

Light-induced current in molecular tunneling junctions excited with intense shaped pulses

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A theory for light-induced current by strong optical pulses in molecular tunneling junctions is described. We consider a molecular bridge represented by its highest occupied and lowest unoccupied levels. We take into account two types of couplings between the molecule and the metal leads: electron transfer that gives rise to net current in the biased junction and energy transfer between the molecule and electron-hole excitations in the leads. Using a Markovian approximation, we derive a closed system of equations for the expectation values of the relevant variables: populations and molecular polarization that are binary, and exciton populations that are tetradic in the annihilation and creation operators for electrons in the molecular states. We have proposed an optical control method using chirped pulses for enhancing charge transfer in unbiased junctions where the bridging molecule is characterized by a strong charge-transfer transition. An approximate analytical solution of the resulting dynamical equations is supported by a full numerical solution. When energy transfer between the molecule and electron-hole excitations in the leads is absent, the optical control problem for inducing charge transfer with a linearly chirped pulse can be reduced to the Landau-Zener transition to a decaying level. When the chirp is fast with respect to the rate of the electron transfer, the Landau theory is recovered. The proposed control mechanism is potentially useful for developing optoelectronic single-electron devices with optical gating based on molecular nanojunctions.

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I. INTRODUCTION

Molecular electronics research attempts to provide substitutes for today's semiconductor electronics. In this relation molecular conduction nanojunctions have been under intense study in the last few years.¹⁻⁴ Recently, a light-induced switching behavior in the conduction properties of molecular nanojunctions has been demonstrated.⁵⁻¹⁰

However, the use of an external electromagnetic field as a controlling tool in the small nanogap between two metal leads is difficult to implement. Currently, techniques available to achieve high spatial resolution with laser illumination are limited by diffraction to about half of the optical wavelength. The introduction of near-field scanning optical microscopes (NSOMs) and tip-enhanced NSOM¹¹ has extended the spatial resolution beyond the diffraction limit. The latter technique uses the strongly confined electromagnetic field generated by optically exciting surface plasmons localized at the apex of a sharp metallic tip, increasing spatial resolution to better than 10 nm.¹¹ Recently, spatial resolution at the atomic scale has also been achieved in the coupling of light to single molecules adsorbed on a surface, using scanning tunneling microscopy.⁸

If experimental setups that can couple biased molecular wires to the radiation field could be achieved, general questions concerning current through the molecular nanojunctions in nonequilibrium situations come to mind. Recently, Galperin and Nitzan investigated a class of molecules characterized by strong charge-transfer transitions into their first excited state.¹² The dipole moment of such molecules changes considerably upon excitation, expressing a strong shift of the electronic charge distribution. For example, the

dipole moment of 4-dimethylamino-4'-nitrostilbene is 7 D in the ground state and ~ 31 D in the first excited singlet state.¹³ For all-*trans* retinal in polymethyl methacrylate films, the dipole increases from ~ 6.6 to 19.8 D upon excitation to the 1B_u electronic state¹⁴ and 40 Å CdSe nanocrystals change their dipole from ~ 0 to ~ 32 D upon excitation to their first excited state.¹⁵ In the independent electron picture, this implies that either the highest occupied (HOMO), $|1\rangle$, or the lowest unoccupied (LUMO) $|2\rangle$, molecular orbital (see Fig. 1) is dominated by atomic orbitals of larger amplitude (and better overlap with metal orbitals) on one side of the molecule than on the other and therefore, when used as molecular wires connecting two metal leads, stronger coupling to one of the leads. They have shown that when such molecular wire connects between two metal leads, a weak steady-state optical pumping can create an internal driving force for charge flow between the leads.

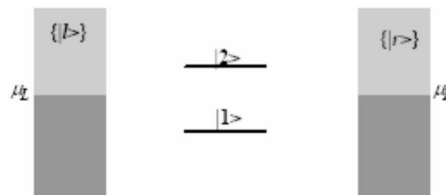


FIG. 1. A model for light-induced effects in molecular conduction. The right ($R=|r\rangle$) and left ($L=|l\rangle$) manifolds represent the two metal leads characterized by electrochemical potentials μ_R and μ_L , respectively. The molecule is represented by its highest occupied molecular orbital (HOMO), $|1\rangle$, and lowest unoccupied molecular orbital (LUMO), $|2\rangle$.

A theory of light-induced effects by weak cw radiation in molecular conduction was developed in Ref. 16. However, there are reasons to consider also molecular junctions subjected to strong electromagnetic fields. First, the structure of such junctions is compatible with configurations considered for large electromagnetic field as in tip-enhanced NSOM.¹¹ Second, it was demonstrated in Ref. 11 that the combination of near-field optics and ultrafast spectroscopy is readily achieved, and the observation of photoinduced processes, such as charge transfer, energy transfer, or isomerization reactions on the nanoscale, is feasible.¹⁷ Third, a consideration of junction stability and integrity suggests that strong radiation fields should be applied as sequences of well separated pulses to allow for sufficient relaxation and heat dissipation. Finally, a consideration of strong time dependent pulses makes it possible to study ways to optimize the desired effect, here the light-induced electron tunneling, i.e., to explore possibilities of coherent control of charge flow between the leads. Our objective in the present work is to extend the theory of Refs. 12 and 16 to strong fields and to apply the theory to studies of coherent control of nanojunction transport.

While these problems are of general and fundamental interest, we note that this study is related to efforts to develop optoelectronic single-electron devices, such as a photon-electron conversion device, optical memory, and single-electron transistors with optical gating.⁶ In addition, the potential significance of molecular nanojunctions for device applications lies in the possibility of creating all-optical switches¹⁸ that could be incorporated in future generations of optical communications systems. It is conceivable that these devices will employ coherent optical manipulations because the speed of coherent manipulations greatly exceeds that of currently available electronic devices.

The outline of the paper is as follows. In Sec. II, we introduce our model. In Sec. III, we derive a closed set of equations for the expectation values of binary and tetradic variables of the annihilation and creation operators for electrons in molecular states $|1\rangle$ and $|2\rangle$, and get formulas for the current and charge transferred during the electromagnetic pulse action. In Sec. IV, we calculate a current induced by the quasistationary intense light pulse. Optical control of current and transferred charge with chirped pulses is considered in Sec. V. We summarize our results in Sec. VI. In the Appendixes, we show that in the absence of the radiative and nonradiative energy transfer couplings, the equations of motion derived in the paper lead to the well-known Landauer formula for the current and present auxiliary calculations.

II. MODEL HAMILTONIAN

We consider a system that comprises a molecule represented by its HOMO, $|1\rangle$, and LUMO, $|2\rangle$, positioned between two leads represented by free electron reservoirs L and R and interacting with the radiation field (Fig. 1). In the independent electron picture, a transition between the ground and excited molecular states corresponds to the transfer of an electron between levels $|1\rangle$ and $|2\rangle$. The electron reservoirs (leads) are characterized by their electronic chemical poten-

tials μ_L and μ_R , where the difference $\mu_L - \mu_R = e\Phi$ is the imposed voltage bias.

The Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (1)$$

where

$$\hat{H}_0 = \sum_{m=1,2} \varepsilon_m \hat{n}_m + \sum_{k \in \{L,R\}} \varepsilon_k \hat{n}_k \quad (2)$$

contains additively terms that correspond to the isolated molecule (m) and the free leads (k). Here, $\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i$ is the population operator in state i , and the operators \hat{c} and \hat{c}^\dagger are annihilation and creation operators of an electron in the various states.

The interaction term \hat{V} can be written as

$$\hat{V} = \hat{V}_M + \hat{V}_P + \hat{V}_N, \quad (3)$$

where \hat{V}_P accounts for the effect of the external radiation field. The latter is represented by the (classical) function

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}^{(+)}(t) + \mathbf{E}^{(-)}(t) = \frac{1}{2} \mathbf{e} \mathcal{E}(t) \exp[-i\omega t + i\varphi(t)] + \text{c.c.} \quad (4)$$

characterized by the pulse envelope $\mathcal{E}(t)$, carrier frequency ω , and (possibly) time-dependent phase $\varphi(t)$. The time-dependent phase corresponds to the time evolution of the pulse frequency (chirp) $\omega(t) = \omega - d\varphi(t)/dt$. Introducing bilinear operators of the excitonic type

$$b_{ij}^+ = b_{ji} \equiv \hat{c}_i^\dagger \hat{c}_j \quad (i \neq j), \quad b_M^+ \equiv b_{21}^+ = \hat{c}_2^\dagger \hat{c}_1, \quad (5)$$

$$b_M = b_{21} = \hat{c}_1^\dagger \hat{c}_2,$$

the molecule-radiation field coupling \hat{V}_P can be written as follows in the resonance or rotating wave approximation (RWA):

$$\hat{V}_P = -\frac{1}{2} (\mathbf{d} \cdot \mathbf{e}) \{b_M^+ \mathcal{E}(t) \exp[-i\omega t + i\varphi(t)] + \text{H.c.}\}, \quad (6)$$

where \mathbf{d} is the transition dipole moment.

