

# Laser Pulse Control of Ultrafast Electron Transfer Reactions

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**Abstract.** The optimal control (OC) scheme for molecular dynamics is applied to the study of ultrafast bridge mediated electron transfer (ET). Utilizing the methods of dissipative quantum dynamics in combination with the OC approach the guided charge motion in a donor–bridge–acceptor system including a single active vibrational coordinate is studied. The control field drives the optical transition from the electronic ground–state of the ET system into the donor–level and can be used to prepare special electronic and vibrational states. In particular, it is demonstrated that charge localization becomes possible at the acceptor or bridge molecule as well as in the electronic ground–state of the ET system.

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## 1 Introduction

Encouraging experimental attempts let become the laser-pulse control of molecular dynamics a subject of physico-chemical research far beyond any pure theoretical speculations [1, 2] (for a recent overview on the whole field see also the contributions in [3]). Nevertheless, theoretical studies and numerical simulations introduced various ideas and concepts which became indispensable for the development of the whole field. At the heart of such simulations lies the optimal control (OC) theory [4, 5]. Defining a particular state of the system at a particular time (target state), OC theory enables one to compute the laser-pulse one needs to achieve this state. The formulation of the OC theory is well documented in a number of reviews and original papers (an actual overview can be found in [3]). Originally it has been formulated for systems which dynamics are governed by the time-dependent Schrödinger equation [4, 5]. A formulation for mixed states could be achieved already in [6]. And recently, the efficient iteration scheme of [7, 8] has been extended to the reduced state dynamics of an open quantum system [9].

The contribution of the present paper is devoted to the application of OC theory to laser pulse control of ultrafast photoinduced ET processes. Such a control task as well as the control of excitation energy motion (Frenkel–exciton transfer) found less interest. Instead, most work has been concentrated on controlling chemical reactions with the main aim to destroy a certain chemical bound. In the field of ET only those reactions have been investigated which are not of the photoinduced type but are characterized by the action of a high-frequency electric field (which mod-

ulates the energetic distance between the donor and the acceptor level) [10–14]. In the present paper, however, we will demonstrate the control of ET reactions by fields in the optical region. An external field-pulse is used to excite the donor level and to initiate ET which proceeds in the sub-picosecond time-domain. We believe that OC theory of such ET processes is of great interest, first because less emphasis has been put on the OC of particle (or quasi-particle) motion in molecular systems, and second because of the increasing number of experiments dealing with such problems (for example [15]).

External field control of ET reactions represents an example for molecular dynamics control where the whole motion of the molecular degrees of freedom (DOF) proceeds within bound states. If one denotes the *eigenstates* of those vibrational coordinates participating in the ET reaction by  $|\psi_\alpha\rangle$  (adiabatic states), the control problem discussed in the following corresponds (i) to the optical preparation of a wavepacket formed by these states, and (ii) involves the motion of this wavepacket guided by the external field into a final superposition state  $|\Psi_f\rangle = \sum_\alpha c_\alpha |\psi_\alpha\rangle$ .

This seems to be a simple problem compared to cases with non-bonding states where one has to carry out the calculation on a grid in the coordinate representation instead in the state (energy) representation. But to cover the aspects of spatial charge redistribution within the ET reaction one usually discusses ET in terms of more localized diabatic states. This results in the fact that spatial charge motion corresponds to the dynamics of a superposition states in the adiabatic representation. For example, introducing the vibrational ground state of the acceptor

$|\psi_{A0}\rangle$  as a possible target state means in the adiabatic representation to try to occupy with high probability a superposition state like the above introduced state  $|\Psi_f\rangle$ .

Usually ET reactions are characterized by vibrational energy dissipation. A common approach to incorporate this process is to account for the coupling to a reservoir of passive vibrational coordinates (see e.g. [16–18] and the various contributions in [19]). In this manner one includes frictional effects on the reaction coordinate and the ET has to be described in the framework of dissipative quantum dynamics (density matrix theory [18, 20–23]). The OC for dissipative dynamics has been studied recently in [9]. The new aspect in the present paper is the foundation of the OC approach on a microscopically justified expression for the (active) system–reservoir (bath) coupling. This ensures that in the density matrix equation those terms being responsible for dissipation are microscopically justified, too.

The paper is organized as follows. In the next section the ET model used for the concrete calculations is shortly introduced. Before discussion the results in Section 4 we establish the OC scheme in Section 3. Any more involved calculation can be found in one of the three appendices. The paper ends with some short conclusions.

## 2 The Model for Ultrafast Electron Transfer Reactions

To study bridge mediated ET the simple donor–bridge–acceptor (DBA) system (where the bridge is represented by a single electronic level) found a widespread application (see [19]). Although it only represents a generalization of the standard curve–crossing problem by an additional level it allows to describe different new aspects of ET. For the present calculations we will introduce such a three–level (three PES) model, too. It is shown in Fig. 1 via the related PES drawn versus a single active coordinate. The actual parameter values can be found in Table 1 (for a detailed explanation see below). Its choice has been inspired by our simulations on ultrafast ET proceeding from a dye molecule attached to a semiconductor surface into the conduction band of the semiconductor [25].

The respective Hamiltonian  $H_S$  (describing the active system) includes a molecular part  $H_{\text{mol}}$  and the coupling to the external field  $H_F(t)$ . We write

$$H_S = H_{\text{mol}} + H_F(t), \quad (1)$$

where the molecular part covers the ground–state contribution  $H_g|\varphi_g\rangle\langle\varphi_g|$  and the ET part  $H_{\text{DBA}}$

$$H_{\text{mol}} = H_g|\varphi_g\rangle\langle\varphi_g| + H_{\text{DBA}}. \quad (2)$$

$|\varphi_g\rangle$  denotes the electronic state vector referring to the ground state of the ET complex, and  $H_g$  is the respective vibrational Hamiltonian. Since we are interested in studying charge localization via external laser pulses the diabatic representation with states localized at the building blocks of the ET system seems to be most appropriate

(compare, e.g. [18, 26, 27]). Accordingly, the ET Hamiltonian reads

$$H_{\text{DBA}} = \sum_{m,n} \left( \delta_{m,n} H_m + (1 - \delta_{m,n}) V_{mn} \right) |\varphi_m\rangle\langle\varphi_n| \quad (3)$$

The diabatic states correspond to the wavefunction of the transferred electron at the donor, acceptor and bridge part and are denoted by  $|\varphi_m\rangle$  ( $m = D, B, A$ ). In the case of the donor the respective level corresponds to an excited level whereas in the case of the bridge molecule as well as the acceptor the diabatic states refer to the presence of an excess electron. All vibrational Hamiltonian  $H_m$ , (note  $m = g, D, B, A$ ) are written here with dimensionless vibrational coordinates  $Q = \{Q_j\}$

$$H_m = T_{\text{vib}} + U_m^{(0)} + \sum_j \frac{\hbar\omega_j}{4} (Q_j - Q_j^{(m)})^2 \quad (4)$$

