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Vibrational effects in laser-driven molecular wires

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The influence of an electron-vibrational coupling on the laser control of electron transport through a molecular wire that is attached to several electronic leads is investigated. These molecular vibrational modes induce an effective electron-electron interaction. In the regime where the wire electrons couple weakly to both the external leads and the vibrational modes, we derive within a Hartree-Fock approximation a nonlinear set of quantum kinetic equations. The quantum kinetic theory is then used to evaluate the laser driven, time-averaged electron current through the wire-leads contacts. This formalism is applied to two archetypical situations in the presence of electron-vibrational effects, namely, (i) the generation of a ratchet or pump current in a symmetrical molecule by a harmonic mixing field and (ii) the laser switching of the current through the molecule.
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I. INTRODUCTION

In recent years, considerable experimental progress in the determination of the current-voltage characteristics of molecular wires has been achieved.[1–4] In these experiments, a single molecule is contacted with two nanoelectrodes such that a transport voltage can be applied. One recent measurement, for example, focused on the influence of the chemical anchor group which couples the molecule, an oligothiophene derivative, to the electrode.[5] In another experiment, the length dependence of the current through a DNA strand[6] was investigated. Most descriptions of such transport experiments rely on generalizations of the scattering approach put forward by Landauer.[7,8] Presently, the main theoretical focus lies on the *ab initio* computation of the orbitals relevant for the motion of excess charges through the molecular wire.[9–13]

Another line of research employs rather generic models to gain a qualitative understanding of the transport mechanisms involved. An important problem addressed in this way is the conduction mechanism in the presence of electron-vibrational coupling.[14–24] With increasing strength of the coupling between the wire electrons and the vibrations, the electrons tend to localize on single wire units. Correspondingly the transport mechanism changes from a purely coherent transfer to a sequential hopping process. The related transfer rates are known from the theory of nonadiabatic electron transfer.[25] Such a special regime of charge transmission can also be described within a Redfield theory after carrying out a so-called polaron transformation.[24,26] If the wire has to be described by spatially extended molecular orbitals, sequential transfer proceeds by jumps from one electrode into a wire orbital, possibly followed by an intrawire relaxation, and then by a jump from a wire orbital into the other electrode. In contrast, the so-called superexchange mechanism enables a direct transfer from one electrode to the other. The crossover from superexchange to a sequential transfer mechanism has been studied in Refs. 18, 21, 23, 24, 27, and 28. In that context, a treatment of inelastic scattering processes profits from an unified theory of the electron transfer through molecular donor-acceptor complexes.[29]

Molecular wires illuminated by laser fields have been proposed for the investigation of ac transport effects such as coherent quantum ratchets,[30,31] optical control of current and noise,[32,33] and resonant current amplification.[34,35] The appropriate treatment of these ac phenomena is based on Floquet theory, which allows to take into account the action of the time-dependent field exactly. A Floquet scattering approach for the fully coherent transport regime has been developed,[33] but it cannot be generalized straightforwardly to the case with additional electron-vibrational coupling. Better suited for this situation is a quantum kinetic equation formalism which, however, is perturbative in both the wire-lead coupling and the electron-vibrational coupling.

In the absence of an external transport voltage, a driving field can induce a so-called pump or ratchet current.[36–39] The same happens even in perfectly symmetric conductors if one adds a higher harmonic to the driving field. The investigation of the corresponding effect for the motion of a particle in a tight-binding lattice revealed that the resulting current depends sensitively on the relative phase between the two components of the driving. For this system, two limits have been studied: the fully coherent dynamics and the overdamped Brownian motion. The dependence of the current on the relative phase is in each case qualitatively different.[40,41] The present model has the advantage that it enables the study of such effects also in the crossover regime between the purely coherent and the purely incoherent transport.

A further intriguing phenomenon in driven transport is the suppression of the dc current caused by properly tailored ac fields.[32] This effect is the transport counterpart of the so-called coherent destruction of tunneling (CDT) found in bistable potentials without any connection to external leads.[42–44] When coupling the bistable system to a heat bath, tunneling becomes a transient, see Ref. 45 for a review. The same is true for coherent destruction of tunneling: ultimately, the driving-induced localization decays via dissipative transitions.[45] Here, we address the role of dissipation for the corresponding transport effect.

The paper is organized as follows: In Sec. II, we introduce a model for the laser driven molecule coupled to several leads and vibrational degrees of freedom. Subsequently, in Sec. III, we derive a kinetic equation approach in the Floquet basis. An expression for the resulting current through the molecule is derived in Sec. IV. Finally, in Sec. V, the formalism is applied to study the influence of the vibrational coupling on nonadiabatic pumping and coherent current suppression.

II. THE MODEL

In the following, we consider a molecular wire which is attached to a number of electrodes and which is driven by an externally applied ac field. We neglect hole transport and start with the Hamiltonian

$$H_0(R) = E_0 + H_{\text{vib}}, \tag{1}$$

of the neutral wire, i.e., in the absence of excess electrons injected via the electrodes. Here, R denotes the set of all involved vibrational coordinates with equilibrium configuration R_0 and $E_0 = H_0(R_0)$ is the electronic ground-state energy of the neutral wire (set equal to zero in the following). In a representation by normal modes with mode index ξ, we find the vibrational Hamiltonian

$$H_{\text{vib}} = \sum_\xi \hbar\omega_\xi b_\xi^\dagger b_\xi \tag{2}$$

with the usual harmonic oscillator operators $b_\xi^\dagger$ and b_ξ. The normal modes may be delocalized over the whole wire or may be localized on specific wire units. We assume that they always remain in thermal equilibrium and are, thus, characterized by the Bose distribution $n_{\text{B}}(\hbar\omega_\xi)$.

We describe the presence of an excess electron on the wire in the representation of N localized wire orbitals $|n\rangle$, $n = 1,\dots,N$, and the corresponding Hamiltonian $H_{nn'}(R,t)$. In the absence of the external driving, the eigenstates of $H_{nn'}$ are the lowest unoccupied molecular orbitals. To account for electron-vibrational coupling this quantity is expanded with respect to deviations from the vibrational equilibrium configuration R_0. To lowest order this results in

$$H_{nn'}(R,t) = H_{nn'}(t) + \sum_\xi K_{nn',\xi}(b_\xi + b_\xi^\dagger). \tag{3}$$

The matrix $H_{nn'}(t) = H_{nn'}(R_0,t)$ taken at the vibrational equilibrium configuration R_0 includes the interaction with the external field. The $\mathcal{T}$-periodic time-dependence $H_{nn'}(t) = H_{nn'}(t+\mathcal{T})$ models the action of the external field on the excess electrons when moving through the wire. We have in mind a dipole-type coupling between electron and field, i.e., a contribution $e\mathbf{E}(t)\mathbf{x}_n\,\delta_{n,n'}$ to the Hamiltonian $H_{nn'}(t)$, where $\mathbf{E}(t)$ is the electric field strength, $\mathbf{x}_n$ the position of site n, and $-e$ the electron charge. The considered action of an external field may in principle also induce a heating of the electron gas in the metallic leads as well as a thermal expansion of the leads. Of course, this can be of importance for any experimental realization of the studied mechanism. Nevertheless, the present approach will not attempt to account for such effects.

We assume that the whole set of vibrational coordinates discerns into subsets, labeled by an index ν. Therefore, we write the electron-vibrational coupling in Eq. (3) as

$$\sum_\xi K_{nn',\xi}(b_\xi + b_\xi^\dagger) = \sum_\nu X_{nn'\nu} \sum_{\xi\in\nu} M_{\nu\xi}(b_\xi + b_\xi^\dagger), \tag{4}$$

where the notation $\xi \in \nu$ indicates that the summation runs only over the modes in the corresponding subset. The related spectral densities read

$$D_\nu(\omega) = \frac{\pi}{\hbar} \sum_{\xi\in\nu} |M_{\nu\xi}|^2 \delta(\omega - \omega_\xi). \tag{5}$$

For notational convenience, we define the spectral density for $\omega < 0$ by $D_\nu(-\omega) = -D_\nu(\omega)$. In our numerical calculations, we restrict ourselves to a situation where each orbital $|n\rangle$ couples to exactly one of these subsets, i.e.,

$$X_{nn'\nu} = \delta_{nn'}\delta_{n\nu}, \tag{6}$$

and assume identical Ohmic spectral densities $D_\nu(\omega) = \kappa\hbar\omega$, where the dimensionless coupling strength κ is identical for all sites. This model has been employed recently for the description of dephasing and relaxation in (time-independent) bridged molecular wires.[18,27]

