Bound states in *ab initio* approaches to quantum transport: A time-dependent formulation

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(Received 19 September 2006; revised manuscript received 24 January 2007; published 15 May 2007)

In this work, we study the role of bound electrons in quantum transport. The partition-free approach by Cini [Phys. Rev. B. **22**, 5887 (1980)] is combined with time-dependent density-functional theory (TDDFT) to calculate total currents and densities in interacting systems. We show that the biased electrode-device-electrode system with bound states does not evolve toward a steady regime. The density oscillates with history-dependent amplitudes and, as a consequence, the effective potential of TDDFT oscillates too. Such time dependence might open new conductive channels, an effect which is not accounted for in any steady-state approach and might deserve further investigations.

I. INTRODUCTION

The progressive miniaturization of electronic devices and their future application in nanoscale circuitry entails the necessity of developing a quantum theory of transport. Such a theory should account for the full atomistic structure of the contacts and the molecular device, and for the dynamical effects of exchange and correlation on the electron motion.

Most theoretical works on quantum transport focus on steady-state properties and are based on a "contacting approach" first introduced by Combescot and co-workers.[1–4] In this approach, the system is separated in isolated parts in the remote past (left and right leads and central device) and the contacts between subsystems are treated as a *time-dependent* perturbation (adiabatic switching). Such a partition is crucial in the formal derivation of the Meir-Wingreen formula,[5] which allows for studying time-dependent phenomena and correlation effects in the device region but is not suitable to include long-range interactions and memory effects in a first-principles manner (see discussion below).

The contacting approach has a severe limitation. In a typical experiment, the whole system is contacted and in equilibrium *before* a driving external field is switched on. Thus, there is an implicit assumption of equivalence between (a) the initially partitioned and biased system once the *contacts* are introduced and (b) the whole system in equilibrium once the *bias* is turned on. This assumption might be reasonable in the long-time limit but is clearly inappropriate at any finite time. As a consequence, the contacting approach is not suitable for describing transient regimes. Also, the memory of initial conditions is not properly accounted for. In a noninteracting system, memory effects are washed out provided the local density of states is smooth in the device region.[6–8] However, this is generally not true in the interacting case.[7,9,10]

Recently, Dhar and Sen[11] have shown that memory effects might also be observed in noninteracting systems with bound states. This finding renders the contacting approach ambiguous since the equilibrium distribution of the initially isolated device is arbitrary. It has also been shown that the one-particle density matrix of the unbiased system does not reduce to the standard equilibrium result but rather oscillates with frequencies $\omega = \varepsilon_b - \varepsilon_{b'}$, where ε_b and $\varepsilon_{b'}$ are bound-state energies. In order to circumvent this problem, Dhar and Sen proposed the introduction of two "extra" reservoirs weakly coupled to the device. For the unbiased system, the equilibrium result is recovered in the limit where the extra couplings tend to zero. However, out of equilibrium the results depend on the limiting procedure.

In this work, we use the "partition-free approach" by Cini[12] which is free from all of the above limitations. In contrast to the contacting approach, the system is not partitioned in the remote past and is in equilibrium at a unique temperature and chemical potential (thermodynamic consistency). The initial equilibrium distribution of the device is unambiguous. The system is driven out of equilibrium by exposing the electrons to a time-dependent electric field. Thus, the external perturbation is a *local* potential and the partition-free approach can be combined with time-dependent density-functional theory[13–16] (TDDFT) to calculate total currents and densities in interacting systems.[7,8] The use of TDDFT in quantum transport is gaining ground[7,8,10,17–29] and several properties of the time-dependent exchange-correlation potential and kernel have recently been discussed.[30–34]

In a previous work,[6] we have shown how a steady current develops under the influence of a constant bias. For noninteracting electrons, we also proved that the steady current is independent of the history of the applied bias and agrees with the steady current calculated in the contacting approach. The theory has been developed assuming a smooth density of states in the device region. Here, we generalize the theory and include bound states in the description of time-dependent quantum-transport phenomena. Our main findings are as follows. For noninteracting electrons (1) in the presence of bound states, the total current and the one-particle density matrix oscillate with frequencies $\omega = \varepsilon_b - \varepsilon_{b'}$, and the amplitude of the oscillations are *unambiguous* calculable quantities. (2) the amplitude of the oscillations depends on the history of the applied bias and on the original equilibrium, meaning that the long-time limit does not wash out the effects of different initial conditions. (3) for the unbiased system, the oscillations vanish and all the time-dependent quantities reduce to their equilibrium value. Thus, in the partition-free approach there is no need of extra reservoirs to recover standard equilibrium properties. For Kohn-Sham
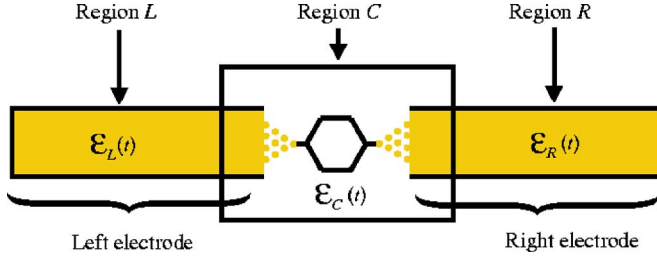
FIG. 1. (Color online) The electrode-device-electrode system described by $\boldsymbol{H}(t)$. It consists of left (L) and right (R) metallic regions coupled to a central scattering region C. Region C contains the actual molecular device and few atomic layers of the L/R electrodes.

electrons (TDDFT) (4) the steady-state assumption is not consistent with the presence of bound states, (5) it is possible to have self-consistent oscillatory solutions even for time-independent external fields, and (6) density oscillations might induce oscillations in the effective potential of TDDFT and hence give rise to new conductive channels. This effect cannot be captured in static DFT calculations.