The minima of the respective PES are denoted by  $U_m^{(0)}$ , and the single  $Q_j$  can be expressed by the respective harmonic oscillator operators  $C_j$  and  $C_j^+$  according to  $Q_j = C_j + C_j^+$ . Their introduction is based on the assumption of equally shaped PES independent on the actual electronic state. The  $Q_j^{(m)}$  refer to the mutual displacement of the PES with respect to the vibrational coordinates. The respective vibrational *eigenfunctions* of the  $H_m$  are denoted as  $|\chi_{mM}\rangle$  with the set  $M$  of vibrational quantum numbers. For simplicity, the transfer integrals  $V_{DB}$  and  $V_{BA}$  coupling the donor with the bridge level, and the bridge level with the acceptor, respectively, have been taken independently on the vibrational coordinates (note the assumption  $V_{DA} = 0$ ). Finally, we give the coupling Hamiltonian to the radiation field

$$H_F(t) = -\mathbf{E}(t)\hat{\mu}, \quad (5)$$

with

$$\hat{\mu} = \mathbf{d}_{Dg}|\varphi_D\rangle\langle\varphi_g| + \text{h.c.}, \quad (6)$$

and with transition dipole moment  $\mathbf{d}_{Dg}$  being independent on the  $Q_j$  (Condon–approximation). The field is assumed to be linearly polarized but remains free otherwise

The model introduced so far is completed by a coupling of the set  $Q$  of active coordinates to remaining passive vibrational coordinates [19, 18]. These coordinates are denoted by  $Z = \{Z_\xi\}$  and act as a dissipative reservoir. They may belong to the ET complex or to a surrounding solvent. The respective coupling Hamiltonian is used in the form

$$H_{S-R} = \sum_m W_m(Q, Z) |\varphi_m\rangle\langle\varphi_m| \quad (7)$$

where the assumption of only diagonal contributions with respect to the electronic states represents an additional assumption. If the  $W_m(Q, Z)$  factorizes into a system and a reservoir part,  $H_{S-R}$  can be identified with the multiple

factorized *ansatz* of dissipative quantum dynamics (see, e.g. [18])

$$H_{S-R} = \sum_u K_u \Phi_u, \quad (8)$$

with  $K_u \equiv K_m(Q)|\varphi_m \rangle \langle \varphi_m|$ , exclusively defined in the state space of active system states and with  $\Phi_u \equiv \Phi_m(Z)$ , defined in the reservoir state space. Such an expression is flexible enough to cover many types of couplings.

### 3 Optimal Control Scheme for Dissipative Molecular Dynamics

Having in mind some generalizations of the computations documented in the present paper on external field control of ET reactions we start with the most general type of OC theory, e.g. the formulation for open quantum systems [9]. A reduction to mixed or pure state dynamics of closed system is straightforward. In order to apply the density matrix theory of dissipative quantum dynamics [18, 20–23] we start with the total Hamiltonian  $H = H_S(t) + H_{S-R} + H_R$ . Here,  $H_R$  governs the dynamics of the environment (thermal reservoir). The active system Hamiltonian  $H_S(t)$  has been already introduced in Eq. (1) and its coupling to the environment,  $H_{S-R}$  in Eq. (8). According to the introduction of an active system (of a selected number of electronic and vibrational DOF) one has to define the reduced density operator

$$\hat{\rho}(t) = \text{tr}_R \{ \hat{W}(t) \}. \quad (9)$$

This quantity is obtained from the complete statistical operator  $\hat{W}(t)$  via a trace operation restricted to the reservoir states. The time evolution of the reduced density operator is governed by a respective time evolution superoperator  $\mathcal{U}(t, t_0)$  which acts according to

$$\hat{\rho}(t) = \mathcal{U}(t, t_0; \mathbf{E}) \hat{\rho}(t_0). \quad (10)$$

The introduction of  $\mathcal{U}$  corresponds to the existence of a particular equation of motion for  $\hat{\rho}$  which is taken here in the following form (Markovian Quantum Master Equation, see e.g. [18])

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i \mathcal{L}_{\text{mol}} \hat{\rho}(t) - i \mathcal{L}_F(t) \hat{\rho}(t) - \mathcal{D} \hat{\rho}(t). \quad (11)$$

The  $\mathcal{L}_{\text{mol}}$  and  $\mathcal{L}_F$  are the Liouville superoperators corresponding to the commutator with  $H_{\text{mol}}$ , Eq. (2) and  $H_F$ , Eq. (5), respectively. Since the electric field–strength has been incorporated in the density operator equation the  $\mathbf{E}$ –dependence of the time evolution superoperator, Eq. (10) has been separately indicated. All effects following from the coupling to the environment are comprised in the action of the superoperator  $\mathcal{D}$ . The concrete form of  $\mathcal{D}$  follows from the system reservoir coupling expressions, Eqs. (7) and (8) (for details see Appendix B).

Finally, we remind on a possible indirect field dependence of Eq. (11) induced via a field dependence of the dissipative superoperator  $\mathcal{D}$ . This effect has been discussed

in Ref. [28] where its relation to continuous–wave driven open quantum systems (see, e.g. [29]) could be underlined. In such a continuous–wave driven situation an external field may change the position and mutual distance of the molecular levels. Since the position of the related transition frequencies within the spectral density (describing the coupling to the reservoir) decides whether or not the dissipation works effectively a change of the transition frequencies may alternate the strength of dissipation. For the field–influence of sub–picosecond pulses, however, one has to change from this frequency domain description to a description in the time–domain. This has been done in [28], where the respective computations showed that a sufficient intense and short pulse (about 10 to 15 fs long) may induce certain modulations of the molecular relaxation rates. Since the numerical calculations given below are aimed to the field control of closed–system dynamics we postpone the inclusion of the indirect field–influence to a forthcoming paper.

Laser pulse control of molecular dynamics is usually formulated as the task to realize at a certain final time  $t_f$  the expectation value

$$O(t_f) = \text{tr}_S \{ \hat{O} \hat{\rho}(t_f) \} \quad (12)$$

of the observable described by the (hermitian) quantum mechanical operator  $\hat{O}$ . To get  $O(t_f)$  one applies a field pulse  $\mathbf{E}(t)$  (the optimal pulse) which should drive the system in the required manner. According to [6] the optimal pulse is defined as the the extremum of the following functional

$$J(t_f; \mathbf{E}) = O(t_f; \mathbf{E}) - \frac{1}{2} \int_{t_0}^{t_f} dt \lambda(t) \mathbf{E}^2(t), \quad (13)$$

where the second term on the right–hand side guarantees an upper limitation of the field intensity. (The penalty factor  $\lambda(t)$  has been taken time–dependent to avoid a sudden switch on and switch off of the control field [24].) A slightly different version of the functional has been suggested by Rabitz [7–9], who used a somewhat larger expression which ensures the use of the correct dynamic equations. In the present approach, however, the concrete dynamic equation to be used is already fixed by the demand how to determine  $O(t_f)$ , Eq. (12).

In order to get a nonlinear functional equation determining the optimal field pulse one sets the functional derivative of  $J$  with respect to  $\mathbf{E}$  equal to zero. One obtains (details of the derivation are given in the Appendix A)

$$\mathbf{E}(t) = \frac{1}{\lambda(t)} \frac{\delta O(t_f)}{\delta \mathbf{E}(t)} = \frac{\mathbf{K}(t_f, t; \mathbf{E})}{\lambda(t)}. \quad (14)$$

This expression has to be understood as a self–consistency relation for the optimal field. The actual value of the field at time  $t$  becomes proportional to the change of  $O(t_f)$  with respect to the field–strength at this time. The quantity

$$\mathbf{K}(t_f, t; \mathbf{E}) = \frac{i}{\hbar} \text{tr}_S \{ \hat{O} \mathcal{U}(t_f, t; \mathbf{E}) \mathcal{M} \mathcal{U}(t, t_0; \mathbf{E}) \hat{\rho}(t_0) \} \quad (15)$$

is known as the (vectorial) control kernel which depends on  $\mathbf{E}$  in a highly nonlinear manner. The kernel is obtained by propagating in a first a step the reduced density operator (under the presence of the external field) from the initial time  $t_0$  up to an intermediate time  $t \leq t_f$ . Then, the commutator with respect to the dipole operator is calculated (abbreviated here by the action of the dipole superoperator  $\mathcal{M}\dots = (\hat{\mu}, \dots)_-$ ). Afterwards, the result has to be propagated from  $t$  to the final time  $t_f$  where the operator  $\hat{O}$  acts. According to Eq. (14) the control kernel has to be calculated in such a manner that it coincides (despite the prefactor  $1/\lambda$ ) with the field. If this became possible the optimal field has been determined.