The other terms in Eq. (3) describe coupling between the molecule and the metal electronic subsystems. In terms of the excitonic operators defined in Eq. (5), they are given by

$$\hat{V}_M = \sum_{K=L,R} \sum_{m=1,2; k \in K} (V_{km}^{(MK)} b_{mk} + \text{H.c.}), \quad (7)$$

$$\hat{V}_N = \sum_{K=L,R} \sum_{k \neq k' \in K} (V_{kk'}^{(NK)} b_{k'k} b_M^+ + V_{k'k}^{(NK)} b_M b_{k'k}^+), \quad (8)$$

where L and R denote the left and right leads, respectively, and H.c. denotes Hermitian conjugate. \hat{V}_M and \hat{V}_N , Eqs. (7) and (8), respectively, denote two types of couplings between the molecule and the metal leads: \hat{V}_M describes electron transfer that gives rise to net current in the biased junction, while \hat{V}_N describes energy transfer between the molecule and

electron-hole excitations in the leads. The latter interaction strongly affects the lifetime of excited molecules near metal surfaces¹⁹ and may also affect the current in a biased junction.²⁰ In Eq. (8), \hat{V}_N is written in the near-field approximation, disregarding retardation effects that will be important at large molecule-lead distances.

III. EQUATIONS OF MOTION

The physics of the system can be described within different approaches. One is the method of nonequilibrium Green's functions.^{12,16,21} It has advantages of a formal treatment due to the possibility of a diagrammatic representation, and it is particularly well suited for stationary processes where the Dyson equation can be cast in the energy representation. For time-dependent processes, such as are the subject of this work, a method based on the equations of motion for the expectation values of the operators provides a more transparent approach since the quantities are more directly related to physical observables. Such a method is adopted here. Using a Markovian approximation for the relaxation induced by the molecule-metal lead coupling, we derive a closed set of equations for the expectation values of binary $\langle \hat{n}_m \rangle = n_m$ and $\langle b_M \rangle = p_M$ and tetradic $\langle b_M^+ b_M \rangle = N_M$ variables of the annihilation and creation operators for electrons in molecular states $|1\rangle$ and $|2\rangle$. The first expression is simply the population of electrons in molecular state m , the second gives the molecular polarization, and the third represents the molecular excitation, referred to below as the molecular excitation population.

Using the Heisenberg equations of motion, one obtains the equation for the expectation value of any operator \hat{F} ,

$$\frac{d}{dt} \langle \hat{F} \rangle = \frac{i}{\hbar} \langle [\hat{H}_0 + \hat{V}, \hat{F}] \rangle \equiv \frac{i}{\hbar} \text{Tr}([\hat{H}_0 + \hat{V}, \hat{F}] \rho), \quad (9)$$

where ρ is the density matrix. Straightforward operator algebra manipulations yield for n_m and p_M in RWA,

$$\begin{aligned} \frac{dn_m}{dt} &= (-1)^m \text{Im} \{ \Omega^*(t) p_M \exp[i\omega t - i\varphi(t)] \} \\ &\quad - \frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \in K} V_{km}^{(MK)} \langle b_{mk} \rangle \\ &\quad - \frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \neq k' \in K} [\delta_{2m} V_{k'k}^{(NK)} \langle b_M b_{k'k}^+ \rangle \\ &\quad + \delta_{1m} V_{kk'}^{(NK)} \langle b_M b_{k'k}^+ \rangle^*], \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{dp_M}{dt} &= \frac{i}{\hbar} (\varepsilon_1 - \varepsilon_2) p_M + \frac{i}{2} \Omega(t) \exp[-i\omega t + i\varphi(t)] (n_1 - n_2) \\ &\quad + \frac{i}{\hbar} \sum_{K=L,R} \sum_{k \in K} (V_{k1}^{(MK)} \langle b_{k2}^+ \rangle - V_{2k}^{(MK)} \langle b_{k1} \rangle) \\ &\quad + \frac{i}{\hbar} \sum_{K=L,R} \sum_{k \neq k' \in K} V_{kk'}^{(NK)} \langle b_{k'k} (\hat{n}_2 - \hat{n}_1) \rangle, \end{aligned} \quad (11)$$

where $\Omega(t) = (\mathbf{d} \cdot \mathbf{e}) \mathcal{E}(t) / \hbar$ is the Rabi frequency. The equa-

tions of motion include couplings to additional correlations of the second order $\langle b_{mk} \rangle$ due to the electron-transfer interaction \hat{V}_M and to higher-order correlations $\langle b_M b_{k'k}^+ \rangle$, etc., due to the energy transfer \hat{V}_N . To obtain expressions for these correlations, we now compute their equations of motion using the Markovian approximation for the relaxations induced by the molecule-metal lead couplings \hat{V}_M and \hat{V}_N . In this work, we assume that the relaxation processes due to \hat{V}_M and \hat{V}_N are not interdependent and also do not depend on the external electromagnetic field. We shall discuss the last approach in Sec. VI.

A. Calculation of terms associated with the electron-transfer interaction \hat{V}_M in the equations for n_m and p_M

In evaluating the effect of the relaxation processes associated with the electron transfer and energy transfer terms in the Hamiltonian, \hat{V}_M and \hat{V}_N , respectively, we make the approximation (known as the noncrossing approximation) that these processes do not affect each other. A similar assumption is made with respect to the effect of the external field. With this in mind, we consider the expectation values $\langle b_{km} \rangle$ and $\langle b_{mk} \rangle$ that enter the terms containing \hat{V}_M on the right-hand side of Eqs. (10) and (11) and omit \hat{V}_P and \hat{V}_N terms in the equations of motion that describe their evolution. This leads to

$$\begin{aligned} \frac{d}{dt} \langle b_{mk} \rangle &= \frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \langle b_{mk} \rangle + \frac{i}{\hbar} \sum_{m'=1,2} V_{m'k}^{(MK)} \langle \hat{c}_{m'}^+ \hat{c}_m \rangle \\ &\quad - \frac{i}{\hbar} V_{mk}^{(MK)} f_K(\varepsilon_k), \end{aligned} \quad (12)$$

where we assumed that the leads are in equilibrium with the expectation values

$$\langle \hat{c}_k^+ \hat{c}_{k'} \rangle = f_K(\varepsilon_k) \delta_{kk'}, \quad (13)$$

where $f_K(\varepsilon_k) = \{\exp[(\varepsilon_k - \mu_k) / k_B T] + 1\}^{-1}$ is the Fermi function and $\delta_{kk'}$ is the Kronecker delta. Formally integrating Eq. (12), we get

$$\begin{aligned} \langle b_{mk} \rangle &= \frac{i}{\hbar} \int_{-\infty}^t dt' \exp\left[\frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) (t - t')\right] \\ &\quad \times \left[\sum_{m'=1,2} V_{m'k}^{(MK)} \langle \hat{c}_{m'}^+ \hat{c}_m \rangle(t') - V_{mk}^{(MK)} f_K(\varepsilon_k) \right]. \end{aligned} \quad (14)$$

In the absence of the \hat{V}_N coupling, this results in a set of integrodifferential equations for $\langle \hat{c}_m^+ \hat{c}_m \rangle = n_m$ and $\langle \hat{c}_1^+ \hat{c}_2 \rangle = p_M$. The dynamics contains memory effects and is therefore non-Markovian. Next, we make a Markovian approximation by transforming $\langle \hat{c}_m^+ \hat{c}_m \rangle$ to the interaction representation: $\langle \hat{c}_m^+ \hat{c}_m \rangle(t') = \langle \hat{c}_m^+ \hat{c}_m \rangle^{int}(t') \exp\left[\frac{i}{\hbar} (\varepsilon_{m'} - \varepsilon_m) t'\right]$ and assuming that a slowly varying function $\langle \hat{c}_m^+ \hat{c}_m \rangle^{int}(t')$ can be moved as $\langle \hat{c}_m^+ \hat{c}_m \rangle^{int}(t)$ to outside the integral.⁴⁶ Equation (14) then becomes

$$\begin{aligned} \langle b_{mk} \rangle &= \langle b_{km} \rangle^* = \frac{i}{\hbar} \left\{ \sum_{m'=1,2} V_{m'k}^{(MK)} \langle \hat{c}_{m'}^+ \hat{c}_m \rangle(t) \right. \\ &\quad \times \left[\frac{i\hbar P}{\varepsilon_k - \varepsilon_{m'}} + \hbar \pi \delta(\varepsilon_k - \varepsilon_{m'}) \right] - V_{mk}^{(MK)} f_K(\varepsilon_k) \\ &\quad \left. \times \left[\frac{i\hbar P}{\varepsilon_k - \varepsilon_m} + \hbar \pi \delta(\varepsilon_k - \varepsilon_m) \right] \right\}, \end{aligned} \quad (15)$$

