Rectification of laser-induced electronic transport through molecules

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We study the influence of laser radiation on the electron transport through a molecular wire weakly coupled to two leads. In the absence of a generalized parity symmetry, the molecule rectifies the laser-induced current, resulting in directed electron transport without any applied voltage. We consider two generic ways of dynamical symmetry breaking: mixing of different harmonics of the laser field and molecules consisting of asymmetric groups. For the evaluation of the nonlinear current, a numerically efficient formalism is derived which is based upon the Floquet solutions of the driven molecule. This permits a treatment in the nonadiabatic regime and beyond linear response. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1536639]

I. INTRODUCTION

During the last several years, we experienced a wealth of experimental activity in the field of molecular electronics.[1–3] Its technological prospects for nanocircuits[4] have created broad interest in the conductance of molecules attached to metal surfaces or tips. In recent experiments[5–8] weak tunneling currents through only a few or even single molecules coupled by chemisorbed thiol groups to the gold surface of leads has been achieved. The experimental development is accompanied by an increasing theoretical interest in the transport properties of such systems.[9,10] An intriguing challenge presents the possibility to control the tunneling current through the molecule. Typical energy scales in molecules are in the optical and the infrared regime, where today's laser technology provides a wealth of coherent light sources. Hence, lasers represent an inherent possibility to control atoms or molecules and to direct currents through them.

A widely studied phenomenon in extended, strongly driven systems is the so-termed ratchet effect,[11–16] originally discovered and investigated for overdamped classical Brownian motion in periodic nonequilibrium systems in the absence of reflection symmetry. Counterintuitively to the second law of thermodynamics, one then observes a directed transport although all acting forces possess no net bias. This effect has been established as well within the regime of dissipative, incoherent quantum Brownian motion.[17] A related effect is found in the overdamped limit of dissipative tunneling in tight-binding lattices. Here the spatial symmetry is typically preserved and the nonvanishing transport is brought about by harmonic mixing of a driving field that includes higher harmonics.[18–20] For overdamped Brownian motion, both phenomena can be understood in terms of breaking a generalized reflection symmetry.[21]

Recent theoretical descriptions of molecular conductivity are based on a scattering approach.[22,23] Alternatively, one can assume that the underlying transport mechanism is an electron transfer reaction and that the conductivity can be derived from the corresponding reaction rate.[9] This analogy leads to a connection between electron transfer rates in a donor–acceptor system and conduction in the same system when operating as a molecular wire between two metal leads.[24] Within the high-temperature limit, the electron transport on the wire can be described by inelastic hopping events.[9,25–27] For a more quantitative *ab initio* analysis, the molecular orbitals may be taken from electronic structure calculations.[28]

Isolated atoms and molecules in strong oscillating fields have been widely studied within a Floquet formalism[29–34] and many corresponding theoretical techniques have been developed in that area. This suggests the procedure followed in Ref. 35: Making use of these Floquet tools, a formalism for the transport through time-dependent quantum systems has been derived that combines Floquet theory for a driven molecule with the many-particle description of transport through a system that is coupled to ideal leads. This approach is devised much in the spirit of the Floquet–Markov theory[36,37] for driven dissipative quantum systems. It assumes that the molecular orbitals that are relevant for the transport are weakly coupled to the contacts, so that the transport characteristics are dominated by the molecule itself. Yet, this treatment goes beyond the usual rotating-wave approximation as frequently employed, such as, e.g., in Refs. 37 and 38.

A time-dependent perturbative approach to the problem of driven molecular wires has recently been described by Tikhonov *et al.*[39,40] However, their one-electron treatment of this essentially inelastic transmission process cannot consistently handle the electronic populations on the leads. Moreover, while their general formulation is not bound to their independent channel approximation, their actual application of this approximation is limited to the small light-molecule interaction regime.

With this work we investigate the possibilities for molecular quantum wires to act as coherent quantum ratchets,

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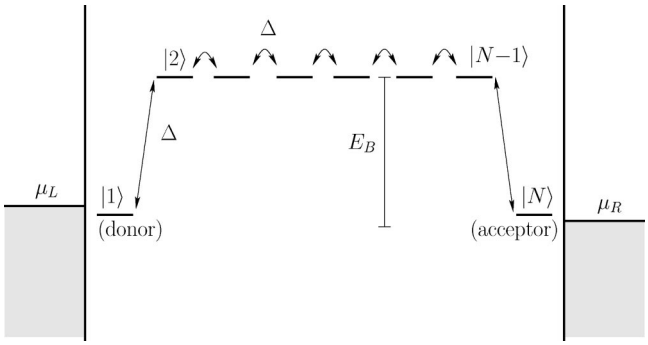

FIG. 1. Level structure of a molecular wire with $N=8$ atomic sites which are attached to two leads.

i.e., as quantum rectifiers for the laser-induced electrical current. In doing so, we provide a full account of the derivation published in letter format in Ref. 35. In Sec. II we present a more detailed derivation of the Floquet approach to the transport through a periodically driven wire. This formalism is employed in Sec. III to investigate the rectification properties of driven molecules. Two generic cases are discussed, namely mixing of different harmonics of the laser field in symmetric molecules and harmonically driven asymmetric molecules. We focus thereby on how the symmetries of the model system manifest themselves in the expressions for the time-averaged current. The general symmetry considerations of a quantum system under the influence of a laser field are deferred to the Appendix.

II. FLOQUET APPROACH TO THE ELECTRON TRANSPORT

The entire system of the driven wire, the leads, and the molecule–lead coupling as sketched in Fig. 1 is described by the Hamiltonian

$$H(t)=H_{\text{wire}}(t)+H_{\text{leads}}+H_{\text{wire-leads}}. \tag{1}$$

The wire is modeled by N atomic orbitals $|n\rangle$, $n=1,\ldots,N$, which are in a tight-binding description coupled by hopping matrix elements. Then, the corresponding Hamiltonian for the electrons on the wire reads in a second quantized form

$$H_{\text{wire}}(t)=\sum_{n,n'} H_{nn'}(t)c_n^\dagger c_{n'}, \tag{2}$$

where the fermionic operators c_n, $c_n^\dagger$ annihilate, respectively, create, an electron in the atomic orbital $|n\rangle$ and obey the anticommutation relation $[c_n,c_{n'}^\dagger]_+=\delta_{n,n'}$. The influence of the laser field is given by a periodic time-dependence of the on-site energies yielding a single particle Hamiltonian of the structure $H_{nn'}(t)=H_{nn'}(t+\mathcal{T})$, where $\mathcal{T}=2\pi/\Omega$ is determined by the frequency Ω of the laser field.

The orbitals at the left and the right end of the molecule, which we shall term donor and acceptor, $|1\rangle$ and $|N\rangle$, respectively, are coupled to ideal leads (cf. Fig. 1) by the tunneling Hamiltonians

$$H_{\text{wire-leads}}=\sum_q (V_{qL}\,c_{qL}^\dagger c_1+V_{qR}c_{qR}^\dagger c_N)+\text{H.c.} \tag{3}$$

The operator c_{qL} (c_{qR}) annihilates an electron on the left (right) lead in state Lq (Rq) orthogonal to all wire states. Later, we shall treat the tunneling Hamiltonian as a perturbation, while taking into account exactly the dynamics of the leads and the wire, including the driving.