In order to take the exclusion principle properly into account, we employ a many-electron description based on a second quantized notation. Neglecting the Coulomb interaction among the electrons, the wire electrons are described by the Hamiltonian

$$H_{\text{wire}}(t) = \sum_{n,n'} H_{nn'}(t) c_n^\dagger c_{n'}. \tag{7}$$

The operators c_n and $c_n^\dagger$ annihilate and create, respectively, an electron in the orbital $|n\rangle$, $n = 1,\dots,N$. We presume vanishing overlap among different orbitals such that the annihilation and creation operators obey the standard anticommutation relations $[c_n, c_{n'}^\dagger]_+ = \delta_{nn'}$. The electron-vibrational coupling Hamiltonian assumes the form

$$H_{\text{el-vib}} = \sum_{n,n',\nu} X_{nn'\nu} \sum_{\xi\in\nu} M_{\nu\xi}(b_\xi + b_\xi^\dagger)\, c_n{}^\dagger c_{n'}. \tag{8}$$

Next, we consider the coupling of the wire to L different macroscopic electronic leads described by the Hamiltonian

$$H_{\text{leads}} = \sum_{\mathbf{k},\ell} \epsilon_{\mathbf{k}\ell} c_{\mathbf{k}\ell}^\dagger c_{\mathbf{k}\ell}. \tag{9}$$

The electrons in each lead ℓ are labeled by wave vectors $\mathbf{k}$ referring to bulk or surface states with energy $\epsilon_{\mathbf{k}\ell}$. All lead states are mutually orthogonal (and also orthogonal to the wire states) and, therefore, the creation and annihilation operators $c_{\mathbf{k}\ell}$ and $c_{\mathbf{k}\ell}^\dagger$, respectively, obey the standard anticommutation relations. We assume that the lead electrons stay in thermal equilibrium and are, thus, described by the Fermi distributions $f(\epsilon_{\mathbf{k}\ell}-\mu_\ell)$ with a common temperature T but possibly different electrochemical potentials μ_ℓ.

The coupling of each lead to exactly one of the suitably labeled molecular orbitals is described by the Hamiltonian

$$H_{\text{wire-leads}}=\sum_{\mathbf{k},\ell} V_{\mathbf{k}\ell}c_{\mathbf{k}\ell}^\dagger c_\ell+\text{H.c.} \tag{10}$$

with $V_{\mathbf{k}\ell}$ being the tunneling matrix elements. As it will turn out, the coupling to the leads is completely characterized by its spectral density

$$\Gamma_\ell(\epsilon)=\frac{2\pi}{\hbar}\sum_{\mathbf{k}} |V_{\mathbf{k}\ell}|^2\delta(\epsilon-\epsilon_{\mathbf{k}\ell}), \tag{11}$$

which becomes a continuous function of the energy ϵ if the lead states are dense. Since we are mainly interested in the behavior of the molecular wire itself and not in the details of the lead-wire coupling,[46] we will assume for all numerical calculations that the conduction bandwidth of the leads is much larger than all remaining relevant energy scales. In this so-called wide-band limit, the spectral densities are constants, $\Gamma_\ell(\epsilon)=\Gamma_\ell$.

The dynamics of the present model is now fully specified by the Hamiltonian

$$H(t)=H_{\text{wire}}(t)+H_{\text{vib}}+H_{\text{leads}}+H_{\text{el-vib}}+H_{\text{wire-leads}}. \tag{12}$$

In the following, we start from the uncoupled subsystems $H_{\text{wire}}(t)+H_{\text{vib}}+H_{\text{leads}}$ and treat the influence of both the wire-lead coupling and the electron-vibrational coupling, subsumed in the Hamiltonian

$$H_{\text{coupl}}=H_{\text{el-vib}}+H_{\text{wire-leads}}, \tag{13}$$

within a master equation approach in second-order perturbation theory.

III. QUANTUM KINETIC EQUATION APPROACH

In this section, which contains the main theoretical body of the present work, we first introduce a master equation which describes the dynamics of the wire electrons in the presence of a weak or intermediately strong coupling to both the vibrational environment and the electronic states in the leads. For the further evaluation of this master equation, we introduce in Sec. III B the so-called Floquet states, which yield an exact solution of the dynamics of the isolated wire electrons. An evaluation of the contributions of the wire-lead (Sec. III C) and electron-vibrational (Sec. III D) coupling in the basis of this Floquet states finally results in a quantum kinetic equation describing the dynamics of the single wire-electron density matrix, which is later, in Sec. IV, required for the calculation of the current through the molecular wire.

A. Quantum master equation

The derivation of a closed equation for the reduced density operator $\varrho_{\text{wire}}(t)$ of the wire electrons, which follows from the total density operator by tracing out those degrees of freedom which correspond to vibrations and lead electrons, to second order in H_{coupl} represents a standard procedure of dissipative quantum dynamics (for a review, see, e.g., Ref. 25). We neglect initial correlations between the wire electrons and the environmental degrees of freedom, which stay in thermal equilibrium, and do not account for non-Markovian dissipative effects. The resulting quantum master equation thus reads

$$\begin{aligned}\dot{\varrho}_{\text{wire}}(t)=&-\frac{i}{\hbar}[H_{\text{wire}}(t),\varrho_{\text{wire}}(t)]\\&-\frac{1}{\hbar^2}\int_0^\infty d\tau\,\text{Tr}_{\text{env}}\{H_{\text{coupl}},[\widetilde{H}_{\text{coupl}}(t-\tau,t),\\&\varrho_{\text{wire}}(t)\otimes\varrho_{\text{env,eq}}]\}.\end{aligned} \tag{14}$$

The trace refers to all environmental states, i.e., the electronic states of the leads as well as the wire vibrations, and the operator $\widetilde{H}_{\text{coupl}}(t,t')=U_0^\dagger(t,t')H_{\text{coupl}}U_0(t,t')$ describes the coupling Hamiltonian (13) in the interaction representation. The related zeroth-order time evolution operator

$$U_0(t,t')=T\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}dt''[H_{\text{wire}}(t'')+H_{\text{vib}}+H_{\text{leads}}]\right) \tag{15}$$

is responsible for the dynamics of the uncoupled subsystems. In this way the external driving field not only determines the coherent dynamics of the wire electrons but also the dissipative part of the master equation (14).[47,48]

Note that Eq. (14) still determines the dynamics of the full many-particle density matrix of the wire electrons. Later on, we will derive an equation of motion for the single wire-electron density matrix defined as

$$P_{nn'}(t)=\text{Tr}_{\text{el}}[\varrho_{\text{wire}}(t)c_{n'}^\dagger c_n], \tag{16}$$

where the trace runs over the many-particle states of the wire electrons. It will be demonstrated below that in the presence of an electron-vibrational coupling, a closed equation for $P_{nn'}(t)$ can only be obtained when an approximation is carried out for the two-electron density matrices by employing a decoupling scheme. We will detail this point when introducing the Hartree-Fock approximation in Sec. III D. However, before doing so, we will briefly review the Floquet method for the treatment of the explicit time dependence appearing in the propagator (15).

B. Introduction of Floquet states

For the evaluation of Eq. (14) it is essential to use an exact expression for the zeroth-order time evolution operator $U_0(t,t')$. The use of any approximation bears the danger of generating artifacts, which, for instance, may lead to a violation of fundamental equilibrium properties.[25,49] In the present case, the only nontrivial contribution to the propagator (15) stems from the periodically time-dependent wire Hamiltonian $H_{nn'}(t)=H_{nn'}(t+\mathcal{T})$. A proper tool for the efficient computation of the corresponding propagator is Floquet theory,[45,50–52] which is based on the fact that there exists a complete set of solutions of the form

$$|\Psi_\alpha(t)\rangle = e^{-i\epsilon_\alpha t/\hbar}|\Phi_\alpha(t)\rangle, \quad |\Phi_\alpha(t)\rangle = |\Phi_\alpha(t+\mathcal{T})\rangle \tag{17}$$

with the so-called quasienergies ϵ_α and corresponding Floquet modes $|\Phi_\alpha(t)\rangle$. The Floquet modes fulfill the quasienergy equation

$$\left(\sum_{n,n'} |n\rangle H_{nn'}(t)\langle n'| - i\hbar\frac{d}{dt}\right)|\Phi_\alpha(t)\rangle = \epsilon_\alpha|\Phi_\alpha(t)\rangle. \tag{18}$$

The practical usefulness of the Floquet ansatz (17) is rooted in the fact that the Floquet modes are periodic functions of time t and can therefore be decomposed in a Fourier series

$$\begin{aligned}|\Phi_\alpha(t)\rangle &= \sum_k e^{-ik\Omega t}|\Phi_{\alpha,k}\rangle,\\ |\Phi_{\alpha,k}\rangle &= \frac{1}{\mathcal{T}}\int_0^{\mathcal{T}} dt e^{ik\Omega t}|\Phi_\alpha(t)\rangle.\end{aligned} \tag{19}$$

This representation makes explicit that each quasienergy ϵ_α is equivalent to the quasienergies

$$\epsilon_{\alpha,k} = \epsilon_\alpha + k\hbar\Omega, \tag{20}$$

where k is an arbitrary integer. Thus, we can restrict ourselves to states with eigenvalues in one Brillouin zone, $E - \hbar\Omega/2 \leqslant \epsilon_\alpha < E + \hbar\Omega/2$.