where P denotes the principal value. Substituting the last result into the corresponding terms containing \hat{V}_M on the right-hand side of Eqs. (10) and (11) and keeping only resonant terms, we have

$$\frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \in K} V_{km}^{(MK)} \langle b_{mk} \rangle = \sum_{K=L,R} [n_m(t) \Gamma_{MK,m} - W_{MK,m}] \quad (16)$$

and

$$\begin{aligned} &\frac{i}{\hbar} \sum_{K=L,R} \sum_{k \in K} (V_{k1}^{(MK)} \langle b_{k2}^+ \rangle - V_{2k}^{(MK)} \langle b_{k1} \rangle) \\ &= -p_M(t) \sum_{K=L,R} \left[\frac{1}{2} (\Gamma_{MK,1} + \Gamma_{MK,2}) + i\Delta_{MK} \right]. \end{aligned} \quad (17)$$

where

$$\Gamma_{MK,m} = \frac{2\pi}{\hbar} \sum_{k \in K} |V_{km}^{(MK)}|^2 \delta(\varepsilon_k - \varepsilon_m). \quad (18)$$

$$\Delta_{MK} = \frac{1}{\hbar} P \sum_{k \in K} \left[\frac{|V_{k1}^{(MK)}|^2}{\varepsilon_k - \varepsilon_1} - \frac{|V_{2k}^{(MK)}|^2}{\varepsilon_k - \varepsilon_2} \right] \quad (19)$$

is the correction to the frequency of molecular transition $(\varepsilon_2 - \varepsilon_1)/\hbar$ due to electron transfer between the molecule and lead K ,

$$W_{MK,m} = \frac{2\pi}{\hbar} \sum_{k \in K} f_K(\varepsilon_k) |V_{km}^{(MK)}|^2 \delta(\varepsilon_k - \varepsilon_m) \quad (20)$$

$$= f_K(\varepsilon_m) \Gamma_{MK,m}. \quad (21)$$

It should be noted that the second equality, Eq. (21), is valid only provided that molecular state ε_m is far from the Fermi level of lead K and, in addition, that the spectral function $\Gamma_{MK,m}(\varepsilon_m) = \frac{2\pi}{\hbar} \sum_{k \in K} |V_{km}^{(MK)}|^2 \delta(\varepsilon_k - \varepsilon_m)$ can be replaced by a constant. The latter condition holds provided that $\Gamma_{MK,m}$ is small relative to the bath correlation frequency ω_c —the range over which its spectral density essentially changes. For metals, ω_c can be estimated as 1–10 eV.²² The situation is different if we assume that the molecular level position is pinned to the Fermi energy of a lead. In the latter case, ω_c for $W_{MK,m}$ is determined also by the frequency interval at which $f_K(\varepsilon)$ is essentially changed, that is, $\sim k_B T/\hbar = 0.026$ eV for room temperature [see Eq. (20)]. Since the value of ω_c places a limit on the used approximation, according to which the relaxation parameters do not depend on exciting electromagnetic field (see Sec. VI), one can use Eq. (21) only in the case

when the bath correlation frequency ω_c is the same for both $W_{MK,m}$ and $\Gamma_{MK,m}$.

One can easily see from Eqs. (10), (11), (16), and (17) that in the absence of energy transfer (\hat{V}_N), equations for the populations of molecular states and molecular polarization form a closed set of the equations of motion.

B. Calculation of terms related to energy transfer in the equations for n_m and p_M

The calculation of terms related to energy transfer in Eqs. (10) and (11) is similar to that of Sec. III A. Invoking again the noncrossing approximation by omitting \hat{V}_P and \hat{V}_M terms in the equations of motion for the expectation values $\langle b_M b_{k'k}^+ \rangle$ and $\langle b_{k'k}(\hat{n}_2 - \hat{n}_1) \rangle$, which appear on the right-hand sides of Eqs. (10) and (11), respectively, we get

$$\begin{aligned} \frac{d}{dt} \langle b_M b_{k'k}^+ \rangle &= \frac{i}{\hbar} (\varepsilon_{k'} - \varepsilon_k - \varepsilon_2 + \varepsilon_1) \langle b_M b_{k'k}^+ \rangle + \frac{i}{\hbar} V_{kk'}^{(NK)} \{ f_K(\varepsilon_k) \\ &\quad \times [1 - f_K(\varepsilon_{k'})] \langle b_M^+ b_M \rangle - f_K(\varepsilon_{k'}) [1 - f_K(\varepsilon_k)] \\ &\quad \times \langle b_M b_M^+ \rangle \}, \end{aligned} \quad (22)$$

$$\begin{aligned} \frac{d}{dt} \langle b_{k'k}(\hat{n}_2 - \hat{n}_1) \rangle &= \frac{i}{\hbar} (\varepsilon_k - \varepsilon_{k'}) \langle b_{k'k}(\hat{n}_2 - \hat{n}_1) \rangle + \frac{i}{\hbar} V_{k'k}^{(NK)} \\ &\quad \times \{ f_K(\varepsilon_{k'}) [1 - f_K(\varepsilon_k)] \\ &\quad + f_K(\varepsilon_k) [1 - f_K(\varepsilon_{k'})] \} p_M. \end{aligned} \quad (23)$$

Formally integrating the last equations, performing Markovian approximation, and substituting the results into the corresponding terms containing \hat{V}_N on the right-hand side of Eqs. (10) and (11), we obtain

$$\begin{aligned} &-\frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \neq k' \in K} V_{k'k}^{(NK)} \langle b_M b_{k'k}^+ \rangle \\ &= \sum_{K=L,R} [B_{NK}(\varepsilon_1 - \varepsilon_2, \mu_K) \langle b_M b_M^+ \rangle \\ &\quad - B_{NK}(\varepsilon_2 - \varepsilon_1, \mu_K) \langle b_M^+ b_M \rangle] \end{aligned} \quad (24)$$

and

$$\begin{aligned} &\frac{i}{\hbar} \sum_{K=L,R} \sum_{k \neq k' \in K} V_{kk'}^{(NK)} \langle b_{k'k}(\hat{n}_2 - \hat{n}_1) \rangle \\ &= -p_M(t) \sum_{K=L,R} \left\{ i\Delta_{NK} \right. \\ &\quad \left. + \frac{1}{2} [B_{NK}(\varepsilon_1 - \varepsilon_2, \mu_K) + B_{NK}(\varepsilon_2 - \varepsilon_1, \mu_K)] \right\}, \end{aligned} \quad (25)$$

where

$$\begin{aligned} B_{NK}(\varepsilon_m - \varepsilon_n, \mu_K) &= \frac{2\pi}{\hbar} \sum_{k \neq k' \in K} |V_{kk'}^{(NK)}|^2 \delta(\varepsilon_k - \varepsilon_{k'} + \varepsilon_m - \varepsilon_n) \\ &\quad \times f_K(\varepsilon_k) [1 - f_K(\varepsilon_{k'})], \end{aligned} \quad (26)$$

and

$$\Delta_{NK} = \frac{1}{\hbar} P \sum_{k \neq k' \in K} \{f_K(\varepsilon_{k'})[1 - f_K(\varepsilon_k)] + f_K(\varepsilon_k)\} \times [1 - f_K(\varepsilon_{k'})] \frac{|V_{kk'}^{(NK)}|^2}{\varepsilon_k - \varepsilon_{k'} + \varepsilon_2 - \varepsilon_1} \quad (27)$$

is the correction to the frequency of molecular transition $(\varepsilon_2 - \varepsilon_1)/\hbar$ due to energy transfer between the molecule and lead K . In deriving Eqs. (24) and (25), we have used the arguments that are similar to those used above in the derivation of Eqs. (16) and (17).