Obviously, one needs a certain iteration procedure to solve Eq. (14). A direct iteration of Eq. (14) has been proposed in [6]. Its inconvenience and sometimes inability to achieve convergency has been discussed in literature [7–9]. To avoid these problems we will follow the suggestion of [9]. For this reason the control kernel is rewritten as

$$K(t_f, t; \mathbf{E}) = \frac{i}{\hbar} \text{tr}_S \{ \hat{\sigma}(t; \mathbf{E}) \mathcal{M} \hat{\rho}(t; \mathbf{E}) \}, \quad (16)$$

where the two time-dependent operators  $\hat{\sigma}(t; \mathbf{E})$  and  $\hat{\rho}(t; \mathbf{E})$  are propagated separately up to the intermediate time  $t$ . The operator at the left part of the trace is given as

$$\hat{\sigma}(t; \mathbf{E}) = \tilde{U}(t_f, t; \mathbf{E}) \hat{O}. \quad (17)$$

It comprises a reverse propagation from the final time  $t_f$  up to the intermediate time starting with  $\hat{O}$  at  $t = t_f$ . The time-evolution superoperator  $\tilde{U}$  is discussed in some more detail in Appendix B.

This possible separate propagation of  $\hat{\sigma}$  and  $\hat{\rho}$  is used to establish an efficient iteration procedure [9]. Therefore, the explicit appearance of the control field  $\mathbf{E}$  via the term proportional to  $\mathcal{L}_F(t)$  is removed in the equations for  $\hat{\rho}$  and  $\hat{\sigma}$  in using Eq. (14) and expression (16) for the control kernel. As a result a coupled set of nonlinear equations of motion is obtained. Since the numerics of the present paper are aimed to study closed system dynamics we only quote these equations in Appendix C and jump to non-dissipative dynamics.

### 3.1 Restriction to Mixed and Pure-State Dynamics

The control scheme explained in the foregoing section provides the introduction of a reduced density operator and is based on dynamic equations including dissipation. Neglecting any coupling to the environment the scheme can be easily specified to closed system dynamics characterized by pure or mixed states. Therefore, the reduced density operator will be identified with the complete statistical operator  $\hat{W}(t)$ . In such a case the time evolution superoperator introduced in Eq. (10) is reduced to

$$\hat{W}(t) = U(t, t_0; \mathbf{E}) \hat{W}(t_0) \equiv U(t, t_0; \mathbf{E}) \hat{W}(t_0) U^\dagger(t, t_0; \mathbf{E}) \quad (18)$$

with the ordinary time-evolution operator  $U(t, t_0; \mathbf{E})$  defined via  $H_S$ , Eq. (1). For the initial value of the statistical

operator we have in mind the canonical equilibrium form written here via an expansion with respect to the *eigenstates*  $|\psi_\alpha\rangle$  of  $H_{\text{mol}}$  ( $f$  is the thermal distribution versus the *eigenenergies*  $E_\alpha$ )

$$\hat{W}(t_0) = \hat{W}_{\text{eq}} = \sum_\alpha f(E_\alpha) |\psi_\alpha\rangle\langle\psi_\alpha|. \quad (19)$$

The pure state version of  $\hat{W}(t_0)$  is given by  $|\psi\rangle\langle\psi|$ .

The reduction of  $\mathcal{U}$  to the action of ordinary time-evolution operators enables a rearrangement of the various terms in Eq. (15) with the following result

$$\begin{aligned} \mathbf{K}(t_f, t; \mathbf{E}) = & \\ - \frac{2}{\hbar} \text{Im} \text{tr} \{ & U^\dagger(t_f, t_0; \mathbf{E}) \hat{O} U(t_f, t; \mathbf{E}) \hat{\mu} U(t, t_0; \mathbf{E}) \hat{W}(t_0) \}. \end{aligned} \quad (20)$$

Introducing Eq. (19) and carrying out the trace gives

$$\mathbf{K}(t_f, t; \mathbf{E}) = -\frac{2}{\hbar} \sum_\alpha f(E_\alpha) \text{Im} \{ \langle \Theta_\alpha(t) | \hat{\mu} | \psi_\alpha(t) \rangle \}, \quad (21)$$

where we defined

$$|\psi_\alpha(t)\rangle = U(t, t_0; \mathbf{E}) |\psi_\alpha\rangle, \quad (22)$$

and

$$|\Theta_\alpha(t)\rangle = U(t, t_f; \mathbf{E}) \hat{O} |\psi_\alpha(t_f)\rangle. \quad (23)$$

The state  $|\psi_\alpha(t)\rangle$  is obtained as the standard propagation (according to the time-dependent Schrödinger equation) of one of the states  $|\psi_\alpha\rangle$  (but, as indicated, with the inclusion of the radiation field). The index  $\alpha$  gives a hint on the particular initial state. In contrast, the state  $|\Theta_\alpha(t)\rangle$  is the result of a reverse propagation from  $t_f$  to the earlier time  $t$  starting with  $\hat{O} |\psi_\alpha(t_f)\rangle$ . Therefore, this propagation requires the complete propagation of  $|\psi_\alpha(t)\rangle$  up to  $t = t_f$ .

In similarity to the general scheme given in Appendix C we introduce the iteration procedure to determine the optimal pulse. We start with a zero-order solution for  $|\psi_\alpha(t)\rangle$  in solving the time-dependent Schrödinger equation corresponding to Eq. (22) with an arbitrary chosen field pulse  $\mathbf{E}(t)$ . With this zero-order solution one can determine the  $n$ 'th order ( $n > 0$ ) solution where the  $n$ 'th iteration step is given by (mixed state version of Eqs. (46) and (47))

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\psi_\alpha^{(n)}(t)\rangle = & H_{\text{mol}} |\psi_\alpha^{(n)}(t)\rangle + \frac{2}{\hbar\lambda(t)} \sum_\beta f(E_\beta) \\ \text{Im} \{ \langle \Theta_\beta^{(n)}(t) | \hat{\mu} | \psi_\beta^{(n)}(t) \rangle \} & \hat{\mu} |\psi_\alpha^{(n)}(t)\rangle, \end{aligned} \quad (24)$$

and

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\Theta_\alpha^{(n)}(t)\rangle = & H_{\text{mol}} |\Theta_\alpha^{(n)}(t)\rangle + \frac{2}{\hbar\lambda(t)} \sum_\beta f(E_\beta) \\ \text{Im} \{ \langle \Theta_\beta^{(n)}(t) | \hat{\mu} | \psi_\beta^{(n-1)}(t) \rangle \} & \hat{\mu} |\Theta_\alpha^{(n)}(t)\rangle, \end{aligned} \quad (25)$$

with

$$|\Theta_\alpha^{(n)}(t_f)\rangle = \hat{O}|\psi_\alpha^{(n-1)}(t_f)\rangle. \quad (26)$$