It is now convenient to define a ‘‘Floquet picture’’ via the time-dependent transformation of the fermionic creation and annihilation operators

$$c_\alpha(t) = \sum_n \langle\Phi_\alpha(t)|n\rangle c_n. \tag{21}$$

The inverse transformation

$$c_n = \sum_\alpha \langle n|\Phi_\alpha(t)\rangle c_\alpha(t) \tag{22}$$

follows from the mutual orthogonality and the completeness of the Floquet states at equal times.[45] Note that the right-hand side of Eq. (22) becomes t independent after the summation over α. In the interaction picture, the operators $c_\alpha(t)$ obey

$$\tilde{c}_\alpha(t,t') = U_0^\dagger(t,t')c_\alpha(t')U_0(t,t') = e^{-i\epsilon_\alpha(t-t')/\hbar}c_\alpha(t'). \tag{23}$$

This is readily verified by differentiating expression (23) with respect to t and using the fact that $|\Phi_\alpha(t)\rangle$ is a solution of the eigenvalue equation (18). The proof is completed by noting that Eq. (23) fulfills the initial condition $\tilde{c}_\alpha(t',t') = c_\alpha(t')$.

It is advantageous to change to the ‘‘Floquet representation’’ of the single-(wire)-electron density operator

$$\begin{aligned}P_{\alpha\beta}(t) &= \sum_{n,n'} \langle n|\Phi_\alpha(t)\rangle\langle\Phi_\alpha(t)|n'\rangle P_{nn'}(t)\\ &= \mathrm{Tr}_{\mathrm{el}}[\varrho_{\mathrm{wire}}(t)c_\beta^\dagger(t)c_\alpha(t)] = \langle c_\beta^\dagger(t)c_\alpha(t)\rangle_t.\end{aligned} \tag{24}$$

Using the relation $\mathrm{Tr}(A[B,C]) = \mathrm{Tr}([A,B]C)$ and the fact that the Floquet states fulfill Eq. (18), we obtain for the dynamics of these expectation values the expression

$$\begin{aligned}\frac{d}{dt}P_{\alpha\beta}(t) = &-\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta)P_{\alpha\beta}(t)\\ &-\frac{1}{\hbar^2}\int_0^\infty d\tau\langle[[c_\beta^\dagger(t)c_\alpha(t),H_{\mathrm{coupl}}],\\ &\tilde{H}_{\mathrm{coupl}}(t-\tau,t)]\rangle_t.\end{aligned} \tag{25}$$

Obviously, the canonical transformation (21) to the basis of the Floquet operators $c_\alpha(t)$ has diagonalized the coherent part of the master equation (25) and the only task left is the evaluation of the incoherent contribution. Here, we use the fact that the contributions resulting from the coupling of the wire electrons to the electronic leads and to the wire vibrations can be treated separately. This is possible due to the assumption that the lead electrons and the vibrations remain uncorrelated at all times. Finally, we will obtain as a main result a quantum kinetic equation of the form

$$\dot{P}_{\alpha\beta} = -\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta)P_{\alpha\beta} + \dot{P}_{\alpha\beta}|_{\text{wire-leads}} + \dot{P}_{\alpha\beta}|_{\text{el-vib}}. \tag{26}$$

Specific expressions for the second and third term on the right-hand side of the last equation will be derived in the following sections.

C. Floquet representation of the wire-leads coupling

For the evaluation of the contribution of the wire-leads coupling to the kinetic equation (26), we have to evaluate the integral in Eq. (25) for the corresponding term in the coupling Hamiltonian (13). Using the relation $\tilde{c}_{q\ell}(t-\tau,t) = \exp(i\epsilon_{q\ell}\tau/\hbar)c_{q\ell}$, we obtain

$$\begin{aligned}\dot{P}_{\alpha\beta}|_{\text{wire-leads}} = &\sum_{\ell=1}^{L}\int_0^\infty \frac{d\tau}{\hbar}\int\frac{d\epsilon}{2\pi}\Gamma_\ell(\epsilon)\\ &\times\{e^{-i\epsilon\tau/\hbar}[\langle[c_\beta^\dagger(t)c_\alpha(t),c_\ell^\dagger],\tilde{c}_\ell]_+\rangle_t\\ &\times f(\epsilon-\mu_\ell) - \langle[c_\beta^\dagger(t)c_\alpha(t),c_\ell^\dagger]\tilde{c}_\ell\rangle_t]\\ &-e^{i\epsilon\tau/\hbar}[\langle[c_\beta^\dagger(t)c_\alpha(t),c_\ell],\tilde{c}_\ell^\dagger]_+\rangle_t\\ &\times f(\epsilon-\mu_\ell) - \langle\tilde{c}_\ell^\dagger[c_\beta^\dagger(t)c_\alpha(t),c_\ell]\rangle_t]\}.\end{aligned} \tag{27}$$

For notational compactness, the time arguments of the interaction picture operators $\tilde{c}_\ell(t-\tau,t)$ have been suppressed.

Using the transformation (22), the commutators in Eq. (27) are readily evaluated to read

$$[c_\beta^\dagger(t)c_\alpha(t),c_\ell] = -\langle\ell|\Phi_\beta(t)\rangle c_\alpha(t), \tag{28}$$

$$[c_\beta^\dagger(t)c_\alpha(t),c_\ell^\dagger] = \langle\Phi_\alpha(t)|\ell\rangle c_\beta^\dagger(t). \tag{29}$$

Moreover, the transformation (22) yields in conjunction with Eqs. (19), (20), and (23) the spectral decomposition of the wire operators in the interaction picture, i.e.,

$$\tilde{c}_\ell(t-\tau,t) = \sum_{\alpha k} e^{-ik\Omega t}e^{i\epsilon_{\alpha,k}\tau/\hbar}\langle\ell|\Phi_{\alpha,k}\rangle c_\alpha(t). \tag{30}$$

With the aid of the last two equations, one may readily carry out the time and the energy integrations in Eq. (27) to obtain

$$\begin{aligned}\dot{P}_{\alpha\beta}\big|_{\text{wire-leads}} &= \frac{1}{2}\sum_{\ell=1}^{L}\sum_{kk'} e^{i(k'-k)\Omega t}\\ &\quad\times\Big\{\Gamma_\ell(\epsilon_{\alpha,k})\langle\Phi_{\alpha,k'}|\ell\rangle\langle\ell|\Phi_{\beta,k}\rangle f(\epsilon_{\alpha,k}-\mu_\ell)\\ &\quad+\Gamma_\ell(\epsilon_{\beta,k})\langle\Phi_{\alpha,k'}|\ell\rangle\langle\ell|\Phi_{\beta,k}\rangle f(\epsilon_{\beta,k}-\mu_\ell)\\ &\quad-\sum_{\alpha'}\Gamma_\ell(\epsilon_{\alpha',k})\langle\Phi_{\alpha,k'}|\ell\rangle\langle\ell|\Phi_{\alpha',k}\rangle P_{\alpha'\beta}(t)\\ &\quad-\sum_{\beta'}\Gamma_\ell(\epsilon_{\beta',k'})\langle\Phi_{\beta',k'}|\ell\rangle\langle\ell|\Phi_{\beta,k}\rangle P_{\alpha\beta'}(t)\Big\}. \qquad (31)\end{aligned}$$

Here, principal value terms stemming from an energy renormalization due to the coupling to the leads have been neglected. The terms containing Fermi functions describe resonant tunneling of electrons from the leads onto the wire, while the reverse processes are captured by the terms proportional to $P_{\alpha\beta}(t)$.