One can see from Eqs. (10) and (24) that in the presence of energy transfer (\hat{V}_N), equations for the populations of molecular states and molecular polarization do not form a closed set of the equations of motion. They must be supplemented, at least, with equations for the expectation values of tetradic variables $\langle b_M b_M^+ \rangle$ and $\langle b_M^+ b_M \rangle = N_M$, where $\langle b_M b_M^+ \rangle$ and N_M are related by the following equation:

$$\langle b_M b_M^+ \rangle = N_M - n_2 + n_1. \quad (28)$$

C. Equation for $\langle b_M b_M^+ \rangle$

Using Eq. (9), straightforward operator algebra manipulations yield for $\langle b_M b_M^+ \rangle$ in RWA,

$$\begin{aligned} \frac{d\langle b_M b_M^+ \rangle}{dt} = & -\frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \in K} (V_{k1}^{(MK)} \langle b_{2k} b_M^+ \rangle - V_{2k}^{(MK)} \langle b_{k1} b_M^+ \rangle) \\ & + \frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \neq k' \in K} V_{k'k}^{(NK)} \langle b_M b_{k'k}^+ \rangle \\ & - \text{Im} \{ \Omega^*(t) \exp[i\omega t - i\varphi(t)] p_M \}, \end{aligned} \quad (29)$$

where the second term on the right-hand side has been calculated above, Eq. (24). The first term on the right-hand sides of Eq. (29) is associated with the electron-transfer process. To evaluate it, we consider the equations of motion for the expectation values $\langle b_{2k} b_M^+ \rangle$ and $\langle b_{k1} b_M^+ \rangle$, omitting \hat{V}_P and \hat{V}_N interactions and keeping only resonant terms,

$$\begin{aligned} \frac{d\langle b_{2k} b_M^+ \rangle}{dt} = & \frac{i}{\hbar} (\varepsilon_k - \varepsilon_1) \langle b_{2k} b_M^+ \rangle + \frac{i}{\hbar} V_{1k}^{(MK)} [\langle b_M b_M^+ \rangle - f_K(\varepsilon_k)] \\ & \times (1 - n_2), \end{aligned} \quad (30)$$

$$\begin{aligned} \frac{d\langle b_{k1} b_M^+ \rangle}{dt} = & \frac{i}{\hbar} (\varepsilon_2 - \varepsilon_k) \langle b_{k1} b_M^+ \rangle + \frac{i}{\hbar} V_{k2}^{(MK)} \{ [1 - f_K(\varepsilon_k)] n_1 \\ & - \langle b_M b_M^+ \rangle \}. \end{aligned} \quad (31)$$

Integrating Eqs. (30) and (31), performing Markovian approximation, and substituting the results into the first term on the right-hand side of Eq. (29), we get

$$\begin{aligned} & -\frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \in K} (V_{k1}^{(MK)} \langle b_{2k} b_M^+ \rangle - V_{2k}^{(MK)} \langle b_{k1} b_M^+ \rangle) \\ & = \sum_{K=L,R} [-\langle b_M b_M^+ \rangle (\Gamma_{MK,1} + \Gamma_{MK,2}) + (1 - n_2) W_{MK,1} \\ & \quad + (\Gamma_{MK,2} - W_{MK,2}) n_1], \end{aligned} \quad (32)$$

where $\Gamma_{MK,m}$ and $W_{MK,m}$ were defined in Eqs. (18), (20), and (21).

D. Closed set of the equations of motion

We are now in a position to get a closed set of the equations of motion. Substituting Eqs. (16) and (24) into Eq. (10) and using Eq. (28), we obtain the equation for the population of electrons in molecular state m . The substitution of Eqs. (17) and (25) into Eq. (11) gives the equation describing the dynamics of molecular polarization p_M . At last, substituting Eqs. (16) and (32) into Eq. (29) and using Eq. (28), we get the equation for molecular exciton population N_M . Then, switching to the system that rotates with instantaneous frequency $\omega(t)$, $\tilde{p}_M(t) = p_M(t) \exp[i\omega t - \varphi(t)]$, we obtain a closed set of equations for the quantities that vary slowly with time during the period of a light wave,

$$\begin{aligned} \frac{dn_m}{dt} = & (-1)^m \text{Im} [\Omega^*(t) \tilde{p}_M] + W_{Mm} - \Gamma_{Mm} n_m - (-1)^m \\ & \times [B_N(\varepsilon_2 - \varepsilon_1) N_M - (n_1 - n_2 + N_M) B_N(\varepsilon_1 - \varepsilon_2)], \end{aligned} \quad (33)$$

$$\frac{d\tilde{p}_M}{dt} = i[\omega(t) - \omega_0] \tilde{p}_M + \frac{i}{2} \Omega(t) (n_1 - n_2) - \frac{1}{2} \Gamma_{MN} \tilde{p}_M, \quad (34)$$

$$\begin{aligned} \frac{dN_M}{dt} = & (\Gamma_{M1} - W_{M1}) n_2 + W_{M2} (1 - n_1) + \text{Im} [\Omega^*(t) \tilde{p}_M] \\ & - [B_N(\varepsilon_2 - \varepsilon_1) + \tilde{\Gamma}_{M1} + \tilde{\Gamma}_{M2}] N_M \\ & + (n_1 - n_2 + N_M) B_N(\varepsilon_1 - \varepsilon_2), \end{aligned} \quad (35)$$

where

$$\Gamma_{Mm} = \sum_{K=L,R} \Gamma_{MK,m}, \quad W_{Mm} = \sum_{K=L,R} W_{MK,m}, \quad (36)$$

$$\sum_{K=L,R} B_{NK}(\varepsilon_m - \varepsilon_n, \mu_K) = B_N(\varepsilon_m - \varepsilon_n), \quad (37)$$

$$\Gamma_{MN} = \Gamma_{M1} + \Gamma_{M2} + B_N(\varepsilon_2 - \varepsilon_1) + B_N(\varepsilon_1 - \varepsilon_2), \quad (38)$$

and $\omega_0 \equiv (\varepsilon_2 - \varepsilon_1)/\hbar + \sum_{K=L,R} (\Delta_{NK} + \Delta_{MK})$ is the frequency of the molecular transition with the corrections due to energy and electron transfer between the molecule and the leads.

As indicated above, equations for the populations of molecular states and molecular polarization, Eqs. (33) and (34), form a closed set of the equations of motion if the energy transfer is absent $[B_N(\varepsilon_m - \varepsilon_n) = 0]$. When energy transfer is present, they must be supplemented with Eq. (35) for the

exciton population. On the other hand, in the absence of electron transfer ($W_{Mm}=\Gamma_{Mm}=0$), Eq. (35) coincides with Eq. (33) for n_2 , which implies that $N_M=n_2$. Indeed, $N_M=\langle\hat{c}_2^\dagger\hat{c}_1\hat{c}_1^\dagger\hat{c}_2\rangle=\langle\hat{n}_2(1-\hat{n}_1)\rangle=\langle\hat{n}_2^2\rangle=\langle\hat{n}_2\rangle=n_2$ when the electron population on the molecule is conserved, i.e., when $\hat{V}_M=0$. It is the combined effect of the electron and energy transfer, represented by the terms \hat{V}_M and \hat{V}_N in the Hamiltonian, that leads to the need to include Eq. (35) in the closed set of the equations of motion.

E. Calculation of current and transferred charge

The electronic current I is given by the rate at which the number of electrons changes in any of the leads, e.g.,^{21,22}

$$I=e\frac{d}{dt}\sum_{k\in L}\langle\hat{n}_k\rangle=\frac{ie}{\hbar}\sum_{k\in L}\langle[\hat{H},\hat{n}_k]\rangle. \quad (39)$$

Evaluating the commutator in Eq. (39), we get

$$I=\frac{2e}{\hbar}\text{Im}\sum_{m=1,2}\sum_{k\in L}V_{km}^{(MK)}\langle b_{mk}\rangle=e\sum_{m=1,2}[n_m(t)\Gamma_{ML,m}-W_{ML,m}], \quad (40)$$

where we used Eq. (16). Correspondingly, the charge transferred during an electromagnetic pulse of finite duration is given by $Q=\int_{-\infty}^{\infty}I(t)dt$.

In Appendix A, we show that in the absence of the radiative and nonradiative energy transfer couplings, \hat{V}_P and \hat{V}_N , Eqs. (18), (20), (21), (33), (36), and (40) lead to the well-known Landauer formula for the current.²³

