

Tailoring current flow patterns through molecular wires using shaped optical pulses

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Combining the features of molecular wires and femtosecond laser pulses gives the unique opportunity to optically switch electron currents in molecular devices with very high speed. Based on a weak-coupling approximation between wire and leads, a quantum master equation for the population dynamics and the electric current through the molecular wire has been developed, which allows for arbitrary time-dependent laser fields interacting with the wire. This formalism is combined with the theory of optimal control, leading to an innovative control of targets distributed in time in open quantum systems. For a tight-binding approximation of the molecular wire, we show how to compute the laser pulses to switch the current through the wire on and off. With this approach, the current flow pattern of the current in time can be chosen in an almost arbitrary fashion.

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I. INTRODUCTION

The field of molecular electronics and especially of molecular wires has attracted much interest recently experimentally as well as theoretically.^{1,2} One rather new aspect is the possibility to switch the current by laser pulses. Experimentally, it is very hard to focus the laser light onto the molecular junction with a width below the diffraction limit of the light. Nevertheless, the development in tip-enhanced near-field scanning optical microscopy looks promising.³ Another possible route with auspicious results is the coupling of a laser field to an adsorbed molecule on a surface with the help of scanning tunneling microscopy.⁴ Several experiments in this general direction have been performed recently (e.g., Refs. 5–8).

To theoretically investigate the effect of time-dependent fields on molecular junctions, one can, for example, apply nonequilibrium Green's functions,⁹ but in most approaches so far, the coupling of the wire to the leads was treated perturbatively.^{10–14} Some of these treatments utilize knowledge from the field of dissipative quantum dynamics and derive quantum master equations (QMEs) to describe the current through a molecular wire. The QMEs easily allow one to apply external optical fields which influence the dynamics in a direct manner by changing the wire part but also in an indirect way by influencing the wire-lead coupling. For monochromatic fields, the Floquet theory has been employed.^{10,15–17} We extended a technique developed in the field of dissipative quantum dynamics in which a special parametrization of the so-called spectral density of the reservoir leads to a set of coupled equations for a primary and several auxiliary density matrices.¹⁸ This formalism allows for an arbitrary time dependence of the laser pulses.^{13,19,20}

So far, only the influence of a given laser field on the current through the molecular junction has been studied. Using, for example, a cw laser with suitable amplitude, the phenomenon of coherent destruction of tunneling (CDT) can be observed.¹⁷ Recently, we demonstrated^{19,20} that one can also suppress the current using short Gaussian laser pulses. The maximum amplitude of these pulses has to fulfill the same conditions as for a cw-laser pulse.

The inverse problem is treated in this paper as follows. Given a predefined current flow pattern, one tries to determine that laser pulse which achieves this current. This kind of control problem was studied in detail for simple chemical reactions in gas phase as well as in liquid phase experimentally²¹ as well as theoretically.²² First approaches to coherent control of molecular dynamics were based on intuitive schemes such as the Brumer-Shapiro procedure in the frequency domain²³ or the pump-dump scheme in the time domain.²⁴ The control algorithms by Judson and Rabitz,²⁵ as well as the Krotov algorithm,²⁶ give complete freedom to the laser pulses to be shaped. Recently, this optimal control formalism was extended to also handle target states distributed in time.^{27–29}

Here, we generalize the control formalism to situations with time-dependent targets in open quantum systems and apply it to molecular wires with a small number of sites. 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. Although we concentrate on the topic of molecular wires here, the techniques described below can, in principle, be applied to coupled quantum dots as well.

II. MODEL

The time-dependent Hamiltonian of the investigated molecular junction is separated into the relevant system $H_S(t)$, mimicking the wire, and reservoirs H_R , modeling the leads,

$$H(t) = H_S + H_F(t) + H_R + H_{SR}, \quad (1)$$

with wire-lead coupling H_{SR} . Denoting the creation (annihilation) operator at site n by c_n^\dagger (c_n), the tight-binding description of the electrons in the molecular wire reads as

$$H_S = \sum_n \varepsilon_n c_n^\dagger c_n - \Delta \sum_n (c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n). \quad (2)$$

The first term describes the on-site energies and the second term the nearest-neighbor hopping. By including electron

spin and interaction, we would expect, in certain parameter regimes, a similar qualitative response of the system on the laser pulse as has also been shown for Gaussian laser pulses.³⁰ Spin and electron interaction of course do introduce extra features which can be influenced by the laser field accordingly. By denoting the dipole operator, which will be detailed below, by μ , the coupling between the wire and the laser field $E(t)$ reads as $H_F(t) = -\mu E(t)$.