D. Floquet representation of the electron vibrational coupling

For ease of notation, we introduce the ''position'' and the ''force'' operators

$$X_\nu=\sum_{n,n'} X_{nn'\nu}c_n^\dagger c_{n'}, \qquad (32)$$

$$F_\nu=\sum_{\xi_\nu} M_{\xi_\nu}(b_{\xi_\nu}+b_{\xi_\nu}^\dagger), \qquad (33)$$

respectively. Then, the vibrational contribution to the dissipative kernel in Eq. (25) becomes

$$\begin{aligned}\dot{P}_{\alpha\beta}\big|_{\text{el-vib}} &= -\frac{1}{\hbar}\sum_\nu\int_0^\infty d\tau S_\nu(\tau)\langle[[c_\beta^\dagger(t)c_\alpha(t),X_\nu],\\ &\quad\tilde{X}_\nu(t-\tau,t)]\rangle_t-\frac{i}{\hbar}\sum_\nu\int_0^\infty d\tau A_\nu(\tau)\\ &\quad\times\langle[[c_\beta^\dagger(t)c_\alpha(t),X_\nu],\tilde{X}_\nu(t-\tau,t)]_+\rangle_t. \qquad (34)\end{aligned}$$

The symmetrized and antisymmetrized autocorrelation functions

$$\begin{aligned}S_\nu(\tau) &= \frac{1}{2\hbar}\langle[\tilde{F}_\nu(\tau),F_\nu]_+\rangle_{\text{eq}}\\ &= \int_0^\infty\frac{d\omega}{\pi}D_\nu(\omega)\coth(\hbar\omega/2k_BT)\cos(\omega\tau), \qquad (35)\end{aligned}$$

$$A_\nu(\tau)=\frac{1}{2i\hbar}\langle[\tilde{F}_\nu(\tau),F_\nu]\rangle_{\text{eq}}=-\int_0^\infty\frac{d\omega}{\pi}D_\nu(\omega)\sin(\omega\tau), \qquad (36)$$

of the ''force'' operators fully characterize the fluctuation properties of the wire vibrations. Note that $\coth(x)=1/x+O(x)$ such that for an Ohmic spectral density no infrared divergence occurs in the integral (35).

For the further evaluation of Eq. (34), we express the operator X_ν and its interaction picture version $\tilde{X}_\nu(t-\tau,t)$ in terms of the Floquet picture operators $c_\alpha(t)$ at time t, obtaining

$$X_\nu=\sum_{\alpha,\beta}\sum_k e^{ik\Omega t}\overline{X}^\nu_{\alpha\beta,k}c_\alpha^\dagger(t)c_\beta(t), \qquad (37)$$

$$\begin{aligned}\tilde{X}_\nu(t-\tau,t) &= \sum_{\alpha,\beta}\sum_k e^{ik\Omega t}e^{i(\epsilon_\beta-\epsilon_\alpha-k\hbar\Omega)\tau/\hbar}\overline{X}^\nu_{\alpha\beta,k}\\ &\quad\times c_\alpha^\dagger(t)c_\beta(t). \qquad (38)\end{aligned}$$

The time-averaged coupling matrix elements in the Floquet basis have been abbreviated as

$$\overline{X}^\nu_{\alpha\beta,k}=\sum_{n,n'}\sum_{k'}\langle\Phi_{\alpha,k+k'}|n\rangle X_{nn'\nu}\langle n'|\Phi_{\beta,k'}\rangle. \qquad (39)$$

When evaluating Eq. (34), it turns out that in addition to terms containing the single-electron density matrix $P_{\alpha\beta}(t)$, two-electron expectation values of the form $\langle c_\delta^\dagger(t)c_\gamma^\dagger(t)c_\beta(t)c_\alpha(t)\rangle_t$ appear. By iteration, one thus generates a hierarchy of equations up to N-electron expectation values. To obtain a description in terms of only the single-electron expectation values, we employ the Hartree-Fock decoupling scheme defined by the approximation

$$\langle c_\delta^\dagger(t)c_\gamma^\dagger(t)c_\beta(t)c_\alpha(t)\rangle_t\approx P_{\alpha\delta}(t)P_{\beta\gamma}(t)-P_{\beta\delta}(t)P_{\alpha\gamma}(t). \qquad (40)$$

Clearly, such a mean-field approximation only covers certain aspects of the full many-particle problem. Nevertheless, it offers a description which is consistent with the second law of thermodynamics, as we will detail in Sec. III F. We remark that in principle one could also include electron-electron interaction in the framework of the mean-field approximation (40), similar to the approach put forward in Refs. 53, 54. However, focusing on the vibration-mediated interaction effects, we here refrain from doing so.

For the description of the transport problem, a scattering approach, i.e., a strict one-particle picture, is frequently employed.[16,18,23,27,55,56] Then, nonlinear terms of the type (40) do not appear. The same happens if one considers a closed system with a single electron; then, the corresponding equation is also of the form (26) but without the terms quadratic in $P_{\alpha\beta}(t)$.[47,57,58]

Upon insertion of the Hartree-Fock approximation (40) into Eq. (34) and disregarding again the principal value integrals, which correspond to an energy renormalization due to the electron-vibrational coupling, we obtain after a straightforward calculation

$$\dot{P}_{\alpha\beta}|_{\text{el-vib}}=\frac{1}{2}\sum_{\alpha'\beta'}\Bigg[\Gamma_{\alpha\alpha'\beta\beta'}(t)+\Gamma^{*}_{\beta\beta'\alpha\alpha'}(t)-\sum_{\alpha''}(\Gamma^{*}_{\alpha''\beta'\alpha\alpha'}(t)+\Gamma_{\beta'\alpha'\alpha''\alpha}(t))P_{\alpha''\beta}-\sum_{\beta''}(\Gamma^{*}_{\alpha'\beta'\beta''\beta}(t)$$
$$+\Gamma_{\beta''\alpha'\beta\beta'}(t))P_{\alpha\beta''}\Bigg]P_{\alpha'\beta'}-\frac{1}{2}\sum_{\alpha'}\Bigg[\sum_{\beta''}\Gamma_{\beta''\alpha'\beta''\alpha}(t)-\sum_{\alpha''\beta''}(\Gamma^{*}_{\alpha''\beta''\alpha\alpha'}(t)+\Gamma_{\beta''\alpha'\alpha''\alpha}(t))P_{\alpha''\beta''}\Bigg]$$
$$\times P_{\alpha'\beta}-\frac{1}{2}\sum_{\beta'}\Bigg[\sum_{\alpha''}\Gamma^{*}_{\alpha''\beta'\alpha''\beta}(t)-\sum_{\alpha''\beta''}(\Gamma^{*}_{\alpha''\beta'\beta''\beta}(t)+\Gamma_{\beta''\alpha''\beta\beta'}(t))P_{\alpha''\beta''}\Bigg]P_{\alpha\beta'}\,. \tag{41}$$

Here, we have introduced the time-dependent, complex-valued coefficients

$$\Gamma_{\alpha\beta\alpha'\beta'}(t)=2\sum_{\nu}\sum_{kk'}e^{i(k'-k)\Omega t}\overline{X}^{\nu}_{\alpha\beta,k'}\overline{X}^{\nu}_{\beta'\alpha',-k}\times N_{\nu}(\epsilon_{\alpha}-\epsilon_{\beta}+k'\hbar\Omega), \tag{42}$$

where the functions $N_{\nu}(\epsilon)$ are defined for each vibrational subsystem ν by $N_{\nu}(\epsilon)=D_{\nu}(\epsilon/\hbar)n_{\mathrm{B}}(\epsilon)/\hbar$. For an Ohmic spectral density, $D_{\nu}(\epsilon/\hbar)\propto\epsilon$, $N_{\nu}(\epsilon)$ is well defined in the limit $\epsilon\to 0$.

Interestingly, the rates (41) resulting from the vibrational coupling render the kinetic equation (26) nonlinear. The physics behind the nonlinear terms is an effective electron-electron coupling mediated by the phonons. This can be illustrated by one electron exciting a phonon while another electron causes the relaxation. In Eq. (41), the transitions between diagonal elements $P_{\alpha\alpha}$ of the single particle density matrix represent collision terms of the quantum Boltzmann equation (45) derived below. However, the transitions between the off-diagonal elements do not have such an intuitive interpretation.