IV. CURRENT INDUCED BY A QUASISTATIONARY LIGHT PULSE

In this section, we calculate the current induced in molecular nanojunctions by a strong quasistationary light pulse. Here and in the next section, we assume that the molecular energy gap $\varepsilon_2-\varepsilon_1$ is much larger than the voltage bias $\mu_L-\mu_R$ and that the HOMO and LUMO energies, ε_1 and ε_2 , are positioned rather far ($\gg k_B T$) from the Fermi levels of both leads, so that the dark (Landauer) current through the junction is small and may be disregarded. Using for this situation $W_{MK,1}\approx\Gamma_{MK,1}$ and $W_{MK,2}\approx B_{NK}(\varepsilon_1-\varepsilon_2,\mu_K)\approx 0$, we obtain the following from Eqs. (33)–(35) and (40):

$$\frac{dn_1}{dt}=-\text{Im}[\Omega^*(t)\tilde{p}_M]+\Gamma_{M1}(1-n_1)+B_N(\varepsilon_2-\varepsilon_1)N_M, \quad (41)$$

$$\frac{dn_2}{dt}=\text{Im}[\Omega^*(t)\tilde{p}_M]-\Gamma_{M2}n_2-B_N(\varepsilon_2-\varepsilon_1)N_M, \quad (42)$$

$$\frac{d\tilde{p}_M}{dt}=i[\omega(t)-\omega_0]\tilde{p}_M+\frac{i}{2}\Omega(t)(n_1-n_2)-\frac{1}{2}\Gamma_{MN}\tilde{p}_M, \quad (43)$$

$$\frac{dN_M}{dt}=\text{Im}[\Omega^*(t)\tilde{p}_M]-[B_N(\varepsilon_2-\varepsilon_1)+\Gamma_{M1}+\Gamma_{M2}]N_M, \quad (44)$$

$$I=e[(n_1-1)\Gamma_{ML,1}+n_2\Gamma_{ML,2}]. \quad (45)$$

Note that although Eqs. (40) and (45) have the form of a rate expression, coherences have not been disregarded, as is evidenced by the fact that the populations n_1 and n_2 depend on the polarization \tilde{p}_M . One can see from Eq. (45) that the current strongly increases when $n_2, 1-n_1\sim 1$, which can be realized for strong light fields. If we further assume that the pulse amplitude $\mathcal{E}(t)$ and frequency $\omega(t)$ change slowly on the time scale of all relaxation times as well as the reciprocal Rabi frequency, one can put all time derivatives on the left-hand sides of Eqs. (41)–(44) equal to zero, and the resulting stationary equations can be easily solved,

$$n_2=\frac{\Omega^2(t)(\Gamma_{M2}+\Gamma_{M1})/(4\Gamma_{M2})}{\frac{(\Gamma_{M2}+\Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}}\Omega^2(t)+(\Gamma_{MN}/2)^2+[\omega_0-\omega(t)]^2}, \quad (46)$$

$$n_1=1-n_2\frac{\Gamma_{M2}}{\Gamma_{M1}}, \quad (47)$$

$$N_M=\frac{\Gamma_{M2}}{\Gamma_{M1}+\Gamma_{M2}}n_2, \quad (48)$$

$$\tilde{p}_M=\frac{\Omega(t)}{2}\frac{i(\Gamma_{MN}/2)-[\omega(t)-\omega_0]}{\Omega^2(t)\frac{(\Gamma_{M2}+\Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}}+(\Gamma_{MN}/2)^2+[\omega_0-\omega(t)]^2}. \quad (49)$$

This solution corresponds to the molecular level and exciton populations as well as polarization adiabatically following the optical pulse. Substituting Eqs. (46) and (47) into Eq. (45), we get

$$I(t)=e\frac{\Gamma_{M2}+\Gamma_{M1}}{4\Gamma_{M1}\Gamma_{M2}}\times\frac{\Omega^2(t)(\Gamma_{ML,2}\Gamma_{MR,1}-\Gamma_{ML,1}\Gamma_{MR,2})}{\Omega^2(t)\frac{(\Gamma_{M2}+\Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}}+\left(\frac{\Gamma_{MN}}{2}\right)^2+[\omega_0-\omega(t)]^2}. \quad (50)$$

At steady state $[\omega(t)=\omega, \Omega(t)=\Omega]$ and small fields, $\Omega^2\frac{(\Gamma_{M2}+\Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}}\ll(\Gamma_{MN}/2)^2$, this becomes

$$I=e\frac{\Omega^2}{4}\frac{\Gamma_{M2}+\Gamma_{M1}}{(\Gamma_{MN}/2)^2+(\omega_0-\omega)^2}\frac{\Gamma_{ML,2}\Gamma_{MR,1}-\Gamma_{ML,1}\Gamma_{MR,2}}{\Gamma_{M1}\Gamma_{M2}}. \quad (51)$$

The last equation is similar to Eq. (50) of Ref. 16, with the only difference that the latter corresponds to the substitution of the sum $\Gamma_{M2}+\Gamma_{M1}$ on the right-hand side of Eq. (51) by

$\Gamma_{MN} = \Gamma_{M2} + \Gamma_{M1} + B_N(\varepsilon_2 - \varepsilon_1) > \Gamma_{M2} + \Gamma_{M1}$. The difference may arise from the fact that Eq. (50) of Ref. 16 is obtained in the much used approximation of strong dephasing²⁴ $N_M = \langle \hat{n}_2(1 - \hat{n}_1) \rangle \approx n_2(1 - n_1)$. For small fields, the latter term is of order Ω^4 since $n_2, 1 - n_1 \sim \Omega^2$. As a matter of fact, when the exciting field is weak, one can neglect the term $B_N(\varepsilon_2 - \varepsilon_1)n_2(1 - n_1) \sim \Omega^4$ with respect to $\Gamma_{M1}(1 - n_1) \sim \Omega^2$ and $\Gamma_{M2}n_2 \sim \Omega^2$ on the right-hand sides of Eqs. (41) and (42), respectively. In other words, the approximation of strong dephasing $N_M \approx n_2(1 - n_1)$ disregards the depletion of state 2 due to energy transfer for small fields, and therefore results in some overestimation of the current. In contrast, our present approach takes the tetradic variable N_M into account exactly (in the framework of the Markovian approximation) and does describe the depletion of state 2 due to energy transfer.

For strong fields and near resonance excitation, $\Omega^2(t) \frac{(\Gamma_{M2} + \Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}} \gg (\Gamma_{MN}/2)^2, [\omega_0 - \omega(t)]^2$, Eqs. (46)–(49) describe the saturation effect,

$$n_1 = n_2 = \frac{\Gamma_{M1}}{\Gamma_{M2} + \Gamma_{M1}}, \quad (52)$$

$$N_M = \frac{\Gamma_{M1}\Gamma_{M2}}{(\Gamma_{M2} + \Gamma_{M1})^2}, \quad (53)$$

$$\tilde{P}_M = \frac{2\Gamma_{M1}\Gamma_{M2}}{(\Gamma_{M2} + \Gamma_{M1})^2} \frac{i(\Gamma_{MN}/2) - [\omega(t) - \omega_0]}{\Omega(t)}, \quad (54)$$

and Eq. (40) gives

$$I = e \frac{\Gamma_{ML,2}\Gamma_{MR,1} - \Gamma_{ML,1}\Gamma_{MR,2}}{\Gamma_{M2} + \Gamma_{M1}}. \quad (55)$$

Equations (50) and (55) show that the optically induced current increases linearly with the pulse intensity $\sim \Omega^2$ for weak fields and saturates at the maximal value given by Eq. (55) for strong fields. As is easy to see from Eqs. (52) and (53), in the latter case, $N_M = n_2(1 - n_1)$ since the strong dephasing limit where \tilde{P}_M can be disregarded is realized under saturation effect [see Eq. (54)].

V. OPTICAL CONTROL OF CURRENT AND TRANSFERRED CHARGE WITH CHIRPED PULSES

In the previous section we have generalized the results of Refs. 12 and 16 to the quasistationary strong electromagnetic field limit. As mentioned in the Introduction, future generations of optical communication systems will employ coherent optical manipulations whose speed greatly exceeds that of currently available electronic devices. We next consider such coherent control processes.

Two well-known procedures based on a coherent excitation can, in principle, produce a complete population inversion in an ensemble of two-level atoms. One of them is the π -pulse excitation,²⁵ which makes use of the Rabi population oscillations. This approach has been successfully demonstrated in atoms as well as semiconductor quantum dots, of-

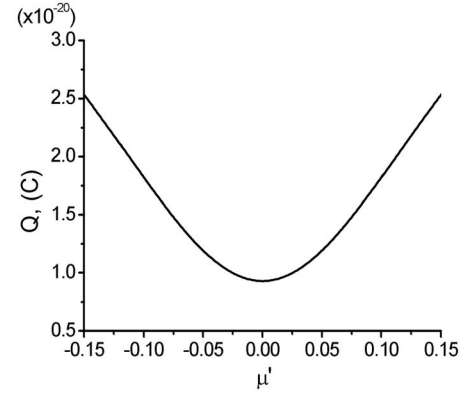


FIG. 2. The charge Q transferred after the completion of the pulse action as a function of the linear chirp rate $\mu' = \bar{\mu}/\omega_0^2$ [ω_0 is defined below Eq. (38)]. Other parameters are as follows: $\omega = \omega_0 = 3$ eV, $\Gamma_{M2}/\omega_0 = 0.03$, $\Gamma_{M1}/\omega_0 = 0.04$, $\Gamma_{MN} = \Gamma_{M1} + \Gamma_{M2}$, $d\mathcal{E}_0/\hbar\omega_0 = 0.2$, $\delta/\omega_0 = 0.1$, $\Gamma_{ML,1} = 0.01$ eV, and $\Gamma_{ML,2} = 0.02$ eV.

ten referred to as artificial atoms.^{26–29} The main disadvantage of the π -pulse excitation method is the requirement for resonant light source and the need for a precise control of the pulse area.³⁰