Since for  $n = 1$  the zero-order solution  $|\psi_\alpha^{(0)}(t)\rangle$  already exist the initial value, Eq. (26) for the first iteration of  $|\Theta_\alpha(t)\rangle$  is well defined, and Eq. (24) (for  $n = 1$ ) can be solved, too. Proceeding in this manner fast convergency can be achieved [9]. For every iteration step two approximations for the optimal field can be given, either

$$\mathbf{E}^{(n)}(t) = -\frac{2}{\hbar\lambda(t)} \sum_\alpha f(E_\alpha) \text{Im} \langle \Theta_\alpha^{(n)}(t) | \hat{\mu} | \psi_\alpha^{(n-1)}(t) \rangle, \quad (27)$$

and a somewhat improved expression with  $|\psi_\alpha^{(n)}(t)\rangle$  instead of  $|\psi_\alpha^{(n-1)}(t)\rangle$ .

The quoted iteration scheme will be applied in the following section to the simple but nontrivial type of ET reaction which Hamiltonian has been described in Section 2.

## 4 Numerical results

For the subsequent discussion, which should serve as simple reference case for more involved further computation, some additional approximations will be taken. First, as already indicated, we neglect any coupling of the reaction coordinates (active coordinates) to a thermal reservoir of passive molecular DOF. And second, the set of active coordinates is reduced to a single one. Furthermore, we will concentrate on the zero-temperature case. Therefore, the set of *eigenstates*  $|\psi_\alpha\rangle$  appearing in the scheme of the preceding section has to be replaced by the electron-vibrational ground state  $|\chi_{g0}\rangle = |\varphi_g\rangle$  of the ET system. It enters Eq. (22) where it acts as a single initial state for the single wavefunction  $|\psi(t)\rangle$  to be determined. To solve Eq. (23) where a backward time propagation has to be carried out, first we have to fix the observable represented by the operator  $\hat{O}$ . Since dynamical electron localization at a single electron-vibrational state (or a superposition of such states) will be of main interest we identify  $\hat{O}$  with a projector on a certain state  $|\psi_{\text{target}}\rangle$  (target state).

To carry out the iteration of the Eqs. (24) and (25) we change to a representation using the diabatic electron-vibrational states  $|\chi_{mM}\rangle = |\varphi_m\rangle$  and use the type of penalty function  $\lambda(t)$ , Eq. (13) suggested in [24]. As the zero-order approximation for the field we took a Gaussian shaped pulse of 20 fs duration, with maximum at 50 fs, and with carrier frequency in the Frank-Condon region of the donor excitation.

To have a reference case at hand where the ET dynamics are not affected by the laser pulse we imagine an impulsive (instantaneous) and complete excitation of the donor level after the action of an infinitely short pulse (where, obviously, the structure of the pulse cannot play any role). This results in a propagation of the Schrödinger equation for the ET system in the absence of an external field but with a initial condition determined by the field. The latter is given by  $|\psi(0)\rangle = |\chi_{g0}\rangle = |\varphi_D\rangle$  and corresponds in the

scheme of PES, Fig. 1 to a vertical displacement of the electronic ground-state vibrational wavefunction  $|\chi_{g0}\rangle$  into the (excited) donor state  $|\varphi_D\rangle$ .

To visualize the dynamics we draw in the following the complete diabatic electronic level populations

$$P_m(t) = \sum_M P_{mM}(t), \quad (28)$$

where  $P_{mM}$  is the electron-vibrational state population. The respective  $P_m(t)$  ( $m = D, B, A$ ) valid for the case of impulsive action of the external field are displayed in Fig. 2 for the first picosecond (system parameters from Table 1). The transferred electron starting with 100% population of the donor state reaches a maximum population of about 70% at the acceptor after  $t \approx 120$  fs. Since any dissipation is absent the populations show a coherent oscillatory behavior. Changing to the corresponding wavepacket motion (in the coordinate representation, not shown here) one notices a fast spread out of the initial wavepacket over a broad range on the  $Q$ -axis.

It is just the question we try to answer whether or not it is possible to control (guide) the ET dynamics in such a manner to reach a chosen state at a chosen time. A first example for the application of OC approach is shown in Fig. 3. Here, the second excited vibrational state of the acceptor electronic state  $|\chi_{A2}\rangle = |\varphi_A\rangle$  has been chosen as the target state which should be reached at time  $t_f = 500$  fs. One notices that the population dynamics under the action of the control pulse turns out to be rather regular and finally the system reaches the desired state with a probability of about 95%. To obtain this result less than 20 iterations of the Eqs. (24) and (25) have been necessary (for more details see the discussion related to Fig. 9). In Fig. 3 we also presented the optimal pulse. It increases up to a time (about 130 fs) at which the ground-state population is nearly completely removed. Afterwards the pulse kicks the ET dynamics (with decreasing amplitude) in such a manner to achieve the required population of the acceptor level. If one takes a look on the related moving wavepacket the regular behavior of the external-field guided ET can be observed, too. The quantity drawn in Fig. 4 is the time-dependent probability distribution  $P(Q, t)$  of the reaction coordinate. It is obtained via the expectation value of the projector on the coordinate operator *eigenstates*

$$P(Q, t) = \langle \psi(t) | Q \rangle \langle Q | \psi(t) \rangle. \quad (29)$$

Introducing an expansion of  $|\psi(t)\rangle$  with respect to the diabatic electron-vibrational states one obtains  $P(Q, t) = \sum_{m,M,N} c_{mM}^*(t) c_{mN}(t) \chi_{mM}^*(Q) \chi_{mN}(Q)$  where the  $c_{mM}^*(t)$  and  $c_{mN}(t)$  denote the related time-dependent expansion coefficients. Thus, the expansion is diagonal with respect to the diabatic electronic states but off-diagonal with respect to the vibrational wavefunctions. The oscillatory behavior which is shown by  $P(Q, t)$  nicely corresponds to the oscillations of the level populations in Fig. 3.

Besides the population of a single electron-vibrational state we can, of course, design pulses which lead to the formation of a wavepacket of Gaussian (or any other) form.

To that end, we introduce the target state as the displaced vibrational ground state of the acceptor level. Using the coordinate representation with respect to the vibrational coordinate it reads  $\langle Q - Q_{\text{dis}} | \chi_{A0} \rangle | \varphi_A \rangle$ . The quantity  $Q_{\text{dis}}$  ( $= 2.4$ , compare Fig. 5) denotes the actual displacement with respect to acceptor equilibrium position  $Q^{(A)}$ . As shown in Fig. 5 the optimization procedure results in a 91% population of the target state. Although the pulse extends over more than  $300 fs$  the main portion of the excitation is achieved in the time period just after  $t = 100 fs$  (compare the the population  $P_g$  of the electronic ground state). Between  $t \approx 150 fs$  and  $t \approx 350 fs$  there is no further probability transfer from the ground-state. The corresponding wavepacket motion (Fig. 6) shows again an oscillatory behavior corresponding to the electronic population dynamics and finally the formation of the required wavepacket.