E. Rotating-wave approximation

For a very weak coupling of the wire electrons to the environmental degrees of freedom, the coherent time evolution dominates the dynamics (26) of the density matrix $P_{\alpha\beta}(t)$. More precisely, the largest time scale of the coherent evolution, which is given by the smallest quasienergy difference, and the dissipative time scale, which is of the order of the coupling rates $\Gamma_{\ell}(\epsilon)$, are well separated, i.e.,

$$\hbar\Gamma_{\ell}(\epsilon)\ll|\epsilon_{\alpha}-\epsilon_{\beta}+k\hbar\Omega|,\quad \kappa\ll 1 \tag{43}$$

for all ℓ, k, ϵ, and $\alpha\neq\beta$. Note that this condition is only satisfiable if the quasienergy spectrum has no degeneracies. Then, it is possible to replace the $\mathcal{T}$-periodic coefficients in Eq. (26) by their time averages. Furthermore, we may assume that in the long-time limit, the solution becomes diagonal and time independent, i.e., we make the ansatz

$$P_{\alpha\beta}(t)=\text{const}=\delta_{\alpha\beta}f_{\alpha}\,. \tag{44}$$

With these approximations, the quantum kinetic equation (26) assumes the form

$$0=\dot{f}_{\alpha}=-w^{\text{leads}}_{\alpha}f_{\alpha}+s^{\text{leads}}+\sum_{\alpha'}w^{\text{vib}}_{\alpha\alpha'}(1-f_{\alpha})f_{\alpha'}-\sum_{\alpha'}w^{\text{vib}}_{\alpha'\alpha}(1-f_{\alpha'})f_{\alpha}\,. \tag{45}$$

Here, the population of the Floquet states α due to the wire-lead coupling is determined by the decay rates

$$w^{\text{leads}}_{\alpha}=\sum_{\ell=1}^{L}\sum_{k}|\langle\ell|\Phi_{\alpha,k}\rangle|^{2}\Gamma_{\ell}(\epsilon_{\alpha,k}) \tag{46}$$

and the source terms

$$s^{\text{leads}}_{\alpha}=\sum_{\ell=1}^{L}\sum_{k}|\langle\ell|\Phi_{\alpha,k}\rangle|^{2}\Gamma_{\ell}(\epsilon_{\alpha,k})f(\epsilon_{\alpha,k}-\mu_{\ell}). \tag{47}$$

In addition, the electron-vibrational interaction contributes a quantum Boltzmann type collision term to Eq. (45), which takes into account the Pauli principle by the blocking factors $1-f_{\alpha}$. The corresponding scattering rates from one state α' into another state α are given by

$$w^{\text{vib}}_{\alpha\alpha'}=2\sum_{\nu}\sum_{k}|\overline{X}^{\nu}_{\alpha\alpha',k}|^{2}N_{\nu}(\epsilon_{\alpha}-\epsilon_{\alpha'}+k\hbar\Omega). \tag{48}$$

F. Thermal equilibrium

An important consistency check of the present theory is a thermal equilibrium situation, where $H_{nn'}$ is time independent and where no external bias is present ($\mu_{\ell}=\mu$ for all ℓ).[59] In order to obtain the static limit of the kinetic equation (26), we have to replace the Floquet states $|\Phi_{\alpha}(t)\rangle$ and the quasienergies ϵ_{α} by the eigenstates $|\varphi_{a}\rangle$ and the eigenenergies E_{a}. One can show that the diagonal ansatz (44) leads to an *exact* stationary solution of the kinetic equation. The populations f_{a} obey also the kinetic equation (45), but with the Floquet states and quasienergies replaced by the (adiabatic wire) eigenstates $|\varphi_{a}\rangle$ and the eigenenergies E_{a}, respectively, of the static Hamiltonian $H_{nn'}$. Moreover, only $k=0$ contributes to the rates (46)–(48).

Thermal equilibrium with respect to the coupling to the vibrational subsystems is characterized by the detailed balance condition

$$w^{\text{vib}}_{aa'}(1-f_{a})f_{a'}=w^{\text{vib}}_{a'a}(1-f_{a'})f_{a}, \tag{49}$$

where the rates $w^{\text{vib}}_{aa'}$ satisfy

$$\frac{w^{\mathrm{vib}}_{aa'}}{w^{\mathrm{vib}}_{a'a}}=\mathrm{e}^{(E_{a'}-E_a)/k_{\mathrm{B}}T}. \tag{50}$$

A solution of Eqs. (49) and (50) is given by the Fermi distribution $f_a=f(E_a-\mu')$, where the chemical potential μ' remains undetermined. It is due to the additional condition $w^{\mathrm{leads}}_a f_a=s^{\mathrm{leads}}$ that μ' adjusts to the chemical potential μ of the leads. Thus, the equilibrium solution of the kinetic equations (26) reads

$$f_a=f(E_a-\mu), \tag{51}$$

in accordance with elementary principles of the statistical physics of noninteracting fermions.

G. Numerical solution of the kinetic equation

For the solution of the nonlinear kinetic equation (26) one generally has to resort to numerical methods. We therefore use a propagation scheme for the computation of the long-time limit of the solutions of the set of nonlinear equations (26), which however, is numerically rather time consuming and, especially in the strongly driven regime, only applicable for not too large systems. We then verify the $\mathcal{T}$ periodicity of the resulting solution and compute its Fourier decomposition

$$P_{\alpha\beta}(t)=\sum_k e^{-\mathrm{i}k\Omega t}P_{\alpha\beta,k}. \tag{52}$$

As we will see in the subsequent section, the Fourier coefficients

$$P_{\alpha\beta,k}=\frac{1}{\mathcal{T}}\int_0^{\mathcal{T}}dt\,e^{\mathrm{i}k\Omega t}P_{\alpha\beta}(t) \tag{53}$$

fully specify the stationary current through the wire.

IV. CURRENT THROUGH THE WIRE

The net (incoming minus outgoing) current through contact ℓ is given by the negative time derivative of the electron number $N_\ell=\Sigma_{\mathbf{k}}c^\dagger_{\mathbf{k}\ell}c_{\mathbf{k}\ell}$ in lead ℓ multiplied by the electron charge $-e$,

$$I_\ell(t)=e\frac{d}{dt}\langle N_\ell\rangle_t=e\frac{\mathrm{i}}{\hbar}\langle[H(t),N_\ell]\rangle_t. \tag{54}$$

For the Hamiltonian (12), the commutator in Eq. (54) is readily evaluated to read

$$I_\ell(t)=-\frac{2e}{\hbar}\mathrm{Im}\sum_{\mathbf{k}}V_{\mathbf{k}\ell}\langle c^\dagger_{\mathbf{k}\ell}c_\ell\rangle_t. \tag{55}$$

For a weak wire-lead coupling, one can assume for all times a factorization of wire and lead degrees of freedom. This assumption allows one to derive from Eq. (55) an explicit expression for the stationary, time-dependent net electrical current through the contact ℓ in terms of one-particle expectation values of the wire electrons,

$$\begin{aligned}I_\ell(t)=\frac{e}{\pi\hbar}\mathrm{Re}\int_0^\infty d\tau\int d\epsilon\,\Gamma_\ell(\epsilon)e^{\mathrm{i}\epsilon\tau/\hbar}\{\langle c^\dagger_\ell\tilde{c}_\ell(t,t-\tau)\rangle_{t-\tau}\\ -[c^\dagger_\ell,\tilde{c}_\ell(t,t-\tau)]_+f(\epsilon-\mu_\ell)\}.\end{aligned} \tag{56}$$

Note that the anticommutator $[c^\dagger_\ell,\tilde{c}_\ell(t,t-\tau)]_+$ is in fact a c-number, which by means of the transformation (22) and the interaction picture dynamics (23) of the wire operators in the Floquet picture reads

$$[c^\dagger_\ell,\tilde{c}_\ell(t,t-\tau)]_+=\sum_\alpha e^{-\mathrm{i}\epsilon_\alpha\tau/\hbar}\langle\Phi_\alpha(t-\tau)|\ell\rangle\langle\ell|\Phi_\alpha(t)\rangle. \tag{57}$$

Similarly, the expectation value appearing in the current formula (56) can be expressed in terms of the density-matrix elements (24) as

$$\begin{aligned}&\langle c^\dagger_\ell\tilde{c}_\ell(t,t-\tau)\rangle_{t-\tau}\\ &\quad=\sum_{\alpha\beta}e^{-\mathrm{i}\epsilon_\alpha\tau/\hbar}\langle\Phi_\beta(t-\tau)|\ell\rangle\langle\ell|\Phi_\alpha(t)\rangle P_{\alpha\beta}(t-\tau).\end{aligned} \tag{58}$$

These relations, together with the spectral decompositions of the Floquet states and of the density matrix, Eqs. (19) and (52), respectively, allow one to carry out the time and energy integrals in expression (56). The current $I_\ell(t)$ obeys the time periodicity of the driving field. However, because we consider here excitations with frequencies in the optical or infrared spectral range, the only experimentally accessible quantity is the time-averaged current. In the wide-band limit—the extension to the general case is straightforward—we thus obtain

$$\begin{aligned}\overline{I}_\ell=e\Gamma_\ell\sum_{\alpha k}\Bigg[\sum_{\beta k'}\langle\Phi_{\beta,k'+k}|\ell\rangle\langle\ell|\Phi_{\alpha,k'}\rangle P_{\alpha\beta,k}\\ -|\langle\ell|\Phi_{\alpha,k}\rangle|^2f(\epsilon_{\alpha,k}-\mu_\ell)\Bigg].\end{aligned} \tag{59}$$