The leads are modeled as noninteracting electrons with the Hamiltonian

$$H_{\text{leads}}=\sum_q (\epsilon_{qL}\,c_{qL}^\dagger c_{qL}+\epsilon_{qR}c_{qR}^\dagger c_{qR}). \tag{4}$$

A typical metal screens electric fields that have a frequency below the so-called plasma frequency. Therefore, any electromagnetic radiation from the optical or the infrared spectral range is almost perfectly reflected at the surface and will not change the bulk properties of the gold contacts. This justifies the assumption that the leads are in a state close to equilibrium and, thus, can be described by a grand-canonical ensemble of electrons, i.e., by a density matrix

$$\varrho_{\text{leads,eq}}\propto\exp[-(H_{\text{leads}}-\mu_L N_L-\mu_R N_R)/k_BT], \tag{5}$$

where $\mu_{L/R}$ are the electrochemical potentials and $N_{L/R}=\Sigma_q c_{qL/R}^\dagger c_{qL/R}$ the electron numbers on the left/right lead. As a consequence, the only nontrivial expectation values of lead operators read

$$\langle c_{qL}^\dagger c_{qL}\rangle=f(\epsilon_{qL}-\mu_L), \tag{6}$$

where ϵ_{qL} is the single particle energy of the state qL and correspondingly for the right lead. Here, $f(x)=(1+e^{x/k_BT})^{-1}$ denotes the Fermi function.

A. Time-dependent electrical current

The net (incoming minus outgoing) current through the left contact is given by the negative time derivative of the electron number in the left lead, multiplied by the electron charge $-e$, i.e.,

$$I_L(t)=e\frac{d}{dt}\langle N_L\rangle_t=\frac{ie}{\hbar}\langle[H(t),N_L]\rangle_t. \tag{7}$$

Here, the angular brackets denote expectation values at time t, i.e., $\langle O\rangle_t=\text{Tr}[O\rho(t)]$. The dynamics of the density matrix is governed by the Liouville–von Neumann equation $i\hbar\dot{\varrho}(t)=[H(t),\varrho(t)]$ together with the factorizing initial condition $\varrho(t_0)=\varrho_{\text{wire}}(t_0)\otimes\varrho_{\text{leads,eq}}$. For the Hamiltonian (1), the commutator in Eq. (7) is readily evaluated to

$$I_L(t)=\frac{2e}{\hbar}\,\text{Im}\sum_q V_{qL}\langle c_{qL}^\dagger c_1\rangle_t. \tag{8}$$

To proceed, it is convenient to switch to the interaction picture with respect to the uncoupled dynamics, where the Liouville–von Neumann equation reads

$$i\hbar\frac{d}{dt}\tilde{\varrho}(t,t_0)=[\tilde{H}_{\text{wire-leads}}(t,t_0),\tilde{\varrho}(t,t_0)]. \tag{9}$$

The tilde denotes the corresponding interaction picture operators, $\tilde{X}(t,t')=U_0^\dagger(t,t')X(t)U_0(t,t')$, where the propagator of the wire and the lead in the absence of the lead–wire coupling is given by the time-ordered product

$$U_0(t,t') = \tilde{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t} dt''[H_{\text{wire}}(t'') + H_{\text{leads}}]\right). \quad (10)$$

Equation (9) is equivalent to the integral equation

$$\tilde{\varrho}(t,t_0) = \tilde{\varrho}(t_0,t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'[\tilde{H}_{\text{wire-leads}}(t',t_0), \tilde{\varrho}(t',t_0)]. \quad (11)$$

Inserting this relation into Eq. (8), we obtain an expression for the current that depends on the density of states in the leads times their coupling strength to the connected sites. At this stage it is convenient to introduce the spectral density of the lead–wire coupling

$$\Gamma_{L/R}(\epsilon) = \frac{2\pi}{\hbar}\sum_q |V_{qL/R}|^2 \delta(\epsilon - \epsilon_{qL/R}), \quad (12)$$

which fully describes the leads' influence. If the lead states are dense, $\Gamma_{L/R}(\epsilon)$ becomes a continuous function. Since we restrict ourselves to the regime of a weak wire–lead coupling, we can furthermore assume that expectation values of lead operators are at all times given by their equilibrium values (6). Then we find after some algebra for the stationary (i.e., for $t_0 \to -\infty$), *time-dependent* net electrical current through the left contact the result

$$I_L(t) = \frac{e}{\pi\hbar}\text{Re}\int_0^\infty d\tau \int d\epsilon\, \Gamma_L(\epsilon) e^{i\epsilon\tau/\hbar}\{\langle c_1^\dagger \tilde{c}_1(t,t-\tau)\rangle_{t-\tau} - [c_1^\dagger, \tilde{c}_1(t,t-\tau)]_+ f(\epsilon-\mu_L)\}. \quad (13)$$

A corresponding relation holds true for the current through the contact on the right-hand side. Note that the anticommutator $[c_1^\dagger, \tilde{c}_1(t,t-\tau)]_+$ is in fact a c-number (see Eq. (22) below). Like the expectation value $\langle c_1^\dagger \tilde{c}_1(t,t-\tau)\rangle_{t-\tau}$, it depends on the dynamics of the isolated wire and is influenced by the external driving.

It is frequently assumed that the attached leads can be described by a one-dimensional tight-binding lattice with hopping matrix elements Δ'. Then, the spectral densities $\Gamma_{L/R}(\epsilon)$ of the lead–wire couplings are given by the Anderson–Newns model,[41] i.e., they assume an elliptical shape with a bandwidth $2\Delta'$. However, because we are mainly interested in the behavior of the molecule and not in the details of the lead–wire coupling, we assume that the conduction bandwidth of the leads is much larger than all remaining relevant energy scales. Consequently, we approximate in the so-called wide-band limit the functions $\Gamma_{L/R}(\epsilon)$ by the constant values $\Gamma_{L/R}$. The first contribution of the ϵ integral in Eq. (13) is then readily evaluated to yield an expression proportional to $\delta(\tau)$. Finally, this term becomes local in time and reads $e\Gamma_L\langle c_1^\dagger c_1\rangle_t$.

B. Floquet decomposition

Let us next focus on the single-particle dynamics of the driven molecule decoupled from the leads. Since its Hamiltonian is periodic in time, $H_{nn'}(t) = H_{nn'}(t+\mathcal{T})$, we can solve the corresponding time-dependent Schrödinger equation within a Floquet approach. This means that we make use of the fact that there exists a complete set of solutions of the form[29–31,33,34]

$$|\Psi_\alpha(t)\rangle = e^{-i\epsilon_\alpha t/\hbar}|\Phi_\alpha(t)\rangle, \quad |\Phi_\alpha(t)\rangle = |\Phi_\alpha(t+\mathcal{T})\rangle \quad (14)$$

with the quasienergies ϵ_α. Since the so-called Floquet modes $|\Phi_\alpha(t)\rangle$ obey the time-periodicity of the driving field, they can be decomposed into the Fourier series

$$|\Phi_\alpha(t)\rangle = \sum_k e^{-ik\Omega t}|\Phi_{\alpha,k}\rangle. \quad (15)$$