Next we chose the population of the vibrational ground-state of the bride state  $|\chi_{B0}\rangle | \varphi_B \rangle$  as the target state. The results of the OC approach are displayed in Fig. 7. In the DAB configuration introduced for the ET transfer system the bridge PES lies symmetrically between donor and acceptor PES. Therefore, the field tries to synchronize the population of the donor and acceptor level. If the respective oscillations of  $P_D$  and  $P_A$  reaches their minimum the bridge population achieves its maximum with a higher and higher population up to the nearly 100% population of the target state at  $t_f = 0.5 ps$ .

The above given results demonstrate the possible laser pulse control of ET reactions. An effective external field control of the deexcitation of the ET system is presented in Fig. 8. After an initial impulsive excitation of the donor state the ET proceeds freely (compare the discussion related to Fig. 2). But at time  $t = 500 fs$  a pulse with a finite duration (see upper part of Fig. 9) is switched on with the task to drive the system back into the electronic ground state. This has been achieved for more than 90% of the population at  $t = 1 ps$ . Since the control problem presented in Figs. 8 and 9 seems a little bit more involved than the foregoing examples we also present the convergency of the iteration procedure to find the optimal pulse. For this aim it is advisable to calculate the overlap  $\langle \psi_{\text{target}} | \psi^{(n)}(t_f) \rangle$  between the target state and the solution of the  $n$ 'th iteration of the OC problem at final time  $t_f$ . The square of this overlap versus the number of actual iterations is shown in the lower part of Fig. 9. The fast convergency of the iteration as reported in literature (see, for example [7–9, 24]) can be confirmed for the present example, too.

## 5 Conclusions

Starting from the OC problem formulated for an open quantum system where the coupling to the environment could be specified according to a microscopic interaction Hamiltonian, laser pulse control of ultrafast photoinduced ET reactions has been studied. In the presented first computations we concentrated on the reference case of closed

system dynamics at zero temperature. The possible guided motion of an electron through a donor–bridge–acceptor system and the charge localization at a certain part of the ET system could be demonstrated.

An extension to ET systems with a larger bridging part (molecular wire) should be possible. And in line with the computations in [9] it seems plausible that similar results can be derived if the dissipation of vibrational excitation energy into passive modes is incorporated. A particular application of the OC scheme to ultrafast ET proceeding from a dye molecule attached to a semiconductor surface [25] is also under work.

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## A Derivation of the Control Kernel

The control kernel Eq. (15) follows as the functional derivative of the expectation value introduced in Eq. (12). The latter expression shows that one has to determine the respective derivate of the reduced density operator. To perform the derivative we first note the more explicite structure of the time–evolution superoperator introduced in Eq. (10). It reads ( $T$  guarantees proper time–ordering)

$$\mathcal{U}(t, t_0; \mathbf{E}) = T \exp \left\{ -i \int_{t_0}^t d\tau (\mathcal{L}_{\text{mol}} + \mathcal{L}_{\text{F}}(\tau) - i\mathcal{D}) \right\}. \quad (30)$$

Accordingly the functional derivate of  $\hat{\rho}(t_f)$  follows as

$$\frac{\delta \hat{\rho}(t_f)}{\delta \mathbf{E}(t)} = -i \int_{t_0}^{t_f} d\tau \mathcal{U}(t_f, \tau; \mathbf{E}) \frac{\delta \mathcal{L}_{\text{F}}(\tau)}{\delta \mathbf{E}(t)} \mathcal{U}(\tau, t_0; \mathbf{E}). \quad (31)$$

Noting

$$\frac{\delta \mathcal{L}_{\text{F}}(\tau)}{\delta \mathbf{E}(t)} = -\frac{1}{\hbar} \delta(\tau - t) \mathcal{M} \quad (32)$$

expression (31) is easily converted into the final result, Eq. (15) for the control kernel.

## B The Reverse Time Evolution Superoperator

To have a more specific version of the time evolution superoperator, Eq. (10) at hand we specify the dissipative superoperator  $\mathcal{D}$  introduced in Eq. (11). According to the standard QME (see for example [18, 30]) we set

$$-\mathcal{D}\hat{\rho} = - \sum_u \left( K_u A_u \hat{\rho} + \hat{\rho} A_u^\dagger K_u - A_u \hat{\rho} K_u - K_u \hat{\rho} A_u^\dagger \right). \quad (33)$$

These dissipative terms correspond to a second–order perturbational treatment of the type of system reservoir coupling introduced in Eq. (8). Although not necessary in

general we will additionally assume that the single operators  $K_u$  are hermitian. The operators  $A_u$  are obtained from the time dependent operators  $K_u(t)$  (defined in the Heisenberg picture with respect to  $H_{\text{mol}}$  and thus incorporating any order in the transfer integrals  $V_{mn}$ ) and the reservoir correlation functions  $C_{uv}(t)$  as [18, 30]

$$A_u = \sum_v \int_0^\infty d\tau C_{uv}(\tau) K_v(-\tau) \quad (34)$$

To justify the representation Eq. (20) for the control kernel and to give a definition of the reverse time evolution superoperator we first note the general form of any superoperator. i.e. of the time evolution superoperator, too. It is given by [30]

$$\begin{aligned} \mathcal{U}(t, t_0) \hat{\rho}(t_0) &= \hat{A}(t, t_0) \hat{\rho}(t_0) + \hat{\rho}(t_0) \hat{B}(t, t_0) \\ &+ \sum_j \hat{C}_j(t, t_0) \hat{\rho}(t_0) \hat{D}_j(t, t_0). \end{aligned} \quad (35)$$

Here, the  $\hat{A}(t, t_0)$ ,  $\hat{B}(t, t_0)$ ,  $\hat{C}_j(t, t_0)$ , and  $\hat{D}_j(t, t_0)$  are ordinary operators acting from the left or from the right on the initial value  $\hat{\rho}(t_0)$  of the reduced density operator. The set of operators can be somewhat restricted if we note that  $\hat{\rho}(t)$  is a hermitian operator

$$\hat{\rho}(t) = \mathcal{U}(t, t_0) \hat{\rho}(t_0) = \hat{\rho}^+(t) = \left( \mathcal{U}(t, t_0) \hat{\rho}(t_0) \right)^+ \quad (36)$$

If all contributions to  $\mathcal{U}$  are considered to be linearly independent one obtains  $\hat{B} = \hat{A}^+$  and  $\hat{D}_j = \hat{C}_j^+$ . This gives

$$\begin{aligned} \mathcal{U}(t, t_0) \hat{\rho}(t_0) &= \hat{A}(t, t_0) \hat{\rho}(t_0) + \hat{\rho}(t_0) \hat{A}^+(t, t_0) \\ &+ \sum_j \hat{C}_j(t, t_0) \hat{\rho}(t_0) \hat{C}_j^+(t, t_0). \end{aligned} \quad (37)$$

We use this relation to change from Eq. (15) to Eq. (16). In a first step we rewrite Eq. (15) in replacing  $\mathcal{U}$  which carries out the time evolution from  $t$  to  $t_f$  according to Eq. (37)

$$\begin{aligned} K(t_f, t; \mathbf{E}) &= \frac{i}{\hbar} \text{tr}_S \left\{ \hat{O} \left( \hat{A}(t_f, t) [\mathcal{M} \hat{\rho}(t)] + [\mathcal{M} \hat{\rho}(t)] \hat{A}^+(t_f, t) \right. \right. \\ &\left. \left. + \sum_j \hat{C}_j(t_f, t) [\mathcal{M} \hat{\rho}(t)] \hat{C}_j^+(t_f, t) \right) \right\}. \end{aligned} \quad (38)$$

A rearrangement of the different terms in the trace leads to

$$\begin{aligned} K(t_f, t; \mathbf{E}) &= \frac{i}{\hbar} \text{tr}_S \left\{ \left( \hat{A}^+(t_f, t) \hat{O} + \hat{O} \hat{A}(t_f, t) \right. \right. \\ &\left. \left. + \sum_j \hat{C}_j^+(t_f, t) \hat{O} \hat{C}_j(t_f, t) \right) \mathcal{M} \hat{\rho}(t) \right\}. \end{aligned} \quad (39)$$

The derived expression confirms the existence of  $\tilde{\mathcal{U}}$ , Eq. (17) and demonstrates how to obtain this quantity if  $\mathcal{U}$  is given in the form of Eq. (37).