Charge conservation, of course, requires that the charge on the wire $Q_{\mathrm{wire}}(t)$ can only change by a current flow, amounting to the continuity equation $\dot{Q}_{\mathrm{wire}}(t)=\Sigma^L_{\ell=1}I_\ell(t)$. Since the charge on the wire is bounded, the long-time average of $\dot{Q}_{\mathrm{wire}}(t)$ must vanish. From the continuity equation one then finds

$$\sum_{\ell=1}^{L}\overline{I}_\ell=0. \tag{60}$$

For a two-terminal configuration, $\ell=\mathrm{L,R}$, we can then introduce the time-averaged current

$$\overline{I}=\overline{I}_{\mathrm{L}}=-\overline{I}_{\mathrm{R}}. \tag{61}$$

To close this section we consider the thermal equilibrium situation described in Sec. III F. It is characterized by $\mu_\ell=\mu$ (absence of any transport voltage) and $|\Phi_{\alpha,k}\rangle=0$ unless $k=0$ (absence of driving). Inserting the equilibrium solution $P_{\alpha\beta,k}=\delta_{\alpha\beta}\delta_{k,0}f(E_\alpha-\mu)$ into Eq. (59), we immediately see that all currents $\overline{I}_\ell$ vanish—despite any possible asymmetry

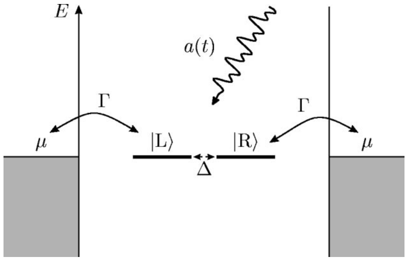

FIG. 1. Symmetric two-site structure coupled to two leads which rectifies an externally applied laser field of the harmonic mixing form $a(t) = A_1 \sin(\Omega t) + A_2 \sin(2\Omega t + \varphi)$.

of the molecule itself or of its coupling to the environment. Thus, the results of our microscopic theory are in accordance with the second law of thermodynamics.

V. CONTROL OF CURRENTS IN TWO-SITE SYSTEMS

With the necessary formalism at hand, we study in this section two aspects of driven transport for which dissipation plays a significant role: (i) the generation of pump currents by means of harmonic mixing fields and (ii) optical current switching. As a rather generic model, which still captures the essential physics, we employ a symmetric wire that consists of two sites in the two-terminal configuration sketched in Fig. 1. The wire sites are coupled by a hopping matrix element Δ while an electromagnetic field causes time-dependent shifts of the on-site energies. Then, the wire Hamiltonian reads

$$H_{\text{wire}}(t) = -\Delta(c_L^\dagger c_R + c_R^\dagger c_L) + \frac{a(t)}{2}(c_L^\dagger c_L - c_R^\dagger c_R), \quad (62)$$

where $a(t) = a(t + \mathcal{T})$ represents the dipole force on the wire electron multiplied by the distance of the two wire sites. Furthermore, we assume that the molecule couples equally strong to both leads, thus, $\Gamma_L = \Gamma_R = \Gamma$.

In a realistic wire molecule, Δ is of the order 0.1 eV. Thus, a wire-lead coupling strength $\Gamma = 0.1\Delta/\hbar$ corresponds to a current $e\Gamma = 2.56 \times 10^{-5}$ A and a laser frequency $\Omega = \Delta/\hbar$ lies in the infrared spectral range. Furthermore, for a distance of 1 Å between two neighboring sites, a driving amplitude $A = \Delta$ is equivalent to an electrical field strength of 10^7 V/cm.

It turns out that for the description of the effects discussed below, the off-diagonal elements of the single-particle density matrix $P_{\alpha\beta}(t)$, $\alpha \neq \beta$, play an essential role. Therefore, we have to go beyond the rotating-wave ansatz (44) and consequently employ the propagation scheme for the full nonlinear kinetic equation (26) described in Sec. III G.

A. Nonadiabatic pump current from harmonic mixing

The Hamiltonian (62) with a driving of the form $a(t) \propto \sin(\Omega t)$ has an intriguing symmetry, the so-called generalized parity, which has been discussed widely in the context of driven tunneling:[42,43] a time translation by half a driving period results for the external field in a minus sign, i.e., $a(t + \mathcal{T}/2) = -a(t)$. Thus, for the dipole coupling given in the Hamiltonian (62), the time shift $t \to t + \mathcal{T}/2$ is equivalent to interchanging the left and the right wire site. In addition, the dc current $\bar{I}$ is also inverted. Consequently, because $\bar{I}$ has to be independent of any (finite) time translation, it must vanish.[31] However, for a time-dependent driving field of the form

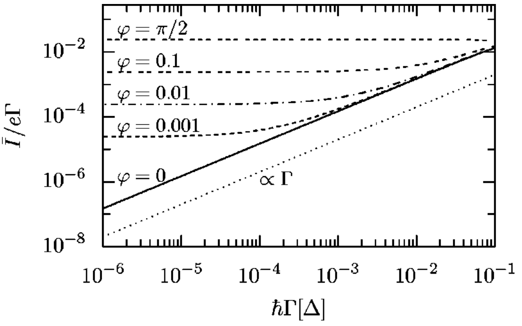

FIG. 2. Average current through the two-site wire from Fig. 1 driven by the harmonic mixing signal (63) with amplitudes $A_1 = 2A_2 = \Delta$ as a function of the wire-lead coupling strength Γ (for $\kappa = 0$) for different values of the phase difference φ. The driving frequency is $\Omega = \Delta/\hbar$, and the temperature is $k_B T = 0.25\Delta$. The dotted line is proportional to Γ, corresponding to a current that is proportional to Γ^2.

$$a(t) = A_1 \sin(\Omega t) + A_2 \sin(2\Omega t + \varphi), \quad (63)$$

with $A_1, A_2 \neq 0$, the generalized parity is no longer present and a nonadiabatic pump current emerges from the harmonic mixing of the two driving frequencies.[31] Its magnitude is generally proportional to the coupling strength between wire and lead, $\bar{I} \propto \Gamma$, with a prefactor that depends on the details such as the phase lag φ or the amplitudes A_1, A_2. The phase lag $\varphi = 0$ represents a particular case because for this value the wire Hamiltonian obeys time-reversal parity, i.e., it is invariant under the operation $(\text{L,R},t) \to (\text{R,L},-t)$. As a consequence, one finds that the dc current vanishes to linear order in Γ such that $\bar{I} \propto \Gamma^2$.[31] Figure 2 demonstrates this behavior and, moreover, reveals that already small phase lags of the order $\varphi \approx 0.001$ are sufficient to alter the qualitative Γ dependence of the dc current.

Harmonic mixing has also been studied recently for the motion of a quantum particle in an infinitely extended tight-binding lattice, both in the purely coherent regime[41,60] and for incoherent, sequential quantum between adjacent sites.[40,41] It turns out that the dependence of the current on the phase lag φ is qualitatively different in these two limiting cases. This raises the question how the phase dependence of the current changes as a function of the dissipation strength.

Generally, quantum dissipation results from a coupling of the quantum system to an environment—here, the metallic leads and the vibrational modes. Figure 3(a) depicts the influence of only the wire-lead coupling: For a very weak coupling strength $\Gamma = 0.001\Delta/\hbar$ and $\kappa = 0$ we find a dc current proportional to $\sin\varphi$. With increasing Γ, the dependence on φ shifts towards $\cos\varphi$. In order to investigate the influence of the vibrational coupling, we choose again $\Gamma = 0.001\Delta/\hbar$ and a finite but small vibrational coupling strength κ. The φ dependence of the pump current is given in Fig. 3(b); it exhibits the same dissipation-induced shift.

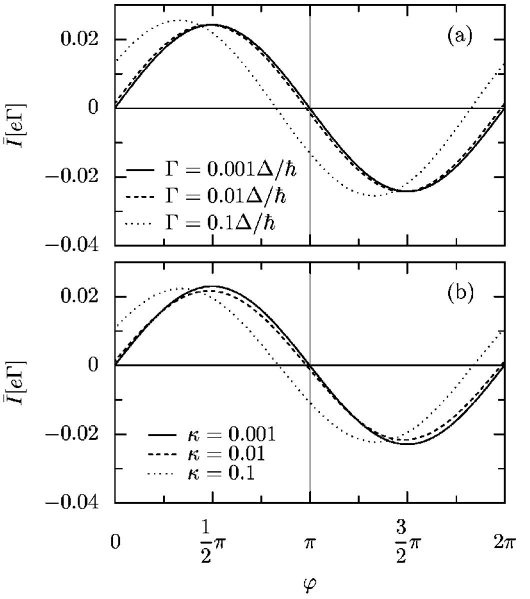

FIG. 3. Average current through the two-site wire sketched in Fig. 1 driven by the harmonic mixing signal (63) as a function of the phase difference φ (a) for different wire-lead coupling strengths Γ (for $\kappa=0$) and (b) for different electron-vibrational coupling κ (for $\Gamma=0.001\Delta/\hbar$). All other parameters are as in Fig. 2.