The environment of the wire consists of two electronic leads that are modeled by two independent reservoirs of uncorrelated electrons in thermal equilibrium. For each lead, the Hamiltonian H_R is given by $H_R = \sum_q \omega_q b_q^\dagger b_q$ with b_q^\dagger creating and b_q annihilating an electron in the corresponding reservoir mode $|q\rangle$ with energy ω_q . We set $\hbar \equiv 1$. In further derivations, we will only refer to the left lead, but the formalism has to be applied as well to the right lead coupled to the last site N of the wire. The coupling of the left electronic lead with the first site of the wire is given by

$$H_{SR} = \sum_{x=1}^2 K_x \Phi_x = \sum_q (V_q c_1^\dagger b_q + V_q^* b_q^\dagger c_1), \quad (3)$$

with $\Phi_1 = \sum_q V_q b_q$, $\Phi_2 = \sum_q V_q^* b_q^\dagger$, $K_1 = c_1^\dagger$, $K_2 = c_1$, and a wire-lead coupling V_q for each reservoir mode.

Starting with the time-convolutionless approach, a time-local QME based on a second-order perturbation theory in the molecule-lead coupling was developed for the reduced density matrix $\rho(t)$ of the molecule,^{13,19}

$$\frac{\partial \rho(t)}{\partial t} = -i\mathcal{L}_S \rho(t) - i\mathcal{L}_F(t) \rho(t) - D(t) \rho(t), \quad (4)$$

$$D(t) \rho(t) = \sum_{xx'} [K_x \Lambda_{xx'}(t) \rho(t) - \Lambda_{xx'}(t) \rho(t) K_x - K_x \rho(t) \hat{\Lambda}_{xx'}(t) + \rho(t) \hat{\Lambda}_{xx'}(t) K_x], \quad (5)$$

with auxiliary operators for the wire-lead coupling,

$$\Lambda_{xx'}(t) = \int_{t_0}^t dt' C_{xx'}(t-t') U_S(t, t') K_{x'}, \quad (6)$$

$$\hat{\Lambda}_{xx'}(t) = \int_{t_0}^t dt' C_{xx'}^*(t-t') U_S(t, t') K_{x'}. \quad (7)$$

Here, we employed the definitions $U_S(t, t') = T_+ \exp\{-i \times \int_{t'}^t d\tau [\mathcal{L}_S + \mathcal{L}_F(\tau)]\}$, $\mathcal{L}_S = [H_S, \bullet]$, and $\mathcal{L}_F(\tau) = [H_F(\tau), \bullet]$ with the time-ordering operator T_+ and the reservoir correlation functions $C_{xx'}(t)$. For later convenience, we also introduce $\mathcal{L}_\mu = [\mu, \bullet]$. Using the electron number operator $N_l = \sum_q c_q^\dagger c_q$ of the left lead with the summation performed over the reservoir degrees of freedom yields

$$I_l(t) = e \frac{d}{dt} \text{tr}_S \{N_l \rho(t)\} = \text{tr}_S \{\mathcal{I}_l(t) \rho(t)\}, \quad (8)$$

with the current operator

$$\mathcal{I}_l(t) \rho(t) = e [c_1^\dagger \hat{\Lambda}_{12}(t) \rho(t) - c_1^\dagger \rho(t) \hat{\Lambda}_{12}(t) + c_1 \rho(t) \hat{\Lambda}_{21}(t) - c_1 \hat{\Lambda}_{21}(t) \rho(t)] \quad (9)$$

and the elementary charge e . This equation describes the current $I_l(t)$ from the left lead into the molecule. A similar expression holds for $I_r(t)$ from the right lead into the molecule. As in a steady-state situation, the net transient current can be defined as $I(t) = [I_l(t) - I_r(t)]/2$. In addition, we define the net current operator $\mathcal{I}(t) = [\mathcal{I}_l(t) - \mathcal{I}_r(t)]/2$.