This suggests that the quasienergies ϵ_α come in classes,

$$\epsilon_{\alpha,k} = \epsilon_\alpha + k\hbar\Omega, \quad k = 0, \pm 1, \pm 2, \ldots, \quad (16)$$

of which all members represent the same solution of the Schrödinger equation. Therefore, the quasienergy spectrum can be reduced to a single "Brillouin zone" $-\hbar\Omega/2 \leqslant \epsilon < \hbar\Omega/2$. In turn, all physical quantities that are computed within a Floquet formalism are independent of the choice of a specific class member. Thus, a consistent description must obey the so-called class invariance, i.e., it must be invariant under the substitution of one or several Floquet states by equivalent ones,

$$\epsilon_\alpha, \ |\Phi_\alpha(t)\rangle \to \epsilon_\alpha + k_\alpha\hbar\Omega, \ e^{ik_\alpha\Omega t}|\Phi_\alpha(t)\rangle, \quad (17)$$

where $k_1, \ldots, k_N$ are integers. In the Fourier decomposition (15), the prefactor $\exp(ik_\alpha\Omega t)$ corresponds to a shift of the side band index so that the class invariance can be expressed equivalently as

$$\epsilon_\alpha, \ |\Phi_{\alpha,k}\rangle \to \epsilon_\alpha + k_\alpha\hbar\Omega, \ |\Phi_{\alpha,k+k_\alpha}\rangle. \quad (18)$$

Floquet states and quasienergies can be obtained from the quasienergy equation[29–34]

$$\left(\sum_{n,n'}|n\rangle H_{nn'}(t)\langle n'| - i\hbar\frac{d}{dt}\right)|\Phi_\alpha(t)\rangle = \epsilon_\alpha|\Phi_\alpha(t)\rangle. \quad (19)$$

A wealth of methods for the solution of this eigenvalue problem can be found in the literature.[33,34] One such method is given by the direct numerical diagonalization of the operator on the left-hand side of Eq. (19). To account for the periodic time-dependence of the $|\Phi_\alpha(t)\rangle$, one has to extend the original Hilbert space by a $\mathcal{T}$-periodic time coordinate. For a harmonic driving, the eigenvalue problem (19) is band-diagonal and selected eigenvalues and eigenvectors can be computed by a matrix-continued fraction scheme.[33,42]

In cases where many Fourier coefficients (in the present context frequently called "sidebands") must be taken into account for the decomposition (15), direct diagonalization is often not very efficient and one has to apply more elaborate schemes. For example, in the case of a large driving amplitude, one can treat the static part of the Hamiltonian as a perturbation.[30,43,44] The Floquet states of the oscillating part of the Hamiltonian then form an adapted basis set for a subsequently more efficient numerical diagonalization.

A completely different strategy to obtain the Floquet states is to propagate the Schrödinger equation for a complete set of initial conditions over one driving period to yield the one-period propagator. Its eigenvalues represent the Flo-

quet states at time $t=0$, i.e., $|\Phi_\alpha(0)\rangle$. Fourier transformation of their time-evolution results in the desired sidebands. Yet another, very efficient propagation scheme is the so-called (t,t') formalism.[45]

As the equivalent of the one-particle Floquet states $|\Phi_\alpha(t)\rangle$, we define a Floquet picture for the fermionic creation and annihilation operators $c_n^\dagger$, c_n, by the time-dependent transformation

$$c_\alpha(t)=\sum_n \langle\Phi_\alpha(t)|n\rangle c_n. \tag{20}$$

The inverse transformation

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

follows from the mutual orthogonality and the completeness of the Floquet states at equal times.[33,34] Note that the right-hand side of Eq. (21) becomes t-independent after the summation. In the interaction picture, the operator $c_\alpha(t)$ obeys

$$\tilde{c}_\alpha(t,t')=U_0^\dagger(t,t')c_\alpha(t)U_0(t,t')=e^{-i\epsilon_\alpha(t-t')/\hbar}c_\alpha(t'). \tag{22}$$

This is easily verified by differentiating the definition in the first line with respect to t and using that $|\Phi_\alpha(t)\rangle$ is a solution of the eigenvalue equation (19). The fact that the initial condition $\tilde{c}_\alpha(t',t')=c_\alpha(t')$ is fulfilled completes the proof. Using Eqs. (21) and (22), we are able to express the anticommutator of wire operators at different times by Floquet states and quasienergies:

$$[c_{n'},\tilde{c}_n^\dagger(t,t')]_+=\sum_\alpha e^{i\epsilon_\alpha(t-t')/\hbar}\langle n'|\Phi_\alpha(t')\rangle \times\langle\Phi_\alpha(t)|n\rangle. \tag{23}$$

This relation together with the spectral decomposition (15) of the Floquet states allows one to carry out the time and energy integrals in expression (13) for the net current entering the wire from the left lead. Thus, we obtain

$$I_L(t)=\sum_k e^{-ik\Omega t}I_L^k, \tag{24}$$

with the Fourier components

$$I_L^k=e\Gamma_L\Bigg[\sum_{\alpha\beta k'k''}\langle\Phi_{\alpha,k'+k''}|1\rangle\langle 1|\Phi_{\beta,k+k''}\rangle R_{\alpha\beta,k'}-\frac{1}{2}\sum_{\alpha k'}(\langle\Phi_{\alpha,k'}|1\rangle\langle 1|\Phi_{\alpha,k+k'}\rangle+\langle\Phi_{\alpha,k'-k}|1\rangle\langle 1|\Phi_{\alpha,k'}\rangle)f(\epsilon_{\alpha,k'}-\mu_L)$$
$$-\frac{i}{2}\sum_{\alpha k'}(\langle\Phi_{\alpha,k'}|1\rangle\langle 1|\Phi_{\alpha,k+k'}\rangle-\langle\Phi_{\alpha,k'-k}|1\rangle\langle 1|\Phi_{\alpha,k'}\rangle)\mathrm{P}\int\frac{d\epsilon}{\pi}\frac{f(\epsilon-\mu_L)}{\epsilon-\epsilon_{\alpha,k'}}\Bigg]. \tag{25}$$

Here, P denotes the principal value of the integral; it does not contribute to the dc component I_L^0. Moreover, we have introduced the expectation values

$$R_{\alpha\beta}(t)=\langle c_\alpha^\dagger(t)c_\beta(t)\rangle_t=R_{\beta\alpha}^*(t) \tag{26}$$

$$=\sum_k e^{-ik\Omega t}R_{\alpha\beta,k}. \tag{27}$$

The Fourier decomposition in the last line is possible because all $R_{\alpha\beta}(t)$ are expectation values of a linear, dissipative, periodically driven system and therefore share in the long-time limit the time-periodicity of the driving field. In the subspace of a single electron, $R_{\alpha\beta}$ reduces to the density matrix in the basis of the Floquet states which has been used to describe dissipative driven quantum systems in Refs. 34, 36, 37, 46–48.