To derive an equation of motion for  $\hat{\sigma}$ , Eq. (17) with respect to a dependence on the intermediate time  $t$  we first take notice of Eq. (30) and get

$$\frac{\partial}{\partial t} \mathcal{U}(t_f, t) = \mathcal{U}(t_f, t) (i\mathcal{L}_{\text{mol}} + i\mathcal{L}_{\text{F}}(t) + \mathcal{D}). \quad (40)$$

Generalizing the control kernel written in the form of Eq. (16) to a quantity which depends via  $\hat{\rho}$  on a second independent time–argument  $\bar{t}$  the time derivative with respect to  $t$  yields

$$\begin{aligned} \frac{\partial}{\partial t} K(t_f, t, \bar{t}; \mathbf{E}) &= \\ \frac{i}{\hbar} \text{tr}_S \{ \hat{\sigma}(t) (i\mathcal{L}_{\text{mol}} + i\mathcal{L}_{\text{F}}(t) + \mathcal{D}) \mathcal{M} \hat{\rho}(\bar{t}) \}, \end{aligned} \quad (41)$$

A rearrangement of the terms in the bracket leads to the required equation of motion for  $\hat{\sigma}$

$$\frac{\partial}{\partial t} \hat{\sigma}(t) = -i\mathcal{L}_{\text{mol}} \hat{\sigma}(t) - i\mathcal{L}_{\text{F}}(t) \hat{\sigma}(t) + \tilde{\mathcal{D}} \hat{\sigma}(t), \quad (42)$$

with the dissipative part

$$\begin{aligned} \tilde{\mathcal{D}} \hat{\sigma}(t) &= \\ \sum_u \left( A_u^+ K_u \hat{\sigma}(t) + \hat{\sigma}(t) K_u A_u - A_u^+ \hat{\sigma}(t) K_u - K_u \hat{\sigma}(t) A_u \right) \end{aligned} \quad (43)$$

which is essentially different from  $\mathcal{D}$ , Eq. (33). Eq. (42) tells us how to perform the reverse time propagation in Eq. (17).

## C Iteration Scheme

As already stated in Section 3 the OC problem can be formulated via the type of control kernel given in Eq. (20). Here, the two time–dependent density operators  $\hat{\sigma}$  and  $\hat{\rho}$  are determined by separate equations. If the control field  $\mathbf{E}$  appearing in the term of the respective equations of motion proportional to  $\mathcal{L}_{\text{F}}$  is replaced via Eq. (14) by the control kernel one obtains

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) &= -i\mathcal{L}_{\text{mol}} \hat{\rho}(t) - \mathcal{D} \hat{\rho}(t) \\ &- \frac{1}{\hbar^2 \lambda(t)} \text{tr}_S \{ \hat{\sigma}(t) \mathcal{M} \hat{\rho}(t) \} \mathcal{M} \hat{\rho}(t), \end{aligned} \quad (44)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\sigma}(t) &= -i\mathcal{L}_{\text{mol}} \hat{\sigma}(t) + \tilde{\mathcal{D}} \hat{\sigma}(t) \\ &- \frac{1}{\hbar^2 \lambda(t)} \text{tr}_S \{ \hat{\sigma}(t) \mathcal{M} \hat{\rho}(t) \} \mathcal{M} \hat{\sigma}(t). \end{aligned} \quad (45)$$

Here, the indirect coupling via the field  $\mathbf{E}$  is replaced by a direct coupling via the terms being nonlinear in both density operators. These nonlinearities ensure a feedback of the dynamics of  $\hat{\rho}$  as well as  $\hat{\sigma}$  via the field–term on

itself. Since the equation for  $\hat{\sigma}(t)$  has to be propagated in reverse time order, i.e. from  $t_f$  to earlier times  $t$  a simultaneous solution of the Eqs. (44) and (45) is not possible. But according to [7–9] an efficient iteration can be constructed. It is based on the idea to determine, e.g.  $\hat{\sigma}(t)$  appearing in Eq. (44) for  $\hat{\rho}(t)$  separately. Then, Eq. (44) for  $\hat{\rho}(t)$  is closed and an approximate version for  $\hat{\rho}(t)$  can be computed. Inserting this  $\hat{\rho}(t)$  together with the used form for  $\hat{\sigma}(t)$  into Eq. (14) an approximate form of the optimal field has been obtained, too. (Note that the role of  $\hat{\sigma}(t)$  and  $\hat{\rho}(t)$  can be interchanged in the present scheme.)

The given procedure is based on the following  $n$ 'th order iteration step for  $\hat{\rho}$  ( $n > 0$ )

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}^{(n)}(t) &= -i\mathcal{L}_{\text{mol}} \hat{\rho}^{(n)}(t) - \mathcal{D} \hat{\rho}^{(n)}(t) \\ - \frac{1}{\hbar^2 \lambda(t)} \text{tr}_S \{ \hat{\sigma}^{(n-1)}(t) \mathcal{M} \hat{\rho}^{(n)}(t) \} \mathcal{M} \hat{\rho}^{(n)}(t), \end{aligned} \quad (46)$$

where  $\hat{\sigma}^{(n-1)}(t)$  is the result of the foregoing iteration step. In a similar manner we obtain for  $\hat{\sigma}^{(n)}(t)$

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\sigma}^{(n)}(t) &= -i\mathcal{L}_{\text{mol}} \hat{\sigma}^{(n)}(t) + \tilde{\mathcal{D}} \hat{\sigma}^{(n)}(t) \\ - \frac{1}{\hbar^2 \lambda(t)} \text{tr}_S \{ \hat{\sigma}^{(n)}(t) \mathcal{M} \hat{\rho}^{(n)}(t) \} \mathcal{M} \hat{\sigma}^{(n)}(t). \end{aligned} \quad (47)$$

The zero-order approximation for  $\hat{\rho}$  follows by replacing the optimal field term by a concrete field expression

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}^{(0)}(t) &= -i\mathcal{L}_{\text{mol}} \hat{\rho}^{(0)}(t) - \mathcal{D} \hat{\rho}^{(0)}(t) \\ &+ \frac{i}{\hbar} \mathbf{E}(t) \mathcal{M} \hat{\rho}^{(0)}(t), \end{aligned} \quad (48)$$

Every iteration step produces two approximation of the optimal field. The first reads