III. OPTIMAL CONTROL

The aim of this study is to determine laser pulses that result in a predefined effect on the current through the molecular wire. This is achieved by extremizing a control functional. Using techniques developed previously for time-dependent targets,^{28,31} we define (as part of the functional) the difference between a preselected current pattern $P(t)$ and the current obtained from the QME as

$$J_0(E) = \int dt \{P(t) - \text{tr}_S [\mathcal{I}(t) \rho(t)]\}^2. \quad (10)$$

To this, we add a second part, ensuring convergence,³¹

$$J(E) = J_0(E) + \frac{\lambda}{2} \int_{t_0}^{t_f} dt \frac{[E(t) - \tilde{E}(t)]^2}{s(t)}, \quad (11)$$

with $\tilde{E}(t)$ being the laser field of the previous iteration step and λ a penalty parameter. Introducing the time-dependent function $s(t)$, we avoid a sudden switch-on and switch-off behavior of the control field at the beginning and the end of the propagation time. In the present study, either a Gaussian or a squared sine function has been employed. The numerical results are rather independent of the actual choice.

In order to calculate the extremum of the functional in Eq. (11), the functional derivative $\delta J(E)/\delta E(t)$ has to vanish. In the present case, this yields

$$E(t) = \tilde{E}(t) - \frac{s(t)}{\lambda} \text{tr}_S \left\{ \chi(t) \left[i\mathcal{L}_\mu \rho(t) - \frac{\delta D(t)}{\delta E(t)} \rho(t) \right] \right\} - \frac{s(t)}{\lambda} \text{tr}_S \left\{ \frac{\delta \mathcal{O}(t)}{\delta E(t)} \rho(t) \right\}, \quad (12)$$

with the operators

$$\chi(t) = \int_t^{t_f} d\tau \mathcal{O}(\tau) U(\tau, t, E), \quad (13)$$

$$\mathcal{O}(\tau) = 2\{\text{tr}_S [\mathcal{I}(\tau) \rho(\tau)] - P(\tau)\} \mathcal{I}(\tau) \quad (14)$$

and the time-evolution operator $U(\tau, t, E)$. The functional derivatives $\delta D/\delta E$ and $\delta \mathcal{O}/\delta E$ are straightforward to evaluate but lengthy and will be given elsewhere. For the operator $\chi(t)$, one can derive the QME

$$\frac{\partial \chi(t)}{\partial t} = -i\mathcal{L}_S\chi(t) - i\mathcal{L}_F(t)\chi(t) + \bar{D}(t)\chi(t) - \mathcal{O}(t), \quad (15)$$

where the inhomogeneous term $\mathcal{O}(t)$ reflects the time-distributed target state. The wire-lead coupling operator $\bar{D}(t)$ in this QME is given by

$$\begin{aligned} \bar{D}(t)\chi(t) = & \sum_{xx'} [\chi(t)K_x\Lambda_{xx'}(t) - K_x\chi(t)\Lambda_{xx'}(t) \\ & - \hat{\Lambda}_{xx'}(t)\chi(t)K_x + \hat{\Lambda}_{xx'}(t)K_x\chi(t)]. \end{aligned} \quad (16)$$

While Eq. (4) is propagated forward in time, Eq. (15) is propagated backward in time. These two equations can now be solved in an iterative fashion. One starts with an equilibrated state on the wire $\rho(0)$ at time $t_0=0$ which is unchanged during the iterative process and chooses an initial guess for the field $E(t)$. The density matrix $\rho(t)$ is propagated forward from initial time $t=t_0$ to final time $t=t_f$ using $E(t)$. In the second step, one obtains a new field $E(t)$ from Eq. (12) in order to propagate the target operator $\chi(t)$ backward from $t=t_f$ to $t=t_0$. One stores the field $E(t)$ as $\tilde{E}(t)$ for the next step, in which we again calculate $E(t)$ and propagate $\rho(t)$ from t_0 to t_f with the initial condition $\rho(t_0)$. This scheme is repeated iteratively until convergence. Some of the density matrices and fields can be stored during the iterative process to save computational effort.²⁹