C. Master equation

The last step toward the stationary current is to find the Fourier coefficients $R_{\alpha\beta,k}$ at asymptotic times. To this end, we derive an equation of motion for the reduced density operator $\varrho_{\mathrm{wire}}(t)=\mathrm{Tr}_{\mathrm{leads}}\varrho(t)$ by reinserting Eq. (11) into the Liouville–von Neumann equation (9). We use that to zeroth order in the molecule–lead coupling the interaction-picture density operator does not change with time, $\tilde{\varrho}(t-\tau,t_0)\approx\tilde{\varrho}(t,t_0)$. A transformation back to the Schrödinger picture results after tracing out the leads' degrees of freedom in the master equation

$$\dot{\varrho}_{\mathrm{wire}}(t)=-\frac{i}{\hbar}[H_{\mathrm{wire}}(t),\varrho_{\mathrm{wire}}(t)] -\frac{1}{\hbar^2}\int_0^\infty d\tau\,\mathrm{Tr}_{\mathrm{leads}}[H_{\text{wire-leads}},[\tilde{H}_{\text{wire-leads}}(t-\tau,t),\varrho_{\mathrm{wire}}(t)\otimes\varrho_{\mathrm{leads,eq}}]]. \tag{28}$$

Since we only consider asymptotic times $t_0\to-\infty$, we have set the upper limit in the integral to infinity. From Eq. (28) follows directly an equation of motion for the $R_{\alpha\beta}(t)$. Since all the coefficients of this equation, as well as its asymptotic solution, are $\mathcal{T}$-periodic, we can split it into its Fourier components. Finally, we obtain for the $R_{\alpha\beta,k}$ the inhomogeneous set of equations

$$\frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta+k\hbar\Omega)R_{\alpha\beta,k}=\frac{\Gamma_L}{2}\sum_{k'}\Bigg(\sum_{\beta' k''}\langle\Phi_{\beta,k'+k''}|1\rangle\langle 1|\Phi_{\beta',k+k''}\rangle R_{\alpha\beta',k'}+\sum_{\alpha' k''}\langle\Phi_{\alpha',k'+k''}|1\rangle\langle 1|\Phi_{\alpha,k+k''}\rangle R_{\alpha'\beta,k'}$$
$$-\langle\Phi_{\beta,k'-k}|1\rangle\langle 1|\Phi_{\alpha,k'}\rangle f(\epsilon_{\alpha,k'}-\mu_L)-\langle\Phi_{\beta,k'}|1\rangle\langle 1|\Phi_{\alpha,k'+k}\rangle f(\epsilon_{\beta,k'}-\mu_L)\Bigg)$$
$$+\text{same terms with the replacement }\{\Gamma_L,\mu_L,|1\rangle\langle 1|\}\rightarrow\{\Gamma_R,\mu_R,|N\rangle\langle N|\}. \tag{29}$$

For a consistent Floquet description, the current formula together with the master equation must obey class invariance. Indeed, the simultaneous transformation with Eq. (18) of both the master equation (29) and the current formula (25) amounts to a mere shift of summation indices and, thus, leaves the current as a physical quantity unchanged.

For the typical parameter values used in the following, a large number of sidebands contributes significantly to the Fourier decomposition of the Floquet modes $|\Phi_\alpha(t)\rangle$. Numerical convergence for the solution of the master equation (29), however, is already obtained by just using a few sidebands for the decomposition of $R_{\alpha\beta}(t)$. This keeps the numerical effort relatively small and justifies *a posteriori* the use of the Floquet representation (21). Yet we are able to treat the problem beyond a rotating-wave approximation.

D. Average current

Equation (24) implies that the current $I_L(t)$ obeys the time-periodicity of the driving field. Since we consider here excitations by a laser field, the corresponding frequency lies in the optical or infrared spectral range. In an experiment one will thus only be able to measure the time average of the current. For the net current entering through the left contact it is given by

$$\overline{I_L}=I_L^0=e\Gamma_L\sum_{\alpha k}\Bigg[\sum_{\beta k'}\langle\Phi_{\alpha,k'+k}|1\rangle\langle 1|\Phi_{\beta,k'}\rangle R_{\alpha\beta,k}$$
$$-\langle\Phi_{\alpha,k}|1\rangle\langle 1|\Phi_{\alpha,k}\rangle f(\epsilon_{\alpha,k}-\mu_L)\Bigg]. \tag{30}$$

Mutatis mutandis we obtain for the time-averaged net current that enters through the right contact

$$\overline{I_R}=e\Gamma_R\sum_{\alpha k}\Bigg[\sum_{\beta k'}\langle\Phi_{\alpha,k'+k}|N\rangle\langle N|\Phi_{\beta,k'}\rangle R_{\alpha\beta,k}$$
$$-\langle\Phi_{\alpha,k}|N\rangle\langle N|\Phi_{\alpha,k}\rangle f(\epsilon_{\alpha,k}-\mu_R)\Bigg]. \tag{31}$$

Total charge conservation of the original wire–lead Hamiltonian (1) of course requires that the charge on the wire can only change by current flow, amounting to the continuity equation $\dot{Q}_{\text{wire}}(t)=I_L(t)+I_R(t)$. Since asymptotically, the charge on the wire obeys at most the periodic time-dependence of the driving field, the time-average of $\dot{Q}_{\text{wire}}(t)$ must vanish in the long-time limit. From the continuity equation one then finds that $\overline{I_L}+\overline{I_R}=0$, and we can introduce the time-averaged current

$$\overline{I}=\overline{I_L}=-\overline{I_R}. \tag{32}$$

For consistency, Eq. (32) must also follow from our expressions for the average current (30) and (31). In fact, this can be shown by identifying $\overline{I_L}+\overline{I_R}$ as the sum over the right-hand sides of the master equation (29) for $\alpha=\beta$ and $k=0$,

$$\overline{I_L}+\overline{I_R}=\sum_\alpha\left[\frac{i}{\hbar}(\epsilon_\alpha-\epsilon_\beta+k\hbar\Omega)R_{\alpha\beta,k}\right]_{\alpha=\beta,k=0}=0, \tag{33}$$

which vanishes as expected.

E. Rotating-wave approximation

Although we can now in principle compute time-dependent currents beyond a rotating-wave approximation (RWA), it is instructive to see under what conditions one may employ this approximation and how it follows from the master equation (29). We note that from a computational viewpoint there is no need to employ a RWA since within the present approach the numerically costly part is the computation of the Floquet states rather than the solution of the master equation. Nevertheless, our motivation is that a RWA allows an analytical solution of the master equation to lowest order in the lead–wire coupling Γ. We will use this solution in the following to discuss the influence of symmetries on the Γ-dependence of the average current.

The master equation (29) can be solved approximately by assuming that the coherent oscillations of all $R_{\alpha\beta}(t)$ are much faster than their decay. Then it is useful to factorize $R_{\alpha\beta}(t)$ into a rapidly oscillating part that takes the coherent dynamics into account and a slowly decaying prefactor. For the latter, one can derive a new master equation with oscillating coefficients. Under the assumption that the coherent and the dissipative time scales are well separated, it is possible to replace the time-dependent coefficients by their time-averages. The remaining master equation is generally of a simpler form than the original one. Because we work here already with a spectral decomposition of the master equation, we give the equivalent line of argumentation for the Fourier coefficients $R_{\alpha\beta,k}$.