The second procedure, known as the adiabatic rapid passage (ARP),^{25,30–36} enables us to transfer the entire population from the ground $|1\rangle$ to the excited $|2\rangle$ electronic state. It is based on sweeping the pulse frequency through a resonance. The mechanism of ARP can be explained by avoided crossing of dressed (adiabatic) states,

$$\Phi_+(t) = \sin \vartheta(t)|1\rangle + \cos \vartheta(t)|2\rangle,$$

$$\Phi_-(t) = \cos \vartheta(t)|1\rangle - \sin \vartheta(t)|2\rangle, \quad (56)$$

as a function of the instantaneous laser pulse frequency $\omega(t)$.³⁰ Here, the mixing angle $\vartheta(t)$ is defined (mod π) as $\vartheta = (1/2)\arctan \frac{\Omega(t)}{\omega_0 - \omega(t)}$, where $\Omega(t)$ is the Rabi frequency. During the excitation, the mixing angle rotates clockwise from $\vartheta(-\infty) = \pi/2$ to $\vartheta(+\infty) = 0$, and the composition of adiabatic states changes accordingly. In particular, starting from state $|1\rangle$, the system follows the adiabatic (dressed) state $\Phi_+(t)$ and eventually ends up in state $|2\rangle$.³³ A scheme based on ARP is robust since it is insensitive to pulse area and the precise location of the resonance. Therefore, we shall focus in what follows on ARP as a way to control optically induced charge transfer in molecular nanojunctions. The application of our formalism to the coherent optoelectronic properties of nanojunctions with quantum dots, using π -pulse excitation,²⁹ will be analyzed elsewhere.

As a particular example, we shall consider a light-induced charge transfer in molecular nanojunctions using linear chirped pulses $\omega(t) = \omega - \bar{\mu}(t - t_0)$, where $\bar{\mu} = d^2\varphi(t)/dt^2 = \text{const}$.

A. Numerical results

Figures 2 and 3 show the influence of $\bar{\mu}$, the chirp rate in the time domain, on the charge transferred during one elec-

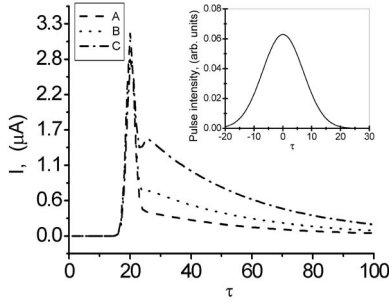


FIG. 3. The current I as a function of time $\tau = \omega_0 t$ for the linear chirp rate $\bar{\mu}/\omega_0^2 = 0$ (A), 0.07 (B), and 0.15 (C). Other parameters are identical to those of Fig. 2. The figure illustrates how signatures of ARP increase the induced current. Inset: the square of electric field amplitude of the exciting pulse in arbitrary units.

tromagnetic pulse action. These results are obtained by a numerical solution of Eqs. (41)–(45) for a Gaussian pulse of the shape,

$$E(t) \equiv \mathcal{E}(t) \exp[i\varphi(t)] = \mathcal{E}_0 \exp\left[-\frac{1}{2}(\delta^2 - i\bar{\mu})(t - t_0)^2\right], \quad (57)$$

and are displayed as a function of $\bar{\mu}$. We see that pulse chirping can increase the transferred charge (Fig. 2) and the induced current (Fig. 3) that can be explained by signatures of ARP (see below).

If chirped pulses are obtained by changing the separation of pulse compression gratings, the parameters δ and $\bar{\mu}$ are determined by the formulas^{37,38}

$$\begin{aligned} \delta^2 &= 2\tau_{p0}^2 [\tau_{p0}^4 + 4\Phi''^2(\omega)]^{-1}, \\ \bar{\mu} &= -4\Phi''(\omega) [\tau_{p0}^4 + 4\Phi''^2(\omega)]^{-1}, \end{aligned} \quad (58)$$

where $\tau_{p0} = t_{p0}/\sqrt{2 \ln 2}$, t_{p0} is the pulse duration of the corresponding transform-limited pulse, and $\Phi''(\omega)$ is the chirp rate in the frequency domain. The latter is defined by writing the electric field at frequency $\bar{\omega}$ as $|E(\bar{\omega})| \exp[i\Phi(\bar{\omega})]$ and expanding the phase term $\Phi(\bar{\omega})$ in a Taylor series about the carrier frequency ω : $\Phi(\bar{\omega}) = \Phi(\omega) + (1/2)\Phi''(\omega)(\bar{\omega} - \omega)^2 + \dots$. Note that the local field in the junction also reflects plasmon excitation in the leads, and taking the incident pulse shape as affected only by the compression gratings used disregards the possible contribution of the near-field response of plasmonic excitations in the leads.^{17,39} Such effects will be considered elsewhere.

Figures 4 and 5 show the calculation results of the transferred charge Q as a function of the chirp rate in the frequency domain $\Phi''(\nu) = 4\pi^2\Phi''(\omega)$. The calculated dependences $Q[\Phi''(\nu)]$ for curves A, B, and C are confined to the values of an argument $|\Phi''(\nu)| > 0$ corresponding to $d\mathcal{E}_0/\hbar\omega_0 \leq 0.3$ [d is the molecular dipole moment (Eq. (6))] since our theory uses RWA. In the course of pulse chirping, the pulse stretches and its intensity decreases with respect to that of the transform-limited pulse of the same energy. This explains the gaps in curves A, B, and C of Figs. 4 and 5. One

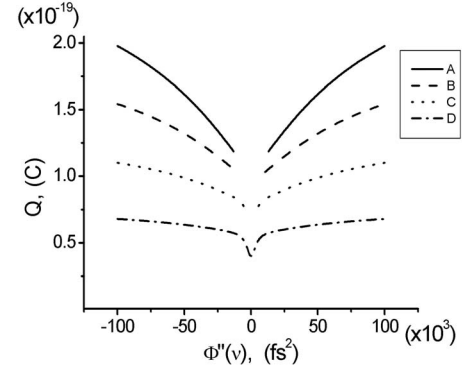


FIG. 4. The charge transferred after the completion of the pulse action as a function of the chirp rate in the frequency domain $\Phi''(\nu)$. The value of $d\mathcal{E}_0/\hbar\omega_0 = 0.6$ (A), 0.5 (B), 0.4 (C), and 0.3 (D) for the transform-limited pulse. In the course of chirping, the pulse energy is conserved so that $\int_{-\infty}^{\infty} \mathcal{E}^2(t) dt = \mathcal{E}_0^2 \sqrt{\frac{\pi}{2}} \left[\tau_{p0}^2 + \frac{4\Phi''^2(\omega)}{\tau_{p0}^2} \right] = \text{const}$, and \mathcal{E}_0 decreases when $|\Phi''(\nu)|$ increases; $\tau_{p0} = 11$ fs. Other parameters are identical to those of Fig. 2.

can see that Q grows rapidly for small $|\Phi''(\nu)|$. The growth of Q slows down for moderate $|\Phi''(\nu)|$, and then Q tends to a constant value for large $|\Phi''(\nu)|$. The larger the pulse energy, the larger value of $|\Phi''(\nu)|$, at which the growth of Q slows down. Figure 4 corresponds to the absence of the energy transfer [$B_N(\varepsilon_2 - \varepsilon_1) = 0$], and Fig. 5 illustrates the influence of the energy transfer [$B_N(\varepsilon_2 - \varepsilon_1) \neq 0$], which diminishes the corresponding values of Q (see also Fig. 6).

The behavior and values of Q shown in Figs. 2 and 4–6 can be rationalized by the theoretical consideration below. Figure 6 illustrates also the influence of detuning between the carrier pulse frequency ω and the corrected frequency of the molecular transition ω_0 on the transferred charge Q .

To end this section, we note that the current that corresponds to the expectation value of $Q = 0.5 \times 10^{-19}$ C/pulse (corresponding to curve D in Fig. 4) and to an estimated pulse repetition frequency of 82 MHz (Ref. 29) results in a small but measurable value of about 4×10^{-12} A.

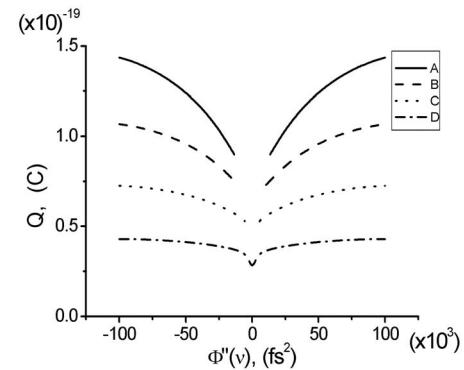


FIG. 5. The charge transferred after the completion of the pulse action as a function of the chirp rate in the frequency domain $\Phi''(\nu)$ in the presence of the energy transfer $B_N(\varepsilon_2 - \varepsilon_1)/\omega_0 = 0.01$. Other parameters are identical to those of Fig. 4.