Interestingly enough, the electron-vibrational coupling can enhance the pumping effect. This enhancement is most pronounced in the presence of the time-reversal parity discussed above, i.e., for $\varphi=0$. Figure 4 shows the pump current as a function of the vibrational coupling strength κ. We find that the dc current can be increased by more than one order of magnitude. For values $\kappa \ll \hbar\Gamma/\Delta$, the main dissipation comes from the leads and the vibrations are practically without influence. Correspondingly, one is back to a the situation of Fig. 2, where the pump current is proportional to Γ^2.

B. Laser-switched current gate

An external driving field cannot only induce a pump current through the molecular wire, but for proper parameters can also cause the opposite effect: A driving of the shape $a(t)=A\sin(\Omega t)$ can suppress almost completely the dc current even in the presence of a large transport voltage V.[32]

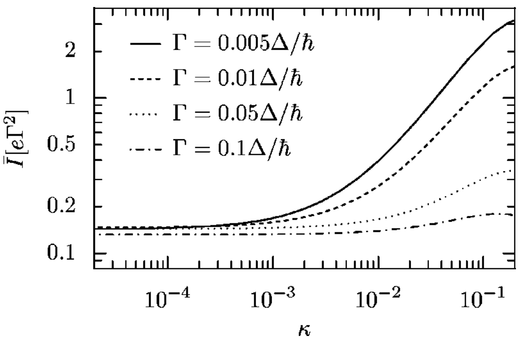

FIG. 4. Average current (in units of $e\Gamma^2$) through the two-site wire sketched in Fig. 1 driven by the harmonic mixing signal (63) with amplitudes $A_1=2A_2=\Delta$ and phase difference $\varphi=0$ as a function of the electron-vibrational coupling strength κ. Different values of the wire-lead coupling strength Γ are shown.

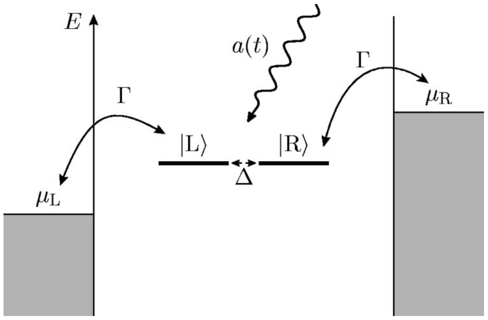

FIG. 5. Two-site wire driving by a harmonic driving field $a(t)=A\sin(\Omega t)$, which is attached to two leads with the chemical potential difference $\mu_{\mathrm{R}}-\mu_{\mathrm{L}}=eV$.

The physics behind these suppressions is the so-called coherent destruction of tunneling (CDT) that has been found in the context of tunneling in time-dependent bistable potentials.[42,43,45,61,62] The central phenomenon observed there is that for a driving with amplitude and frequency such that the ratio $A/\hbar\Omega$ equals a zero of the Bessel function J_0 (i.e., for the values 2.405.., 5.520.., 8.654.., ...), the coherent tunneling dynamics comes to a standstill.[61] As a related effect for the transport through such a tunnel system, one finds pronounced suppressions of the dc current.[32] The fact that coherent destruction of tunneling is disrupted by finite dissipation,[45,57,58,63–65] motivates our investigation of the influence of dissipation on these current suppressions.

We model the transport voltage V by shifting the chemical potential of the left (right) lead, μ_{L} (μ_{R}), by $-eV/2$ $(+eV/2)$, cf. Fig. 5. Due to the external voltage, the electric field can in principle also cause a static bias to the wire levels. We do not take this effect into account in the present work, but remark only that in the absence of a vibrational coupling, the current suppressions are stable against an internal bias.[31]

Before focussing on the influence of electron-vibrational coupling, let us first substantiate the discussion of the current suppressions by the numerical results depicted in Fig. 6. The time-averaged current $\bar{I}$ as a function of the laser amplitude A exhibits, besides a global decay, pronounced minima whenever the CDT condition is fulfilled, i.e., when the ratio

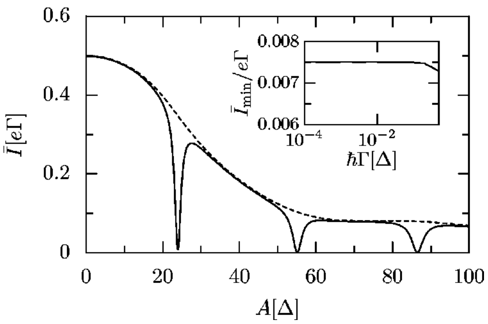

FIG. 6. Average current (solid) vs driving amplitude for the setup sketched in Fig. 5. The leads' chemical potentials are $\mu_{\mathrm{R}}=-\mu_{\mathrm{L}}=10\Delta$; the other parameters read $\hbar\Omega=10\Delta$, $k_{\mathrm{B}}T=0.25\Delta$, $\hbar\Gamma=0.1\Delta$. The dashed line marks the result obtained within a rotating-wave approximation. The inset depicts the minimal current $\bar{I}_{\min}$ at the first suppression as a function of the wire-lead coupling strength Γ.

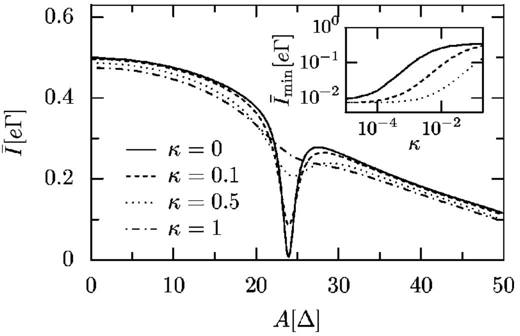

FIG. 7. Average current vs driving amplitude for the setup sketched in Fig. 5 in the presence of dissipation of the form (6). The inset depicts the minimal current $\bar{I}_{\min}$ at the first suppression as a function of the electron-phonon coupling strength κ for $\Gamma = 0.001\Delta/\hbar$ (solid line), $0.01\Delta/\hbar$ (dashed), and $0.1\Delta/\hbar$ (dotted). All other parameters are as in Fig. 6.

$A/\hbar\Omega$ assumes a zero of the Bessel function J_0. However, the current does not vanish exactly, but a residual current remains; its value is proportional to the molecule-lead coupling Γ, as can be appreciated from the inset of Fig. 6. Since the current in the undriven situation is also proportional to Γ, we thus can conclude that the maximal suppression is determined by a factor which is *independent* of Γ.

The inspection of the quasienergy spectrum reveals that CDT is related to crossings of the quasienergies.[61] Thus, at the center of the current suppressions, the quasienergies are degenerate and the condition (43) for the applicability of the rotating-wave approximation is *not* fulfilled. Indeed, the dashed line in Fig. 6 demonstrates that a rotating-wave approximation fails completely in the vicinity of current suppressions.

A central question to be addressed is the robustness of the current suppressions against dissipation. In the corresponding tunneling problem, the CDT driving alters both the coherent and the dissipative time scale by the same factor.[58] Thus, one might speculate that a vibrational coupling leaves the effect of the driving on the current qualitatively unchanged. Figure 7, however, demonstrates that this is not the case. With increasing dissipation strength κ, the characteristic current suppressions become washed out until they finally disappear when κ becomes of the order unity. This detracting influence underlines the importance of quantum coherence for the observation of those current suppressions. Note that the dissipation affects only the depth of the suppressions while the width remains unchanged. We close this section with the remark that within the present setup of two driven tunnel-coupled orbitals (cf. Fig. 5) and within our chosen parameter range, we do not detect the analog of the effect of a stabilization of CDT within a certain temperature range[57,66–70] or, likewise, with increasing external noise,[71] as it has been reported for driven, dissipative symmetric bistable systems.

VI. CONCLUSIONS

We have derived a nonlinear quantum kinetic equation that allows one to investigate for a molecule the simultaneous influence of a laser field, a coupling to leads, and in addition, a coupling to vibrational modes. The use of Floquet states as a basis set for the reduced single-particle density matrix represents a most important technical cornerstone. It enables both the exact inclusion of the driving field and an efficient treatment of the dissipative couplings. Since the vibrational modes provide an *effective electron-electron interaction*, a formalism for general situations requires one to resort to further approximations such as a Hartree-Fock decoupling scheme.

Within this kinetic equation formalism, we have investigated the influence of quantum dissipation on recently proposed transport effects caused by the action of laser fields on molecular wires. For the nonadiabatic electron pumping that emerges from harmonic mixing, we find that dissipation can play a constructive role to the extent that it can significantly enhance the current.