It is clear from the master equation (29) that if

$$\epsilon_\alpha-\epsilon_\beta+k\hbar\Omega\gg\Gamma_{L/R}, \tag{34}$$

then the corresponding $R_{\alpha\beta,k}$ emerge to be small and, thus, may be neglected. Under the assumption that the wire–lead

couplings are weak and that the Floquet spectrum has no degeneracies, the RWA condition (34) is well satisfied except for

$$\alpha=\beta, \quad k=0, \tag{35}$$

i.e., when the prefactor of the left-hand side of Eq. (34) vanishes exactly. This motivates the ansatz

$$R_{\alpha\beta,k}=P_\alpha\delta_{\alpha,\beta}\delta_{k,0}, \tag{36}$$

which means physically that the stationary state consists of an incoherent population of the Floquet modes. The occupation probabilities P_α are found by inserting the ansatz (36) into the master equation (29) and read

$$P_\alpha=\frac{\Sigma_k[w^1_{\alpha,k}f(\epsilon_{\alpha,k}-\mu_L)+w^N_{\alpha,k}f(\epsilon_{\alpha,k}-\mu_R)]}{\Sigma_k(w^1_{\alpha,k}+w^N_{\alpha,k})}. \tag{37}$$

Thus, the populations are determined by an average over the Fermi functions, where the weights

$$w^1_{\alpha,k}=\Gamma_L|\langle 1|\Phi_{\alpha,k}\rangle|^2, \tag{38}$$

$$w^N_{\alpha,k}=\Gamma_R|\langle N|\Phi_{\alpha,k}\rangle|^2, \tag{39}$$

are given by the effective coupling strengths of the kth Floquet sideband $|\Phi_{\alpha,k}\rangle$ to the corresponding lead. The average current (32) is within RWA readily evaluated to read

$$\overline{I}_{\mathrm{RWA}}=e\sum_{\alpha,k,k'}\frac{w^1_{\alpha,k}w^N_{\alpha,k'}}{\Sigma_{k''}(w^1_{\alpha,k''}+w^N_{\alpha,k''})}\times[f(\epsilon_{\alpha,k'}-\mu_R)-f(\epsilon_{\alpha,k}-\mu_L)]. \tag{40}$$

III. RECTIFICATION OF THE DRIVING-INDUCED CURRENT

In the absence of an applied voltage, i.e., $\mu_L=\mu_R$, the average force on the electrons on the wire vanishes. Nevertheless, it may occur that the molecule rectifies the laser-induced oscillating electron motion and consequently a nonzero dc current through the wire is established. In this section we investigate such ratchet currents in molecular wires.

As a working model we consider a molecule consisting of a donor and an acceptor site and $N-2$ sites in between (cf. Fig. 1). Each of the N sites is coupled to its nearest neighbors by a hopping matrix elements Δ. The laser field renders each level oscillating in time with a position-dependent amplitude. The corresponding time-dependent wire Hamiltonian reads

$$H_{nn'}(t)=-\Delta(\delta_{n,n'+1}+\delta_{n+1,n'})+[E_n-a(t)x_n]\delta_{nn'}, \tag{41}$$

where $x_n=(N+1-2n)/2$ is the scaled position of site $|n\rangle$, the energy $a(t)$ equals the electron charge multiplied by the time-dependent electrical field of the laser and the distance between two neighboring sites. The energies of the donor and the acceptor orbitals are assumed to be at the level of the chemical potentials of the attached leads, $E_1=E_N=\mu_L=\mu_R$. The bridge levels E_n, $n=2,\ldots,N-1$, lie E_B above the chemical potential, as sketched in Fig. 1. Later, we will also study the modified bridge sketched in Fig. 6. We remark that for the sake of simplicity, intra-atomic dipole excitations are neglected within our model Hamiltonian.

In all numerical studies, we will use the hopping matrix element Δ as the energy unit; in a realistic wire molecule, Δ is of the order 0.1 eV. Thus, our chosen wire–lead hopping rate $\Gamma=0.1\Delta/\hbar$ yields $e\Gamma=2.56\times10^{-5}$ A and $\Omega=3\Delta/\hbar$ corresponds to a laser frequency in the infrared. Note that for a typical distance of 5 Å between two neighboring sites, a driving amplitude $A=\Delta$ is equivalent to an electrical field strength of 2×10^6 V/cm.

A. Symmetry

It is known from the study of deterministically rocked periodic potentials[49] and of overdamped classical Brownian motion[21] that the symmetry of the equations of motion may rule out any nonzero average current at asymptotic times. Thus, before starting to compute ratchet currents, let us first analyze what kind of symmetries may prevent the sought-after effect. Apart from the principle interest, such situations with vanishing average current are also of computational relevance since they allow one to test numerical implementations.

The current formula (25) and the master equation (29) contain, besides Fermi factors, the overlap of the Floquet states with the donor and the acceptor orbitals $|1\rangle$ and $|N\rangle$. Therefore, we focus on symmetries that relate these two. If we choose the origin of the position space at the center of the wire, it is the parity transformation $\mathcal{P}:x\to-x$ that exchanges the donor with the acceptor, $|1\rangle\leftrightarrow|N\rangle$. Since we deal here with Floquet states $|\Phi_\alpha(t)\rangle$, respectively, with their Fourier coefficients $|\Phi_{\alpha,k}\rangle$, we must also take into account the time t. This allows for a variety of generalizations of the parity that differ by the accompanying transformation of the time coordinate. For a Hamiltonian of the structure (41), two symmetries come to mind: $a(t)=-a(t+\pi/\Omega)$ and $a(t)=-a(-t)$. Both are present in the case of a purely harmonic driving, i.e., $a(t)\propto\sin(\Omega t)$. We shall derive their consequences for the Floquet states in the Appendix and shall argue here why they yield a vanishing average current within the present perturbative approach.

1. Generalized parity

As a first case, we investigate a driving field that obeys $a(t)=-a(t+\pi/\Omega)$. Then, the wire Hamiltonian (41) is invariant under the so-called generalized parity transformation

$$\mathcal{S}_{\mathrm{GP}}:(x,t)\to(-x,t+\pi/\Omega). \tag{42}$$

Consequently, the Floquet states are either even or odd under this transformation, i.e., they fulfill the relation (A5), which reduces in the tight-binding limit to

$$\langle 1|\Phi_{\alpha,k}\rangle=\sigma_\alpha(-1)^k\langle N|\Phi_{\alpha,k}\rangle, \tag{43}$$

where $\sigma_\alpha=\pm1$, according to the generalized parity of the Floquet state $|\Phi_\alpha(t)\rangle$.

The average current $\overline{I}$ is defined in Eq. (32) by the current formulas (30) and (31) together with the master equation (29). We apply now the symmetry relation (43) to them in order to interchange donor state $|1\rangle$ and acceptor state $|N\rangle$. In

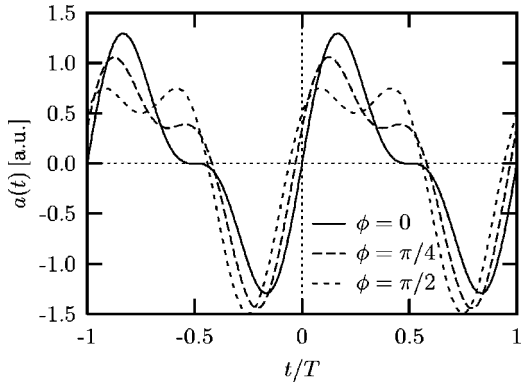

FIG. 2. Shape of the harmonic mixing field $a(t)$ in Eq. (47) for $A_1=2A_2$ for different phase shifts ϕ. For $\phi=0$, the field changes its sign for $t\rightarrow -t$ which amounts to the time-reversal parity (45).