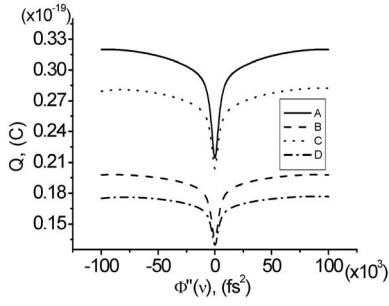


FIG. 6. Influence of energy transfer and the frequency detuning $\omega_0 - \omega$ on the charge transferred after the completion of the pulse action for $d\mathcal{E}_0/\hbar\omega_0=0.2$. A: $B_N(\varepsilon_2 - \varepsilon_1)=0$, $\omega_0 - \omega=0$; B: $B_N(\varepsilon_2 - \varepsilon_1)/\omega_0=0.01$, $\omega_0 - \omega=0$; C: $B_N(\varepsilon_2 - \varepsilon_1)=0$, $(\omega_0 - \omega)/\omega_0=0.05$; D: $B_N(\varepsilon_2 - \varepsilon_1)/\omega_0=0.01$, $(\omega_0 - \omega)/\omega_0=0.05$. Other parameters are identical to those of Fig. 4.

B. Analytical consideration

The problem under consideration above can be solved analytically in certain conditions.

1. Chirped pulse control of charge transfer in molecular nanojunctions as the Landau-Zener transition to a decaying level

Consider first an excitation of the molecular nanojunction with a linear chirped pulse $\omega(t)=\omega_0 - \bar{\mu}t$ ($t_0=0$, $\omega=\omega_0$) of a constant amplitude ($|\Omega|=\text{const}$) in the absence of energy transfer: $B_N(\varepsilon_2 - \varepsilon_1)=\Delta_{NK}=0$, $\Gamma_{MN}=\Gamma_{M2}+\Gamma_{M1}$ [Γ_{MN} was defined by Eq. (38)]. If in addition, $\Gamma_{M1}=\Gamma_{M2}\equiv\Gamma_M$ and provided that level 1 is below and level 2 is above both Fermi energies, then it can be shown that $n_1=1-n_2$ (see Appendix B) and

$$Q = e(\Gamma_{ML,2} - \Gamma_{ML,1}) \int_{-\infty}^{\infty} n_2(t) dt. \quad (59)$$

Under these conditions, our electron problem [Eqs. (41)–(44)] becomes mathematically equivalent to the Landau-Zener transition to a decaying level⁴⁷ solved analytically by Akulin and Schleich.⁴⁰ The magnitude $\Gamma_{ML,2} \int_{-\infty}^{\infty} n_2(t) dt$ on the right-hand side of Eq. (59) represents the expectation value of the number of electrons passed from the molecule to the left lead after the completion of the pulse action, and $\Gamma_{ML,1} \int_{-\infty}^{\infty} n_2(t) dt = \Gamma_{ML,1} \int_{-\infty}^{\infty} (1 - n_1(t)) dt$ is the same for the electrons passed from the left lead to the molecule.

Using Eq. (59) and Eq. (25) of Ref. 40 for the magnitude $I_{AS} \equiv \Gamma_M \int_{-\infty}^{\infty} n_2(t) dt$, we obtain in terms of our representation:

$$Q = e \frac{\Gamma_{ML,2} - \Gamma_{ML,1}}{\Gamma_M} I_{AS} = 2\pi e \frac{\Gamma_{ML,2} - \Gamma_{ML,1}}{\Gamma_M} \frac{\Omega^2}{4|\bar{\mu}|} \times \exp\left(\frac{-\pi\Omega^2}{4|\bar{\mu}|}\right) \left| W_{i\Omega^2/4|\bar{\mu}|, -1/2}\left(-\frac{i\Gamma_M^2}{|\bar{\mu}|}\right) \right|^2, \quad (60)$$

where $W_{i\Omega^2/4|\bar{\mu}|}(z)$ is the Whittaker function.⁴¹ The graph of I_{AS} as a function of the Landau-Zener parameter and quenching parameter, which correspond to $\Omega^2/|\bar{\mu}|$ and $\Gamma_M^2/|\bar{\mu}|$, re-

spectively, in terms of our representation, can be found in Fig. 1 of Ref. 40.

When the chirp is fast with respect to the rate of the electron transfer, $\frac{\Gamma_M^2}{|\bar{\mu}|} \ll 1$, one gets the following from Eq. (60):

$$Q = e \frac{\Gamma_{ML,2} - \Gamma_{ML,1}}{\Gamma_M} \left[1 - \exp\left(\frac{-\pi\Omega^2}{2|\bar{\mu}|}\right) \right], \quad (61)$$

where we have used the integral representation⁴¹ of the Whittaker function to calculate $|\lim_{z \rightarrow 0} W_{i\Omega^2/4|\bar{\mu}|}(z)|^2 = (a\pi)^{-1} \sinh(\pi a)$. The expression in the brackets on the right-hand side of Eq. (61) is simply the probability of the Landau-Zener transition, which is indeed identical to the probability of the electron transfer from the excited molecule to the leads in the case of fast passage through the resonance. Indeed, in this case, $\Gamma_M \int_{-\infty}^{\infty} n_2(t) dt = \Gamma_M \int_0^{\infty} n_2(0) \exp(-\Gamma_M t) dt = n_2(0)$, where $n_2(0)$ is the population of molecular state 2 immediately following the passage through the resonance. The highest charge transfer is therefore obtained if $n_2(0)=1$. Equation (61) shows that $n_2(0)$ approaches 1 for a strong interaction, $\pi\Omega^2 \gg 2|\bar{\mu}|$, which corresponds to ARP. In other words, when the interaction with light is short in comparison with the electron transfer, the transferred charge is maximal when ARP is realized. Really, $Q \rightarrow |e| \left| \frac{\Gamma_{ML,2} - \Gamma_{ML,1}}{\Gamma_M} \right| \rightarrow 1$. This issue is of importance for developing single-electron devices with optical gating based on molecular nanojunctions.

When $\frac{\Omega^2 \Gamma_M^2}{4\bar{\mu}^2} \gg 1$, the magnitude I_{AS} is given by⁴⁰

$$I_{AS} = \frac{\pi\Gamma_M\Omega^2}{2|\bar{\mu}|\sqrt{\Gamma_M^2 + \Omega^2}},$$

and we get a simple formula for the charge transferred in the course of slow passage through the resonance (with respect to both the electron-transfer rate and the reciprocal Rabi frequency),

$$Q = \frac{\pi\Omega^2 e (\Gamma_{ML,2} - \Gamma_{ML,1})}{2|\bar{\mu}| \sqrt{\Omega^2 + \Gamma_M^2}}. \quad (62)$$

Equation (62) gives $Q = e (\Gamma_{ML,2} - \Gamma_{ML,1}) \frac{\pi\Omega}{2|\bar{\mu}|} \gg e$ at least for a strong interaction when $\Omega^2 \gg \Gamma_M^2$.

2. Slow passage through the resonance and strongly chirped pulses

Equation (62) can be obtained directly by integrating Eq. (50) with respect to time for $\omega(t)=\omega_0 - \bar{\mu}t$ and $\Omega=\text{const}$. Indeed, integrating Eq. (50) yields

$$Q = \int_{-\infty}^{\infty} I(t) dt = \frac{\Gamma_{M2} + \Gamma_{M1}}{4\Gamma_{M1}\Gamma_{M2}} \frac{\pi\Omega^2 e (\Gamma_{ML,2}\Gamma_{MR,1} - \Gamma_{ML,1}\Gamma_{MR,2})}{|\bar{\mu}| \sqrt{\Omega^2 \frac{(\Gamma_{M2} + \Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}} + (\Gamma_{MN}/2)^2}}. \quad (63)$$

In the special case $\Gamma_{M1}=\Gamma_{M2}\equiv\Gamma_M$ and $B_N(\varepsilon_2 - \varepsilon_1)=0$, Eq.

(63) leads to Eq. (62). As a matter of fact, Eq. (63) extends the case of slow passage through the resonance beyond the treatment of Ref. 40.