For the model under investigation, we observed an enhancement of the pump current by more than one order of magnitude. Moreover, the present scheme allows one to trace back the dependence of the pump current on the phase lag between the two harmonic mixing fields to the increasing influence of dissipation. The situation is less promising for effects that depend intrinsically on quantum coherence. We have found that the coherent current suppressions are derogated by the coupling to vibrational modes. Nevertheless, the effect persists provided that the quantum dynamics of the wire electrons remains predominantly coherent. Finally, we share the hope that our general theoretical findings will provide motivation and prove useful to experimentalists to initiate corresponding, tailored experiments on driven molecular wires in the not too distant future.

ACKNOWLEDGMENTS

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[1] See Special Issue on *Process in Molecular Wires* [Chem. Phys. **281**, 111 (2002)].
[2] A. Nitzan and M. A. Ratner, Science **300**, 1384 (2003).
[3] T. Seideman, J. Phys. C **15**, R521 (2003).
[4] J. R. Heath and M. A. Ratner, Phys. Today **56(11)**, 43 (2003).
[5] L. Patrone *et al.*, Phys. Rev. Lett. **91**, 096802 (2003).
[6] T. Shigematsu *et al.*, J. Chem. Phys. **118**, 4245 (2003).
[7] R. Landauer, IBM J. Res. Dev. **1**, 223 (1957).
[8] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1995).
[9] M. Di Ventra, S. T. Pantelides, and N. D. Lang, Phys. Rev. Lett. **84**, 979 (2000).
[10] M. Di Ventra and N. D. Lang, Phys. Rev. B **65**, 045402 (2002).
[11] Y. Xue, S. Datta, and M. A. Ratner, Chem. Phys. **281**, 151 (2002).
[12] P. Damle, A. W. Ghosh, and S. Datta, Chem. Phys. **281**, 171 (2002).
[13] J. Heurich, J. C. Cuevas, W. Wenzel, and G. Schön, Phys. Rev. Lett. **88**, 256803 (2002).
[14] M. Olson *et al.*, J. Chem. Phys. **102**, 941 (1998).
[15] Z. G. Yu, D. L. Smith, A. Saxena, and A. R. Bishop, Phys. Rev. B **59**, 16001 (1999).
[16] E. G. Emberly and G. Kirczenow, Phys. Rev. B **61**, 5740 (2000).
[17] M. K. Okuyama and F. G. Shi, Phys. Rev. B **61**, 8224 (2000).
[18] D. Segal *et al.*, J. Phys. Chem. **104**, 3817 (2000).
[19] H. Ness, S. A. Shevlin, and A. J. Fisher, Phys. Rev. B **63**, 125422 (2001).
[20] D. Boese and H. Schoeller, Europhys. Lett. **54**, 668 (2001).
[21] E. G. Petrov and P. Hänggi, Phys. Rev. Lett. **86**, 2862 (2001).
[22] E. G. Petrov, V. May, and P. Hänggi, Chem. Phys. **281**, 211 (2002).

[23] V. May, Phys. Rev. B **66**, 245411 (2002).
[24] E. G. Petrov, V. May, and P. Hänggi, Chem. Phys. **296**, 251 (2004).
[25] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, 2nd ed. (Wiley, Weinheim, 2003).
[26] D. Segal and A. Nitzan, Chem. Phys. **281**, 235 (2002).
[27] D. Segal and A. Nitzan, Chem. Phys. **268**, 315 (2001).
[28] E. G. Petrov, I. S. Tolokh, A. A. Demidenko, and V. V. Gorbach, Chem. Phys. **193**, 237 (1995).
[29] E. G. Petrov and V. May, J. Phys. Chem. A **105**, 10176 (2001).
[30] J. Lehmann, S. Kohler, P. Hänggi, and A. Nitzan, Phys. Rev. Lett. **88**, 228305 (2002).
[31] J. Lehmann, S. Kohler, P. Hänggi, and A. Nitzan, J. Chem. Phys. **118**, 3283 (2003).
[32] J. Lehmann, S. Camalet, S. Kohler, and P. Hänggi, Chem. Phys. Lett. **368**, 282 (2003).
[33] S. Camalet, J. Lehmann, S. Kohler, and P. Hänggi, Phys. Rev. Lett. **90**, 210602 (2003).
[34] A. Keller, O. Atabek, M. Ratner, and V. Mujica, J. Phys. B **35**, 4981 (2002).
[35] S. Kohler, J. Lehmann, S. Camalet, and P. Hänggi, Isr. J. Chem. **42**, 135 (2002).
[36] M. Switkes, C. M. Marcus, K. Campman, and A. C. Gossard, Science **283**, 1905 (1999).
[37] P. Reimann, Phys. Rep. **361**, 57 (2002).
[38] P. Reimann and P. Hänggi, Appl. Phys. A: Mater. Sci. Process. **75**, 169 (2002).
[39] R. D. Astumian and P. Hänggi, Phys. Today **55(5)**, 33 (2002).
[40] I. Goychuk and P. Hänggi, Europhys. Lett. **43**, 503 (1998).
[41] I. Goychuk and P. Hänggi, J. Phys. Chem. B **105**, 6642 (2001).
[42] F. Grossmann, T. Dittrich, P. Jung, and P. Hänggi, Phys. Rev. Lett. **67**, 516 (1991).
[43] F. Großmann, P. Jung, T. Dittrich, and P. Hänggi, Z. Phys. B: Condens. Matter **84**, 315 (1991).
[44] R. Bavli and H. Metiu, Phys. Rev. Lett. **69**, 1986 (1992).
[45] M. Grifoni and P. Hänggi, Phys. Rep. **304**, 229 (1998).
[46] S. N. Yaliraki and M. A. Ratner, J. Chem. Phys. **109**, 5036 (1998).
[47] S. Kohler, T. Dittrich, and P. Hänggi, Phys. Rev. E **55**, 300 (1997).
[48] S. Kohler, R. Utermann, P. Hänggi, and T. Dittrich, Phys. Rev. E **58**, 7219 (1998).
[49] T. Novotný, Europhys. Lett. **59**, 648 (2002).
[50] J. H. Shirley, Phys. Rev. **138**, B979 (1965).
[51] H. Sambe, Phys. Rev. A **7**, 2203 (1973).
[52] A. G. Fainshtein, N. L. Manakov, and L. P. Rapoport, J. Phys. B **11**, 2561 (1978).
[53] V. May, J. Mol. Electron. **6**, 187 (1990).
[54] V. May, Phys. Lett. A **161**, 118 (1991).
[55] J. Bonča and S. A. Trugman, Phys. Rev. Lett. **75**, 2566 (1995).
[56] H. Ness and A. J. Fisher, Phys. Rev. Lett. **83**, 452 (1999).
[57] T. Dittrich, B. Oelschlägel, and P. Hänggi, Europhys. Lett. **22**, 5 (1993).
[58] K. M. Fonseca-Romero, S. Kohler, and P. Hänggi, Chem. Phys. **296**, 307 (2004).
[59] Of course, thermal equilibrium requires all baths to be at a common temperature, as was put into our model from the very beginning.
[60] I. Goychuk and P. Hänggi, in *Stochastic Processes in Physics, Chemistry, and Biology*, Lecture Notes in Physics Vol. 557, edited by J. Freund and T. Pöschel (Springer, Berlin, 2000), pp. 7–20.
[61] F. Großmann and P. Hänggi, Europhys. Lett. **18**, 571 (1992).
[62] I. A. Goychuk, E. G. Petrov, and V. May, Chem. Phys. Lett. **253**, 428 (1996).
[63] M. Morillo and R. I. Cukier, J. Chem. Phys. **98**, 4548 (1993).
[64] Y. Kayanuma, Phys. Rev. B **47**, 9940 (1993).
[65] M. Grifoni, M. Sassetti, P. Hänggi, and U. Weiss, Phys. Rev. E **52**, 3596 (1995).
[66] T. Dittrich *et al.*, Physica A **194**, 173 (1993).
[67] B. Oelschlägel, T. Dittrich, and P. Hänggi, Acta Phys. Pol. B **24**, 845 (1993).
[68] M. Thorwart, M. Grifoni, and P. Hänggi, Phys. Rev. Lett. **85**, 860 (2000).
[69] M. Thorwart, M. Grifoni, and P. Hänggi, Ann. Phys. (N.Y.) **293**, 15 (2001).
[70] D. E. Makarov and N. Makri, Phys. Rev. E **52**, R2257 (1995).
[71] F. Grossmann, T. Dittrich, P. Jung, and P. Hänggi, J. Stat. Phys. **70**, 229 (1993).