IV. NUMERICAL RESULTS AND CONCLUSIONS

For the calculations shown below, we consider a wire consisting of two sites without spin, equal site energies $\varepsilon_1 = \varepsilon_2$, intersite coupling $\Delta=0.1$ eV, and a dipole operator $\mu = (c_1^\dagger c_1 - c_2^\dagger c_2)/2$. A bias $V_b=0.4$ eV symmetric with respect to the site energies ε_n determines the Fermi energies $\varepsilon_{F,l} = \varepsilon_1 + V_b/2$ and $\varepsilon_{F,r} = \varepsilon_2 - V_b/2$, which describe the occupation of the reservoir modes. The coupling between the wire and the leads is almost in the wide-band limit and the maximum coupling strength is 0.1Δ . For the first and third examples below, λ was set to 0.003 and for the second calculation to 0.0006.

As a first simple example of current control, we consider a case in which the current is initially constant and the goal is to suppress the current following a half-Gaussian form, a constant part, and, again, a half-Gaussian shape for the increasing current. In Fig. 1, the current target $P(t)$ is shown together with the obtained current and the corresponding laser field $E(t)$. Before $t_0=0$, the laser field is turned off and the system is equilibrated, i.e., in a steady state, leading to a time-independent current. As can be seen, the optimal control current matches the target very well. This optimal laser pulse mainly moves the levels of the wire out of and back into the energetic conduction window. In the middle of the time interval, the energy levels have to be readjusted because of the population decay on the wire sites.

In the second example, the complexity of the control task is increased. As shown in Fig. 2, the current target $P(t)$ is a symmetric double step function and the goal is achieved by the optimal control algorithm rather accurately. Only at the

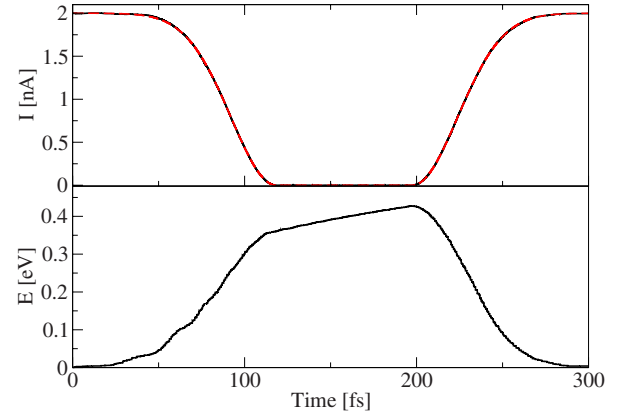


FIG. 1. (Color online) Target current $P(t)$ (dashed) and calculated current $I(t)$ (solid) in the upper panel. The control field $E(t)$ is shown in the lower panel.

last step there some visible deviation between the target and achieved currents. The optimized laser field in the lower panel of Fig. 2 also shows steplike features but, additionally, oscillations and peaks. In contrast to the previous control target, the rapidly changing target current pattern requires larger changes in the electric field. To compensate the effect of these large peaks on the current at later times, additional oscillations of the field are needed to achieve constant values of the current at the plateaus.

In many experimental setups, the laser field has a high carrier frequency and a more slowly varying envelope function. To mimic such a scenario, we created a target for the current which consists of a fast oscillating pattern with $\omega = 1$ eV modulated by a slowly varying envelope function, namely, a form as in Fig. 1. This pattern, together with the current achieved by the optimal control algorithm, is shown in the middle panel of Fig. 3. Despite the rapidly varying target function, the goal is accurately achieved. Similar to previous studies of CDT, we also calculated a mean current which is determined by averaging the current over a few cycles of the carrier frequency (here five periods). This procedure can, of course, be performed for the target as well as

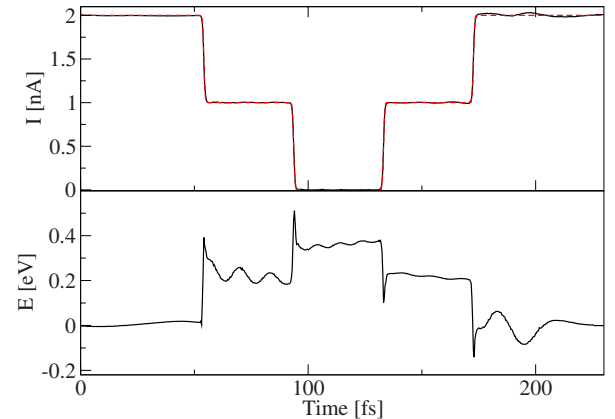


FIG. 2. (Color online) Same as in Fig. 1 for a different control target.