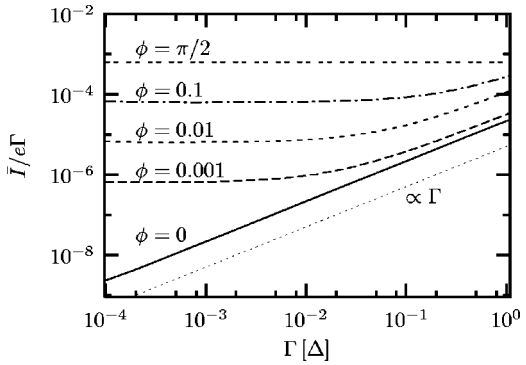

FIG. 3. Average current response to the harmonic mixing signal with amplitudes $A_1=2A_2=\Delta$, as a function of the coupling strength for different phase shifts ϕ. The remaining parameters are $\Omega=10\Delta/\hbar$, $E_B=5\Delta$, $k_BT=0.25\Delta$, $N=10$. The dotted line is proportional to Γ; it represents a current which is proportional to Γ^2.

addition we substitute in both the master equation and the current formulas $R_{\alpha\beta,k}$ by $\tilde{R}_{\alpha\beta,k}=\sigma_\alpha\sigma_\beta(-1)^k R_{\alpha\beta,k}$. The result is that the new expressions for the current, including the master equation, are identical to the original ones except for the fact that $\bar{I}_L$, Γ_L and $\bar{I}_R$, Γ_R are now interchanged (recall that we consider the case $\mu_L=\mu_R$). Therefore, we can conclude that

$$\frac{\bar{I}_L}{\Gamma_L}=\frac{\bar{I}_R}{\Gamma_R}, \tag{44}$$

which yields together with the continuity relation (32) a vanishing average current $\bar{I}=0$.

2. Time-reversal parity

A further symmetry is present if the driving is an odd function of time, $a(t)=-a(-t)$. Then, as detailed in the Appendix, the Floquet eigenvalue equation (19) is invariant under the time-reversal parity

$$\mathcal{S}_{\mathrm{TP}}:(\Phi,x,t)\rightarrow(\Phi^*,-x,-t), \tag{45}$$

i.e., the usual parity together with time-reversal and complex conjugation of the Floquet states Φ. The consequence for the Floquet states is the symmetry relation (A7) which reads for a tight-binding system

$$\langle 1|\Phi_{\alpha,k}\rangle=\langle N|\Phi_{\alpha,k}\rangle^*=\langle\Phi_{\alpha,k}|N\rangle. \tag{46}$$

Inserting this into the current formulas (30) and (31) would yield, if all $R_{\alpha\beta,k}$ were real, again the balance condition (44) and, thus, a vanishing average current. However, the $R_{\alpha\beta,k}$ are in general only real for $\Gamma_L=\Gamma_R=0$, i.e., for very weak coupling such that the condition (34) for the applicability of the rotating-wave approximation holds. Then, the solution of the master equation is dominated by the RWA solution (36), which is real. In the general case, the solution of the master equation (29) is however complex and consequently the symmetry (46) does not inhibit a ratchet effect. Still we can conclude from the fact that within the RWA the average current vanishes, that $\bar{I}$ is of the order Γ^2 for $\Gamma\rightarrow 0$, while it is of the order Γ for broken time-reversal symmetry.

B. Rectification from harmonic mixing

The symmetry analysis in Sec. III A explains that a symmetric bridge like the one sketched in Fig. 1 will not result in an average current if the driving is purely harmonic since a nonzero value is forbidden by the generalized parity (42). A simple way to break the time-reversal part of this symmetry is to add a second harmonic to the driving field, i.e., a contribution with twice the fundamental frequency Ω, such that it is of the form

$$a(t)=A_1\sin(\Omega t)+A_2\sin(2\Omega t+\phi), \tag{47}$$

as sketched in Fig. 2. While now shifting the time t by a half period π/Ω changes the sign of the fundamental frequency contribution, the second harmonic is left unchanged. The generalized parity is therefore broken and we find generally a nonvanishing average current.

Here, the phase shift ϕ plays a subtle role. For $\phi=0$ (or equivalently any multiple of π) the time-reversal parity is still present. Thus, according to the above-mentioned symmetry considerations, the current vanishes within the rotating-wave approximation. However, as discussed earlier, we expect beyond RWA for small coupling a current $\bar{I}\propto\Gamma^2$. Figure 3 confirms this prediction. Yet one observes that al-

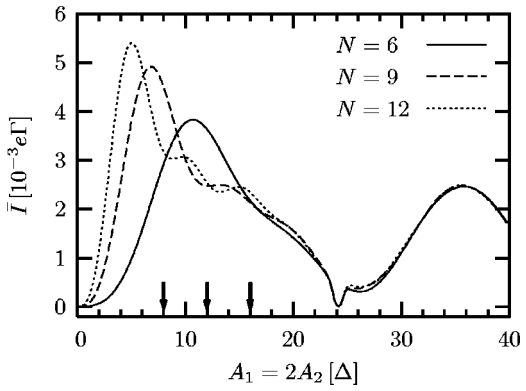

FIG. 4. Average current response to the harmonic mixing signal (47) for $\Omega=10\Delta/\hbar$ and phase $\phi=\pi/2$. The wire–lead coupling strength is $\Gamma=0.1\Delta$, the temperature $k_BT=0.25\Delta$, and the bridge height $E_B=5\Delta$. The arrows indicate the driving amplitudes used in Fig. 5.

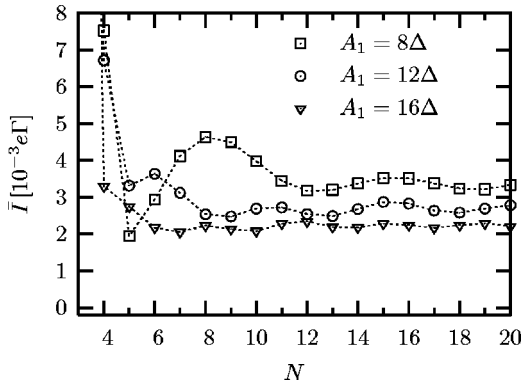

FIG. 5. Length dependence of the average current for harmonic mixing with phase $\phi=\pi/2$ for different driving amplitudes; the ratio of the driving amplitudes is fixed by $A_1=2A_2$. The other parameters are as in Fig. 4; the dotted lines serve as a guide to the eye.

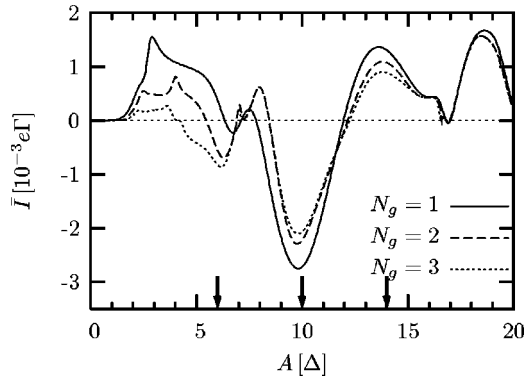

FIG. 7. Time-averaged current through a molecular wire that consists of N_g bridge units as a function of the driving strength A. The bridge parameters are $E_B=10\Delta$, $E_S=\Delta$, the driving frequency is $\Omega=3\Delta/\hbar$, the coupling to the leads is chosen as $\Gamma_L=\Gamma_R=0.1\Delta/\hbar$, and the temperature is $k_BT=0.25\Delta$. The arrows indicate the driving amplitudes used in Fig. 9.

ready a small deviation from $\phi=0$ is sufficient to restore the usual weak coupling behavior, namely a current which is proportional to the coupling strength Γ.