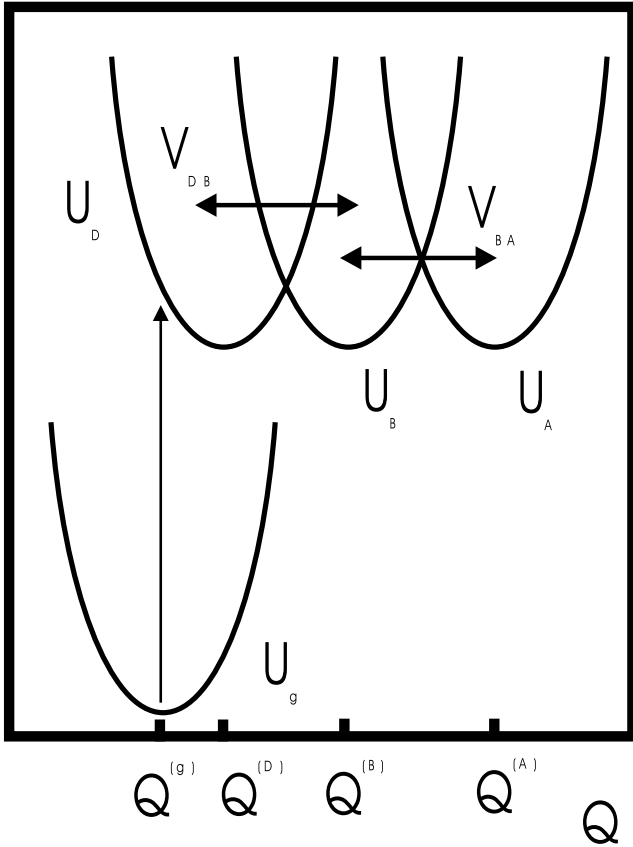
$$\mathbf{E}^{(n)}(t) = \frac{i}{\hbar \lambda(t)} \text{tr}_S \{ \hat{\sigma}^{(n-1)}(t) \mathcal{M} \hat{\rho}^{(n)}(t) \}. \quad (49)$$

If  $\hat{\sigma}^{(n-1)}(t)$  is replaced by the  $n$ 'th iteration  $\hat{\sigma}^{(n)}(t)$  the second approximation for the field is obtained. The fast convergence of this iteration could be demonstrated in [9].

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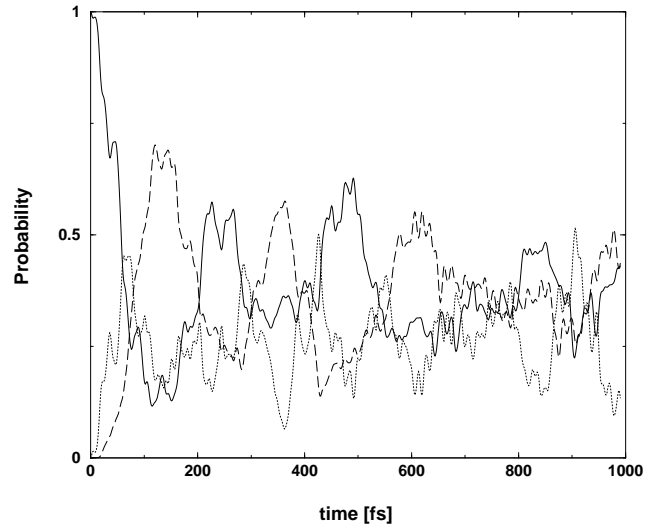




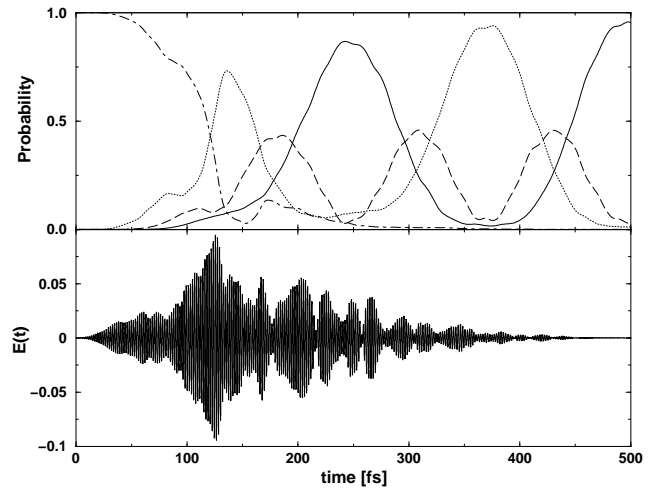
**Fig. 1.** PES referring to the discussed ET system. The position of the PES are somewhat oriented at the system of a dye molecule attached to a semiconductor surface which shows ET on a time scale below 100 fs [25].

$m$	$U_m^{(0)} - U_g^{(0)}$	$\hbar\omega_{\text{vib}}$	$Q^{(m)}$
$g$	0	0.1 eV	-4
$D$	2 eV	0.1 eV	-1.172
$B$	2 eV	0.1 eV	1.414
$A$	2 eV	0.1 eV	4

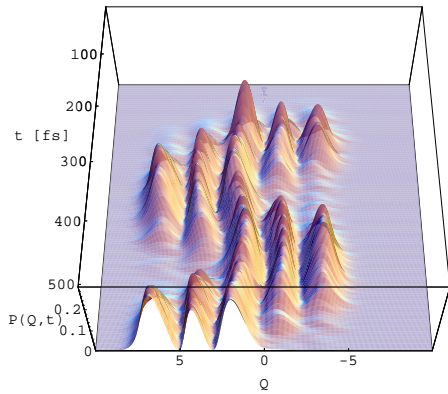
**Table 1.** Parameters of the single-mode version of the ET model introduced in Section 2. The transfer integrals among the three PES responsible for the ET have been taken as  $V_{DB} = V_{BA} = 0.03$  eV, and  $V_{DA} = 0$ . The transition dipole moment  $d_{Dg}$  has been set equal to 12 D.



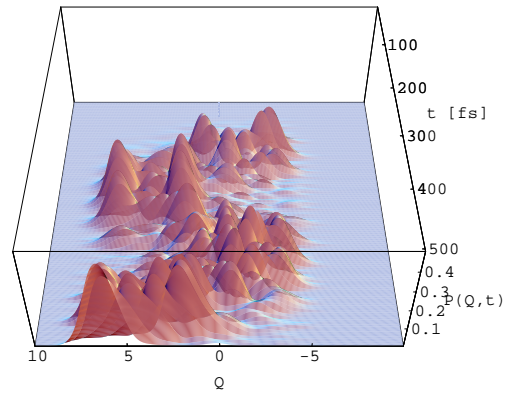
**Fig. 2.** Reference ET dynamics in the DBA-system (parameters see Tab. 1) after an impulsive excitation at  $t = 0$ . The excitation process results in a complete probability transfer into the donor level. The total populations  $P_m$ , Eq. (28) of the donor level (solid line), the bridge level (dotted line) and the acceptor level (dashed line) are shown.