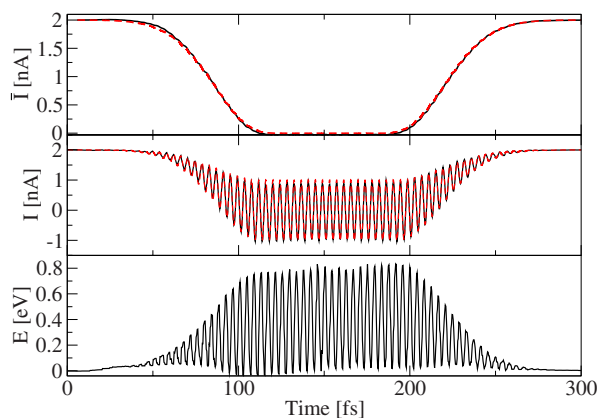


FIG. 3. (Color online) A control target including a highly oscillating pattern. The control target (dashed) and the achieved current (solid) are displayed in the middle panel, while in the top panel, an average over five oscillatory periods is shown. The control field is given in the lowest part of the figure.

for the shaped current, and the results are shown in the top panel of Fig. 3. As can be seen, the average current is suppressed nicely in such a scenario.

In previous studies,^{17,19,20} CDT was utilized to suppress the current, which is possible for certain values of the amplitude A of the laser field. The fraction A/ω has to be equal to a root of the zeroth-order Bessel function. In the present case, the maximal value of the field is about $A/\omega=0.8$, which is certainly far from a root of the zeroth-order Bessel function. Therefore, the present current depletion cannot be explained by the high-frequency limit of CDT but seems to be as efficient as CDT. Finding solutions other than well-known ones is actually a major advantage of the optimal control theory. Nevertheless, it would be very useful to understand the actual process behind this suppression of the current. Work in this direction is in progress.

The convergence of the iterative control algorithm for the second and third examples is displayed in Fig. 4. It shows how the value of J decreases with increasing number of it-

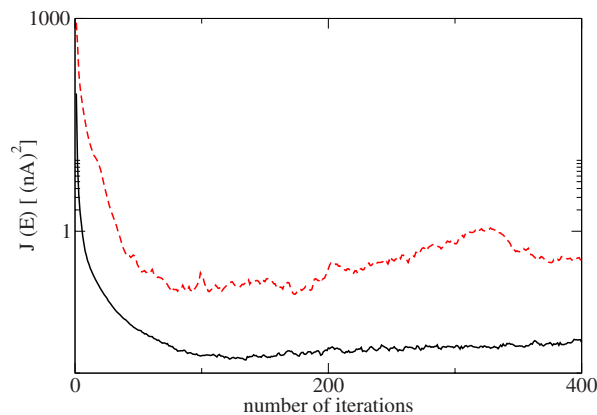


FIG. 4. (Color online) The value of the control function $J(E)$. The solid line is for the step function as shown in Fig. 2 and the dashed line is for the symmetric Gaussian shape in Fig. 3.

erations. For a simple target such as a step function, J decreases very fast and then gets more or less constant. In contrast, for a complex target with a fast oscillating function, it decreases not as fast in the beginning and later even increases slightly. To further decrease the control function, one could increase the Lagrange parameter λ for large iteration numbers.

In conclusion, we have demonstrated that it is theoretically possible to achieve a time-dependent pattern of the current through a molecular junction. The optimized current can be obtained using an optimal control field. Although we used a simplified model for a molecular wire, the present investigation shows that it is worthwhile to study the combination of molecular wires and optimal control theory on the femto-second time scale theoretically as well as experimentally. In experiment, feedback coherent control for complex systems has been successful²¹ so that an experimental implementation of the ideas described above might be feasible in the future.

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¹A. Nitzan and M. A. Ratner, *Science* **300**, 1384 (2003).

²A. W. Ghosh, P. S. Damle, S. Datta, and A. Nitzan, *MRS Bull.* **6**, 391 (2004).