The average current for such a harmonic mixing situation is depicted in Fig. 4. For large driving amplitudes, it is essentially independent of the wire length and, thus, a wire that consists of only a few orbitals, mimics the behavior of an infinite tight-binding system. Figure 5 shows the length dependence of the average current for different driving strengths. The current saturates as a function of the length at a nonzero value. The convergence depends on the driving amplitude and is typically reached once the number of sites exceeds a value of $N\approx 10$. For low driving amplitudes the current response is more sensitive to the wire length.

C. Rectification in ratchet-like structures

A second possibility to realize a finite dc current is to preserve the symmetries of the time-dependent part of the Hamiltonian by employing a driving field of the form

$$a(t)=A\sin(\Omega t), \tag{48}$$

while making the level structure of the molecule asymmetric. Asymmetry in molecular structures can be achieved in many ways, and was explored as a source of molecular rectifying since the early paper of Aviram and Ratner.[50] In general, it can be controlled by attaching different chemical groups to the opposite sides of an otherwise symmetric molecular wire.[8,51] A tight-binding model of such a structure is sketched in Fig. 6.[35,52] In this molecular wire model, the inner wire states are arranged in N_g groups of three, i.e., $N-2=3N_g$. The levels in each such group are shifted by $\pm E_S/2$, forming an asymmetric saw-tooth-like structure.

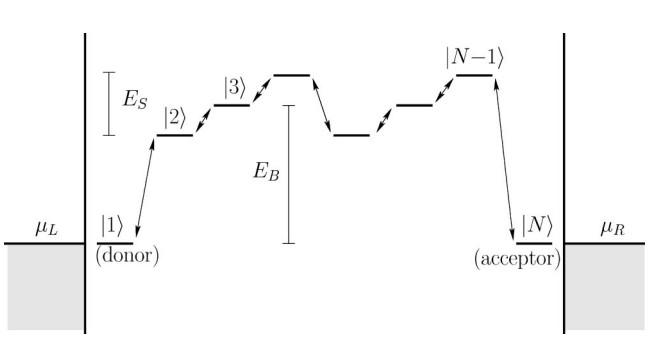

FIG. 6. Level structure of the wire ratchet with $N=8$ atomic sites, i.e., $N_g=2$ asymmetric molecular groups. The bridge levels are E_B above the donor and acceptor levels and are shifted by $\pm E_S/2$.

Figure 7 shows for this model the stationary time-averaged current $\bar{I}$ as a function of the driving amplitude A. In the limit of a very weak laser field, we find $\bar{I}\propto A^2E_S$, as can be seen from Fig. 8. This behavior is expected from symmetry considerations: On one hand, the asymptotic current must be independent of any initial phase of the driving field and therefore is an even function of the field amplitude A. On the other hand, $\bar{I}$ vanishes for zero step size E_S since then both parity symmetries are restored. The A^2 dependence indicates that the ratchet effect can only be obtained from a treatment *beyond linear response*. For strong laser fields, we find that $\bar{I}$ is almost independent of the wire length. If the driving is moderately strong, $\bar{I}$ depends in a short wire sensitively on the driving amplitude A and the number of asymmetric molecular groups N_g; even the sign of the current may change with N_g, i.e., we find a current reversal as a function of the wire length. For long wires that comprise five or more wire units (corresponding to 17 or more sites), the

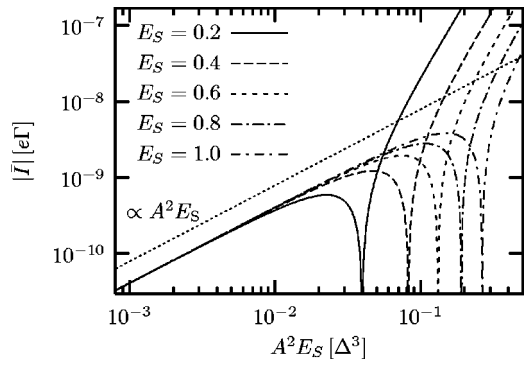

FIG. 8. Absolute value of the time-averaged current in a ratchet-like structure with $N_g=1$ as a function of A^2E_S demonstrating the proportionality to A^2E_S for small driving amplitudes. All other parameters are as in Fig. 7. At the dips on the right-hand side, the current $\bar{I}$ changes its sign.

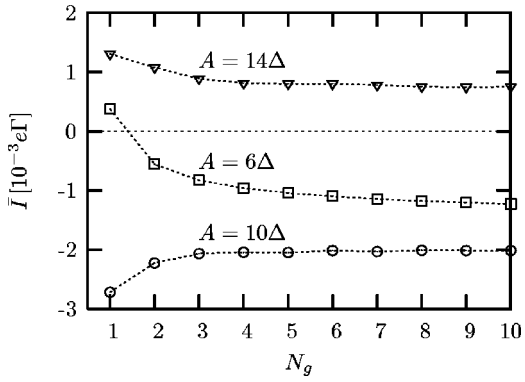

FIG. 9. Time-averaged current as a function of the number of bridge units N_g, $N=3N_g+2$, for the laser amplitudes indicated in Fig. 7. All other parameters are as in Fig. 7. The connecting lines serve as a guide to the eye.

average current becomes again length-independent, as can be observed in Fig. 9. This identifies the current reversal as a finite size effect.

Figure 10 depicts the average current versus the driving frequency Ω, exhibiting resonance peaks as a striking feature. Comparison with the quasienergy spectrum reveals that each peak corresponds to a nonlinear resonance between the donor/acceptor and a bridge orbital. While the broader peaks at $\hbar\Omega \approx E_B = 10\Delta$ match the 1:1 resonance (i.e., the driving frequency equals the energy difference), one can identify the sharp peaks for $\hbar\Omega \lesssim 7\Delta$ as multiphoton transitions. Owing to the broken spatial symmetry of the wire, one expects an asymmetric current–voltage characteristic. This is indeed the case as depicted with the inset of Fig. 10.

IV. CONCLUSIONS

With this work we have detailed our recently presented approach[35] for the computation of the current through a time-dependent nanostructure. The Floquet solutions of the isolated wire provide a well-adapted basis set that keeps the numerical effort for the solution of the master equation relatively low. This allows an efficient theoretical treatment that is feasible even for long wires in combination with strong laser fields.

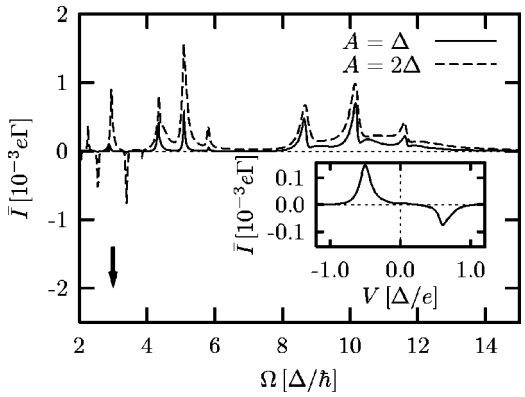

FIG. 10. Time-averaged current as a function of the angular driving frequency Ω for $N_g=1$. All other parameters are as in Fig. 7. The inset displays the dependence of the average current on an externally applied static voltage V, which we assume here to drop solely along the molecule. The driving frequency and amplitude are $\Omega=3\Delta/\hbar$ (cf. arrow in main panel) and $A=\Delta$, respectively.

