory behavior present in the non-damped case disappears when the phonon–bath coupling is introduced.

In figure 6, we show the partial currents $I_+$ and $I_-$ as well as the intersite current $I_{12}$ with and without coupling to a phonon bath. As can be seen, the net current between lead and wire $I_l$ is mainly determined by $I_+$ for the current parameters and $I_-$ only has very small nonzero values while the laser field is non-vanishing. The suppression of the current $I_l$ therefore is mainly a suppression of $I_+$. Interestingly enough the intersite current $I_{12}$ transiently behaves different from the other currents discussed for this setup so far. In the case without damping there is a current peak going to values of roughly twice the value of the steady-state current without laser field. Also $I_l$ shows a peak at this moment in time but this is less pronounced. With damping $\xi = 10\Delta$ the current $I_{12}$ still shows quite some oscillatory behavior which is visible neither for $I_l$ nor for the partial currents $I_+$ and $I_-$. This detailed analysis clearly shows that under the influence of time-dependent laser pulses the current in different parts of the system behaves rather differently though in the steady-state limit all these currents behave as expected.
Figure 6. Average values of the partial currents $I_+$ and $I_-$ between lead and wire and $I_{12}$ as function of time for the laser pulse given in figure 5. In the top panel the upper two lines show the current $I_-$ and the lower two show $I_+$.

As mentioned previously [40], the average current $I$ induced by a time-dependent laser pulse is of course dependent on the number $n_{av}$ of periods used in the averaging procedure. Any averaging procedure will not only average over the highly oscillating carrier field but also smooth the envelope function. For a Gaussian shape of the laser pulse the averaged current will still be close to a Gaussian form although slightly shifted but there are only minor changes when changing $n_{av}$ between 2 and 10. The averaging process does not depend much on $n_{av}$ for monochromatic laser pulses.

4.2. Optimal control theory

For the current suppression in the CDT case we employed a predefined pulse and calculated the corresponding current. Also the inverse situation is possible: first a desired electron flow pattern is defined and then the corresponding laser field is determined which achieves this goal by applying optimal control theory. As detailed in a previous publication [15], such an optimal control field to suppress the current can be calculated for simple setups. So like CDT, optimal control theory can be used to suppress the current through the wire. One difference is that no high-frequency carrier field is necessary and so the simplest situation as displayed in figure 7 shows a rather simple external control field. This field was calculated without the coupling to a phonon bath [15]. The field mainly moves one site of the wire out of the energetical conduction window. At the same time the field has to correct for population flowing onto and off the wire sites which can also result in transient currents. In a next step a phonon bath is coupled to the system while the laser field is not changed, i.e. it is still optimized to suppress the current in the undamped setup. Nevertheless the current is still roughly suppressed in the desired time frame. In contrast to the previously discussed CDT situation the damping does not simply destroy the current suppression but for the second half of the time window the current is even in a way over-suppressed, i.e. the current flows in the opposite direction.

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Figure 7. In the upper panel the time-dependent current $I$ for different phonon–bath coupling parameters $\xi$ is shown for the laser field displayed in the lower panel.

Figure 8. Same as in figure 6 but for the laser pulse shown in figure 7.

As in the previous subsection for the CDT situation, figure 8 shows the partial currents $I_+$ and $I_-$ as well as the intersite current $I_{12}$ with and without coupling to a phonon bath. In the CDT situation discussed above mainly $I_+$ was suppressed while here $I_+$ and $I_-$ are of the same absolute value which is rather large compared to the values in figure 6 but of opposite sign, so that $I_l$ becomes very small. The intersite current is also very small in the undamped case but remains nonzero. Here we have to emphasize that the target was to suppress $I_l$ and not $I_{12}$ so it is consistent with the theory of optimal control that $I_{12}$ is nonzero. Turning on damping without further adapting the laser field, the cancellation of $I_+$ and $I_-$ is not exact anymore leading to a nonzero current $I_l$. In principle, a new laser field would have to be determined after turning on the coupling to the phonon bath as has been done here for electron transfer in [56]. This has
Figure 9. The lower panel shows the laser field obtained by optimal control theory for $\xi = 0$. The upper panel shows the highly oscillating current $I$ and its average value $\bar{I}$. The average value $\bar{I}$ is also shown for two different phonon–bath coupling strengths.

not been done here for the situation of electron transport so far since in this case, it results in a coupling to two fermionic reservoirs and one bosonic reservoir. For such a task special care has to be taken of an optimal implementation of the numerical solution of the QME and the equations for the auxiliary operators.

To study situations closer to that of CDT a high-frequency carrier field was added to the target pattern of the current flow so that only the average current becomes zero. This leads to an oscillating electric field as shown in figure 9 and also discussed in [15]. Interestingly enough the mechanism found by optimal control theory is still a shift of the levels out of the energetical conduction window. In principle, the CDT mechanism would also be a valid solution of the inverse problem. The influence of the phonon bath is very similar to that in the case without the high-frequency terms.

5. Conclusions

In this paper, we described and analyzed two different approaches to suppress the current through a tight-binding model of a molecular wire using ultra-fast laser pulses. Both formalisms succeed in reducing the current through the wire when using short laser pulses, even in the presence of a weak phonon–bath coupling. But the two theories use different physical approaches to achieve the goal: in the first formalism the phenomena of CDT is employed basically reducing the effective coupling between the leads and the wire and between the sites within the wire. As discussed above the influence of the laser field on the transport between a lead and the wire behaves qualitatively different from the influence of the transport between the sites of the wire, i.e. localizing the electrons at the individual sites. Within the wire the effective coupling $\Delta_{\text{eff}}$ is reduced to zero while in the case of coupling between a lead and the wire the partial currents might be non-vanishing but cancel out each other.
The solutions found by optimal control theory in a previous publication [15] do move at least one of the levels of the wire out of the energetical conduction window while at the same time controlling the decay and increase of the population of these sites. The population decay or increase of individual levels would otherwise lead to transient currents itself. This optimal control method has the advantage of a free choice of the predefined current flow pattern. The solution of this formalism is also more stable against dephasing effects since the effect is based on a shift of the energy levels. These levels are not influenced by the coupling to the phonon bath, at least when neglecting the minor Lamb shift. Only the population of the sites is changed by the relaxation effects. On the other hand, the suppression of tunneling in CDT is certainly influenced much more by the dephasing since it is intrinsically based on the coherences in the system to quench the transfer between the sites. These coherences are certainly very sensitive to adding dephasing effects. Furthermore, an important advantage of the coherent control approach is the possibility to include the phonon bath while determining the laser pulse suppressing the current as has been shown, for example, for electron transfer processes [56]. In the current paper, we calculated the effect of a phonon bath on the current through the wire under the effect of a laser pulse from optimal control theory. Such a determination of damping effects on the corresponding laser fields is so far not possible for pulses based on CDT.

With the present study, we hope to show some possible future direction of controlling the current through a molecular wire by ultra-fast laser pulses creating ideal optoelectrical switches and also to stimulate further experimental investigations in this direction. Here we restricted ourselves to two-site systems but extensions to general \(N\)-site systems shall be possible by using the fact that coherences between system states with different numbers of electrons, (Fock space coherences) do not contribute to the transport to second order in the system–lead coupling [57]. Concerning possible systems, recent theoretical investigations discuss trans-polyacetylene oligomers [23] or oligophenylene molecules [58] as candidates for an experimental implementation of light-induced effects. It is also shown how to derive tight-binding models for such systems. Furthermore, our present study can be extended to lower temperatures and therefore double quantum dots might be possible candidates for experiments as well.

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