³A. Hartschuh, M. R. Beversluis, A. Bouhelier, and L. Novotny, *Philos. Trans. R. Soc. London, Ser. A* **362**, 807 (2004).

⁴S. W. Wu, N. Ogawa, and W. Ho, *Science* **312**, 1362 (2006).

⁵C. Meyer, J. M. Elzerman, and L. P. Kouwenhoven, *Nano Lett.* **7**, 295 (2007).

⁶J. M. Simmons, I. In, V. E. Campbell, T. J. Mark, F. Leonard, P. Gopalan, and M. A. Eriksson, *Phys. Rev. Lett.* **98**, 086802 (2007).

⁷M. Ikeda, N. Tanifuji, H. Yamaguchi, M. Irie, and K. Matsuda, *Chem. Commun. (Cambridge)* **2007**, 1355.

⁸N. Katsonis, M. Lubomska, M. M. Pollard, B. L. Feringa, and P. Rudolf, *Prog. Surf. Sci.* **82**, 407 (2007).

⁹Y. Meir and N. S. Wingreen, *Phys. Rev. Lett.* **68**, 2512 (1992).

¹⁰S. Kohler, J. Lehmann, and P. Hänggi, *Phys. Rep.* **406**, 379 (2005).

¹¹X. Q. Li, J. Luo, Y. G. Yang, P. Cui, and Y. J. Yan, *Phys. Rev. B* **71**, 205304 (2005).

¹²I. V. Ovchinnikov and D. Neuhauser, *J. Chem. Phys.* **122**, 024707 (2005).

¹³S. Welack, M. Schreiber, and U. Kleinekathöfer, *J. Chem. Phys.* **124**, 044712 (2006).

¹⁴U. Harbola, M. Esposito, and S. Mukamel, *Phys. Rev. B* **74**, 235309 (2006).

¹⁵J. Lehmann, S. Kohler, P. Hänggi, and A. Nitzan, *Phys. Rev. Lett.* **88**, 228305 (2002).

¹⁶A. Tikhonov, R. D. Coalson, and Y. Dahnovsky, *J. Chem. Phys.* **117**, 567 (2002).

- ¹⁷J. Lehmann, S. Camalet, S. Kohler, and P. Hänggi, *Chem. Phys. Lett.* **368**, 282 (2003).
- ¹⁸C. Meier and D. J. Tannor, *J. Chem. Phys.* **111**, 3365 (1999).
- ¹⁹U. Kleinekathöfer, G.-Q. Li, S. Welack, and M. Schreiber, *Europhys. Lett.* **75**, 139 (2006).
- ²⁰G.-Q. Li, M. Schreiber, and U. Kleinekathöfer, *Europhys. Lett.* **79**, 27006 (2007).
- ²¹T. Brixner and G. Gerber, *ChemPhysChem* **4**, 418 (2003).
- ²²M. Shapiro and P. Brumer, *Rep. Prog. Phys.* **66**, 859 (2003).
- ²³P. Brumer and M. Shapiro, *Chem. Phys. Lett.* **126**, 541 (1986).
- ²⁴D. J. Tannor, R. Kosloff, and S. A. Rice, *J. Chem. Phys.* **85**, 5805 (1986).
- ²⁵R. S. Judson and H. Rabitz, *Phys. Rev. Lett.* **68**, 1500 (1992).
- ²⁶D. J. Tannor, V. Kazakov, and V. Orlov, in *Time Dependent Quantum Molecular Dynamics*, edited by J. Broeckhove and L. Lathouwers (Plenum, New York, 1992), pp. 347–360.
- ²⁷A. Kaiser and V. May, *J. Chem. Phys.* **121**, 2528 (2004).
- ²⁸A. Kaiser and V. May, *Chem. Phys.* **320**, 95 (2006).
- ²⁹I. Serban, J. Werschnik, and E. K. U. Gross, *Phys. Rev. A* **71**, 053810 (2005).
- ³⁰U. Kleinekathöfer, G.-Q. Li, S. Welack, and M. Schreiber, *Phys. Status Solidi B* **243**, 3775 (2006).
- ³¹C. P. Koch, J. P. Palao, R. Kosloff, and F. Masnou-Seeuws, *Phys. Rev. A* **70**, 013402 (2004).