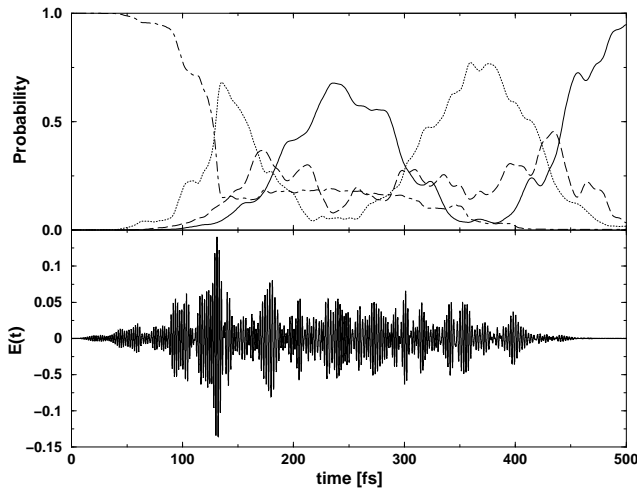
**Fig. 3.** Laser-pulse control of photoinduced ET in the DBA-system. Optical excitation proceeds in the Frank-Condon transition region of the donor level. The second excited vibrational state of the acceptor level  $|\chi_{A2}\rangle > |\varphi_A\rangle$  has been chosen as the target state. Upper part: population  $P_g$  of the ground-state of the ET-system (dashed-dotted line), population  $P_D$  of the donor level (dotted line), population  $P_B$  of the bridge level (dashed line), and population  $P_A$  of the acceptor level (solid line). Lower part: shape of the optimal laser pulse, field in units of  $10^7$  V/cm.



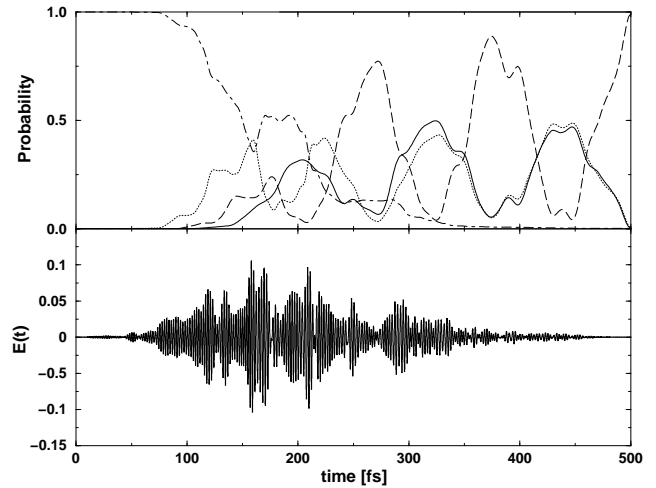
**Fig. 4.** Wavepacket motion (probability distribution  $P(Q, t)$  of the vibrational coordinate, Eq. (29)) related to the controlled ET dynamics shown in Fig. 3. (Note that time increases from the backward part of the figure to the foreground.) The shape of the probability distribution corresponding mainly to a wavepacket with two nodes indicating that the correct target state  $|\chi_{A2} > |\varphi_A >$  has been reached.



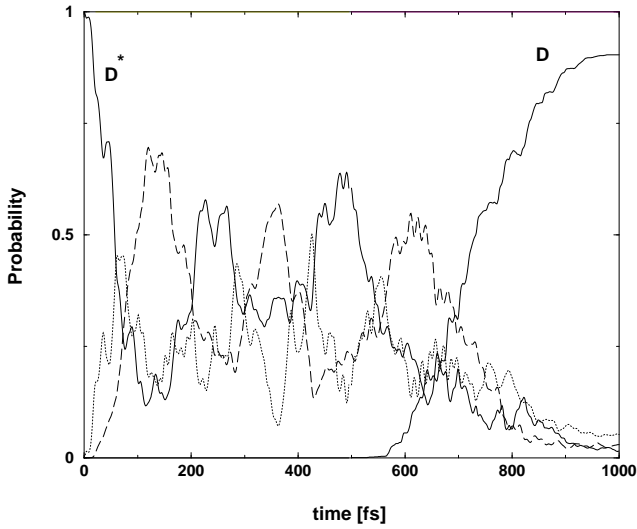
**Fig. 6.** Wavepacket motion (probability distribution  $P(Q, t)$  of the vibrational coordinate) related to the controlled ET dynamics shown in Fig. 5. (Note that time increases from the backward part of the figure to the foreground.) The Gaussian shape of the probability distribution corresponding to the displaced acceptor vibrational ground-state can be clearly identified at  $t = 500 fs$ .



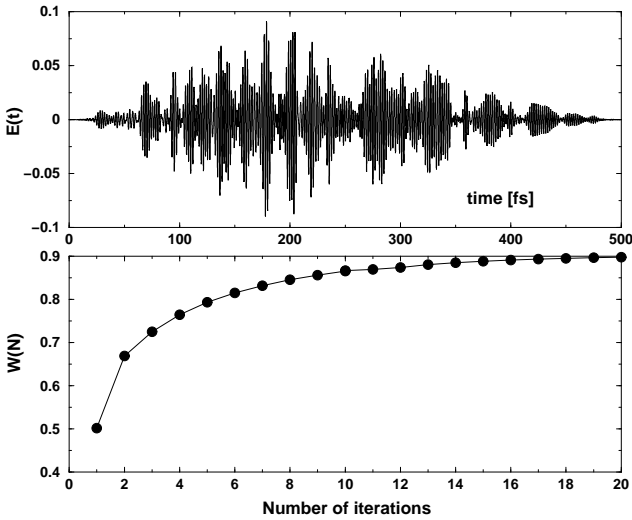
**Fig. 5.** Laser-pulse control of photoinduced ET in the DBA-system. Optical excitation proceeds in the Frank-Condon transition region of the donor level. The target state is given by the vibrational ground-state of the acceptor level but displaced from  $Q^{(A)} = 4$  to the new position 6.4. Upper part: population  $P_g$  of the ground-state of the ET-system (dashed-dotted line), population  $P_D$  of the donor level (dotted line), population  $P_B$  of the bridge level (dashed line), and population of the target state (solid line). Lower part: shape of the optimal laser pulse, field in units of  $10^7 V/cm$ .



**Fig. 7.** Laser-pulse control of photoinduced ET in the DBA-system. Optical excitation proceeds in the Frank-Condon transition region of the donor level. The target state is given by the vibrational ground-state of the bridge level  $|\chi_{B0} > |\varphi_B >$ . Upper part: population  $P_g$  of the ground-state of the ET-system (dashed-dotted line), population  $P_D$  of the donor level (dotted line), population  $P_B$  of the bridge level (dashed line), and population  $P_A$  of the acceptor level (solid line). Lower part: shape of the optimal laser pulse, field in units of  $10^7 V/cm$ .



**Fig. 8.** Laser-pulse induced deexcitation of the DBA-system after photoinduced ET. To excite the system an impulsive mechanism with complete population transfer into the donor level has been assumed (compare Fig. 2). The control pulse is switched on at  $t = 500\text{ fs}$  with the task to transfer all the electronic population back to the vibrational ground-state of the electronic ET system ground-state  $|\chi_{g0}\rangle > |\varphi_g\rangle$  at time  $t = 1000\text{ fs}$ . Shown are the population  $P_g$  of the ground-state of the ET-system, the population  $P_D$  of the donor level (solid line), the population  $P_B$  of the bridge level (dotted line), and the population  $P_A$  of the acceptor level (dashed line). The optimal pulse found after 20 iteration steps of the OC equations has been able to remove about 90% of the population back into the ground-state level.



**Fig. 9.** Laser-pulse induced deexcitation of the DBA-system after photoinduced ET. Upper part: shape of the laser pulse corresponding to the controlled ET displayed in Fig. 8. Field in units of  $10^7\text{ V/cm}$ . Lower part: square of the wavefunction overlap between the  $n$ 'th iteration of the OC equations at  $t = 1000\text{ fs}$  and the target state  $|\chi_{g0}\rangle > |\varphi_g\rangle$  versus iteration steps  $n$ .