Equation (63) can be used for the excitation of a bridging molecule by Gaussian pulses, Eqs. (57) and (58), as well when the pulses are strongly chirped⁴²

$$2|\Phi''(\omega)| \gg \tau_{p0}^2. \quad (64)$$

For a strongly chirped pulse, one can ascribe to different instants of time the corresponding frequencies,⁴² i.e., different frequency components of the field are determined via values of the instantaneous pulse frequency $\omega(t)$ for different instants of time. Then, one can integrate $\int_{-\infty}^{\infty} I(t) dt$ similar to Eq. (63), bearing in mind that $\Omega(t) = \left(\frac{d\varepsilon_0}{\hbar}\right) \exp\left(-\frac{1}{2}\delta^2 t^2\right) \approx \left(\frac{d\varepsilon_0}{\hbar}\right) \exp\left(-\frac{\tau_{p0}^2}{4\Phi''(\omega)} t^2\right)$ is a much slower function of time than $\omega(t) = \omega_0 - \dot{\mu}t \approx \omega_0 + \frac{1}{\Phi''(\omega)}t$. Using Eqs. (57), (58), (63), and (64), we then get

$$Q \approx \frac{\Gamma_{M2} + \Gamma_{M1}}{4\Gamma_{M1}\Gamma_{M2}} \frac{\sqrt{\pi} \left(\frac{d}{\hbar}\right)^2 \mu_0 c E_p \tau_{p0} e^{(\Gamma_{ML,2}\Gamma_{MR,1} - \Gamma_{ML,1}\Gamma_{MR,2})}}{\sqrt{\left(\frac{d}{\hbar}\right)^2 \frac{\mu_0 c E_p \tau_{p0}}{\sqrt{\pi}|\Phi''(\omega)|} \frac{(\Gamma_{M2} + \Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}} + (\Gamma_{MN}/2)^2}}, \quad (65)$$

where $\varepsilon_0^2 \approx \frac{\mu_0 c E_p \tau_{p0}}{\sqrt{\pi}|\Phi''(\omega)|}$ since the magnitude $\int_{-\infty}^{\infty} \mathcal{E}^2(t) dt = 2\mu_0 c E_p = \text{const}$ is conserved in the course of chirping. Here, E_p is the pulse energy per unit area, μ_0 is the permeability constant, c is the light velocity in vacuum. According to Eq. (65), in the case of slow passage through the resonance, $Q \sim \sqrt{|\Phi''(\omega)|}$ for strong interaction when $\left(\frac{d}{\hbar}\right)^2 \frac{\mu_0 c E_p \tau_{p0}}{\sqrt{\pi}|\Phi''(\omega)|} \frac{(\Gamma_{M2} + \Gamma_{M1})^2}{4\Gamma_{M1}\Gamma_{M2}} \gg (\Gamma_{MN}/2)^2$, and Q tends to a constant value for large $|\Phi''(\omega)|$. This elucidates the behavior observed in our simulations shown in Figs. 4 and 5 for moderate and large values of $|\Phi''(\nu)|$. In addition, Eq. (65) explains why the growth of Q slows down for a larger value of $|\Phi''(\nu)|$ if pulse energy increases.

VI. CONCLUSION

In this work, a theory for light-induced current by strong optical pulses in molecular-tunneling junctions has been developed. We have considered a molecular bridge represented by its highest occupied and lowest unoccupied levels, HOMO and LUMO, respectively, and have derived a closed set of equations for electron populations, of molecular states, molecular polarization, and molecular excitation (exciton population) when two types of couplings between the molecule and the metal leads are presented: electron transfer that gives rise to net current in the biased junction and energy transfer between the molecule and electron-hole excitations in the leads.

We have used this formalism to analyze a control mechanism by which the charge flow is enhanced by chirped pulses. For a linear chirp and when the energy transfer be-

tween the molecule and electron-hole excitations in the leads is absent, this control model can be reduced to the Landau-Zener transition to a decaying level, which has an exact analytical solution.

The relaxation parameters in the derived closed set of the equations of motion do not depend on the exciting electromagnetic field. This is true if the Rabi frequency Ω is much smaller than the bath correlation frequency ω_c . If molecular states ε_m are far from the Fermi levels of both leads, ω_c is determined by the frequency interval for the system-bath interaction matrix elements $V_{km}^{(MK)}$ and $V_{kk'}^{(NK)}$ and the density of states of metal leads. The last can be evaluated as 1–10 eV.²² As a matter of fact, the approximation of constant relaxation parameters, which do not depend on exciting electromagnetic radiation, is consistent with the RWA used in our theory.

The situation is different if we assume that the molecular level position is pinned to the Fermi energy of a lead, which may lead to highly nonlinear current voltage dependence.¹⁶ In this case, ω_c is determined also by the frequency interval at which $f_K(\varepsilon)$ is essentially changed, that is, $\sim k_B T / \hbar$ [see Eqs. (20) and (26)]. In the last case, Ω can be of the same order of magnitude as ω_c in the RWA, and the dependence of the relaxation parameters on the exciting electromagnetic field²² must be included into the theory.

To end this discussion, we note that in this work we have investigated a model process driven by light absorption in a molecular bridge connecting metal leads. As already discussed, the geometry considered is potentially advantageous because of the possible local field enhancement due to plasmon excitation in the leads. It should be emphasized, however, that other processes not considered in this work may play important roles in nanojunction response to incident light. First, direct electron-hole excitations of the metal leads^{43,44} may affect the response in an adsorbed molecule that goes beyond the local field enhancement associated with plasmon excitation. Second, an experimental realization of strong local excitations in nanojunctions requires a careful consideration of heating and heat dissipation and conduction.⁴⁵ Heating may be kept under control by driving the junction using a sequence of well separated optical pulses, as envisioned in the proposed experiment, but it should be kept in mind that a more detailed consideration of this issue may be needed.

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APPENDIX A

Consider the steady-state current in the absence of the radiative and nonradiative energy transfer couplings, \hat{V}_p and \hat{V}_N . The corresponding solution of Eq. (33) is as follows: $n_m = W_{Mm} / \Gamma_{Mm}$. Substituting it into Eq. (40) and using Eq. (21), we get

$$I = e \sum_{m=1,2} \frac{\Gamma_{ML,m} \Gamma_{MR,m}}{\Gamma_{Mm}} [f_R(\varepsilon_m) - f_L(\varepsilon_m)]. \quad (\text{A1})$$

The last formula can be written as

$$\begin{aligned} I &= e \sum_{m=1,2} \frac{\Gamma_{ML,m} \Gamma_{MR,m}}{\Gamma_{Mm}} \int d\varepsilon [f_R(\varepsilon) - f_L(\varepsilon)] \delta(\varepsilon - \varepsilon_m) \\ &= \frac{e}{2\pi\hbar} \sum_{m=1,2} \lim_{\Gamma_{Mm}/2 \rightarrow 0} \Gamma_{ML,m} \Gamma_{MR,m} \int d\varepsilon \\ &\quad \times \frac{f_R(\varepsilon) - f_L(\varepsilon)}{(\varepsilon - \varepsilon_m)^2 \hbar^{-2} + [\Gamma_{Mm}/2]^2} \end{aligned} \quad (\text{A2})$$

using the well-known representation for $\delta(x)$,

$$\delta(x) = \frac{1}{\pi} \lim_{\sigma \rightarrow 0} \frac{\sigma}{x^2 + \sigma^2}. \quad (\text{A3})$$

The limit $\lim_{\Gamma_{Mm}/2 \rightarrow 0}$ on the right-hand side of Eq. (A2) is consistent with the Markovian approximation in the sense that relaxation parameters $\Gamma_{Mm}/2$ are small in comparison to the bath correlation frequency ω_c .

The term $\lim_{\Gamma_{Mm}/2 \rightarrow 0} \frac{1}{(\varepsilon - \varepsilon_m)^2 \hbar^{-2} + [\Gamma_{Mm}/2]^2}$ on the right-hand side of Eq. (A2) can be written as

$$\lim_{\Gamma_{Mm}/2 \rightarrow 0} \frac{1}{(\varepsilon - \varepsilon_m)^2 \hbar^{-2} + [\Gamma_{Mm}/2]^2} = G_{mm}^r(\varepsilon) G_{mm}^a(\varepsilon), \quad (\text{A4})$$

where $G_{mm}^r(\varepsilon)$ and $G_{mm}^a(\varepsilon)$ are the retarded and advanced Green's functions, respectively,¹⁶ in the Markovian approximation. The substitution of Eq. (A4) into Eq. (A2) leads to the well-known Landauer formula for the current.²³ Note that this does not constitute a general derivation of the Landauer formula since our formalism is limited to the Markovian approximation.

APPENDIX B

Let us show that $n_1 = 1 - n_2$ when $\Gamma_{M1} = \Gamma_{M2} \equiv \Gamma_M$. Summing Eqs. (41) and (42) at a given condition, we have

$$\frac{dy}{dt} = -\Gamma_M y, \quad (\text{B1})$$

where we denoted $y = n_1 + n_2 - 1$. The solution of the last equation is as follows:

$$y(t) = y(0) \exp(-\Gamma_M t), \quad (\text{B2})$$

where $y(0) = 0$. This gives $n_1(t) + n_2(t) = 1$ even in the presence of energy transfer when $B_N(\varepsilon_2 - \varepsilon_1) \neq 0$.

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