With this formalism we have investigated the possibility to rectify with a molecular wire an oscillating external force brought about by laser radiation, thereby inducing a nonvanishing average current without any net bias. A general requirement for this effect is the absence of any reflection symmetry, even in a generalized sense. A most significant difference between ''true'' ratchets and molecular wires studied here is that the latter lack the strict spatial periodicity owing to their finite length. However, as demonstrated earlier, already relatively short wires that consist of approximately 5 to 10 units can mimic the behavior of an infinite ratchet. If the wire is even shorter, we find under certain conditions a current reversal as a function of the wire length, i.e., even the sign of the current may change. This demonstrates that the physics of a coherent quantum ratchet is richer than the one of its units, i.e., the combination of coherently coupled wire units, the driving, and the dissipation resulting from the coupling to leads bears new intriguing effects. A quantitative analysis of a tight-binding model has demonstrated that the resulting currents lie in the range of 10^{-9} A and, thus, can be measured with today's techniques.

An experimental realization of the phenomena discussed in this paper is obviously not a simple problem. The requirement for asymmetric molecular structures is easily realized as discussed earlier, however difficulties associated with the many possible effects of junction illumination have to be surmounted.[53] First is the issue of bringing the light into the junction. This is a difficult problem in a break-junction setup but possible in a STM configuration. Second, in addition to the mechanism discussed in this paper, which is associated with modulation of electronic states on the molecular bridge, other processes involving excitation of the metal surface may also affect electron transport. A complete theory of illuminated molecular junction should consider this possible effect. Also, part of the junction response to an oscillating electromagnetic field may involve displacement currents associated with the junction capacity. Finally, junction heating may constitute a severe problem when strong electromagnetic fields are applied. On the other hand, the light-induced rectification phenomenon discussed in this paper is generic in the sense that it does not require a particular molecular electronic structure as long as an inherent molecular asymmetry is present. The prediction that with proper illumination one might induce a unidirectional current without applied voltage suggests a possibility to observe the effect without the background of a direct current component.

An alternative experimental realization of the presented results is possible in semiconductor heterostructures, where, instead of a molecule, coherently coupled quantum dots[54] form the central system. A suitable radiation source that matches the frequency scales in this case must operate in the microwave spectral range.

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APPENDIX: PARITY OF A SYSTEM UNDER DRIVING BY A DIPOLE FIELD

Although we describe in this work the molecule within a tight-binding approximation, it is more convenient to study its symmetries as a function of a continuous position and to regard the discrete sites as a special case. Let us first consider a Hamiltonian that is an even function of x and, thus, is invariant under the parity transformation $\mathcal{P}: x \to -x$. Then, its eigenfunctions φ_α can be divided into two classes: even and odd ones, according to the sign in $\varphi_\alpha(x) = \pm \varphi_\alpha(-x)$.

Adding a periodically time-dependent dipole force $xa(t)$ to such a Hamiltonian evidently breaks parity symmetry since $\mathcal{P}$ changes the sign of the interaction with the radiation. In a Floquet description, however, we deal with states that are functions of both position and time—we work in the extended space $\{x,t\}$. Instead of the stationary Schrödinger equation, we address the eigenvalue problem

$$\mathcal{H}(x,t)\Phi(x,t) = \epsilon\,\Phi(x,t) \tag{A1}$$

with the so-called Floquet Hamiltonian given by

$$\mathcal{H}(t) = H_0(x) + xa(t) - i\hbar\frac{\partial}{\partial t}, \tag{A2}$$

where we assume a symmetric static part, $H_0(x) = H_0(-x)$. Our aim is now to generalize the notion of parity to the extended space $\{x,t\}$ such that the overall transformation leaves the Floquet equation (A1) invariant. This can be achieved if the shape of the driving $a(t)$ is such that an additional time transformation ''repairs'' the acquired minus sign. We consider two types of transformation: generalized parity and time-reversal parity. Both occur for purely harmonic driving, $a(t) = \sin(\Omega t)$. In the following two sections we derive their consequences for the Fourier coefficients

$$\Phi_k(x) = \frac{1}{T}\int_0^T dt\, e^{ik\Omega t}\Phi(x,t) \tag{A3}$$

of a Floquet states $\Phi(x,t)$.

1. Generalized parity

It has been noted[55–57] that a Floquet Hamiltonian of the form (A2) with $a(t) = \sin(\Omega t)$ may possess degenerate quasienergies due to its symmetry under the so-called generalized parity transformation

$$\mathcal{S}_{\mathrm{GP}}: \quad (x,t) \to (-x, t + \pi/\Omega), \tag{A4}$$

which consists of spatial parity plus a time shift by half a driving period. This symmetry is present in the Floquet Hamiltonian (A2), if the driving field obeys $a(t) = -a(t + \pi/\Omega)$, since then $\mathcal{S}_{\mathrm{GP}}$ leaves the Floquet equation invariant. Owing to $\mathcal{S}_{\mathrm{GP}}^2 = 1$, we find that the corresponding Floquet states are either even or odd, $\mathcal{S}_{\mathrm{GP}}\Phi(x,t) = \Phi(-x, t + \pi/\Omega) = \pm\Phi(x,t)$. Consequently, the Fourier coefficients (A3) obey the relation

$$\Phi_k(x) = \pm(-1)^k \Phi_k(-x). \tag{A5}$$

2. Time-inversion parity

A further symmetry is found if a is an odd function of time, $a(t) = -a(-t)$. Then, time inversion transforms the Floquet Hamiltonian (A2) into its complex conjugate so that the corresponding symmetry is given by the antilinear transformation

$$\mathcal{S}_{\mathrm{TP}}: \quad (\Phi,x,t) \to (\Phi^*, -x, -t). \tag{A6}$$

This transformation represents a further generalization of the parity $\mathcal{P}$; we will refer to it as *time-inversion parity* since in the literature the term generalized parity is mostly used in the context of the transformation (A4).

Let us now assume that that the Floquet Hamiltonian is invariant under the transformation (A6), $\mathcal{H}(x,t) = \mathcal{H}^*(-x, -t)$, and that $\Phi(x,t)$ is a Floquet state, i.e., a solution of the eigenvalue equation (A1) with quasienergy ϵ. Then, $\Phi^*(-x,-t)$ is also a Floquet state with the same quasienergy. In the absence of any degeneracy, both Floquet states must be identical and, thus, we find as a consequence of the time-inversion parity $\mathcal{S}_{\mathrm{TP}}$ that $\Phi(x,t) = \Phi^*(-x,-t)$. This is not necessarily the case in the presence of degeneracies, but then we are able to choose linear combinations of the (degenerate) Floquet states which fulfill the same symmetry relation. Again we are interested in the Fourier decomposition (A3) and obtain

$$\Phi_k(x) = \Phi_k^*(-x). \tag{A7}$$

The time-inversion discussed here can be generalized by an additional time-shift to read $t \to t_0 - t$. Then, we find by the same line of argumentation that $\Phi_k(x)$ and $\Phi_k^*(-x)$ differ at most by a phase factor. However, for convenience one may choose already from the start the origin of the time axis such that $t_0 = 0$.

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