The plan of the paper is as follows. In Sec. II, we give a brief introduction to the extended Keldysh formalism which properly accounts for the effects of initial correlations. A general formula for the total current is derived in Sec. III. Such a formula explicitly contains the distribution function of the system in equilibrium and allows for working in both the contacting approach and the partition-free approach. In Sec. IV, we generalize the theory of Ref. 6 to include bound states in quantum transport. The implications of our findings in a formulation based on TDDFT are discussed in Sec. V. In Sec. VI, we summarize the main results and draw our conclusions.

II. KELDYSH-GREEN FUNCTION

Let us consider a system of noninteracting electrons (or mean-field electrons or Kohn-Sham electrons) described by

$$\hat{H}(t) = \sum_{m,n} [\boldsymbol{H}(t)]_{m,n} c_m^\dagger c_n, \tag{1}$$

where the matrix

$$\boldsymbol{H}(t) = \begin{bmatrix} \boldsymbol{\mathcal{E}}_L(t) & \boldsymbol{V}_{LC}(t) & 0 \\ \boldsymbol{V}_{CL}(t) & \boldsymbol{\mathcal{E}}_C(t) & \boldsymbol{V}_{CR}(t) \\ 0 & \boldsymbol{V}_{RC}(t) & \boldsymbol{\mathcal{E}}_R(t) \end{bmatrix} \tag{2}$$

models the electrode-device-electrode system of Fig. 1. (Here and in the following, we use boldface to indicate matrices in one-electron labels.)

Without loss of generality, we assume that the system is in equilibrium for negative times $t<0$. Letting μ be the chemical potential and β be the inverse temperature, all equilibrium quantities can be expressed in terms of the density matrix
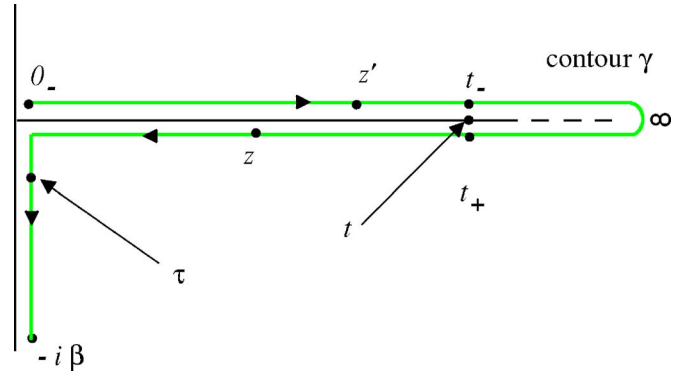

FIG. 2. (Color online) The oriented contour γ is composed by a forward and a backward branch between 0 and ∞ and a vertical track going from 0 to $-i\beta$. According to the orientation, the point z is later than z' and any point lying on the vertical track is later than both z and z'. For any physical time t, we have two points $t_\pm$ on γ at the same distance from the origin. In the main text, we choose the Greek letter τ for z on the vertical track.

$$\hat{\rho} = e^{-\beta(\hat{H}^0 - \mu\hat{N})}, \tag{3}$$

with $\hat{N} = \sum_m c_m^\dagger c_m$ the operator of the total number of particles and $\hat{H}^0 = \hat{H}(t<0)$. The Matsubara-Green function technique is a well established theory for calculating $\hat{\rho}$-averaged quantities but is limited to equilibrium problems. A very powerful tool for dealing with nonequilibrium (as well as equilibrium) problems is provided by the non-equilibrium Green's function (NEGF) theory.[35,36]

The basic quantity in NEGF is the Keldysh-Green function

$$[\boldsymbol{\mathcal{G}}(z;z')]_{m,n} = \frac{1}{i} \frac{\text{Tr}\left(\mathcal{T}\left\{ \exp\left[-i \int_\gamma d\bar{z}\hat{H}(\bar{z}) \right] c_m(z) c_n^\dagger(z') \right\} \right)}{\text{Tr}[\hat{\rho}]}, \tag{4}$$

where Tr denotes the trace over all many-body states. In Eq. (4), the integral is over the Keldysh contour γ of Fig. 2, $\mathcal{T}$ is the contour ordering operator, and $\hat{H}(z) = \hat{H}(t)$ for $z = t_\pm$ while $\hat{H}(z) = \hat{H}^0$ for $z = \tau$. The fermion operators $c_m(z) = c_m$ and $c_n^\dagger(z') = c_n^\dagger$ do not depend on the contour variables z and z'; the reason of the contour argument stems from the need of specifying their positions in the contour ordering. The Green's function $\boldsymbol{\mathcal{G}}$ obeys an important cyclic relation[37,38]

$$\boldsymbol{\mathcal{G}}(0_-;z') = -e^{\beta\mu}\boldsymbol{\mathcal{G}}(-i\beta;z'), \tag{5}$$

$$\boldsymbol{\mathcal{G}}(z;0_-) = -e^{-\beta\mu}\boldsymbol{\mathcal{G}}(z;-i\beta), \tag{6}$$

which is used as boundary condition for the solution of the equation of motion

$$\left\{ i\frac{d}{dz}\mathbf{1} - H(z) \right\} \mathcal{G}(z;z') = \delta(z;z')\mathbf{1}, \qquad (7)$$

with $\mathbf{1}$ the unity matrix. The Keldysh-Green function reduces to the Matsubara-Green function for z and z' on the vertical track of the contour γ.

In the NEGF formulation of quantum transport, the non-local Hamiltonian connecting regions L and R to the central region C is treated perturbatively to all orders. This is possible by rewriting H as $\mathcal{E} + V$ where

$$\mathcal{E} = \begin{bmatrix} \mathcal{E}_L & 0 & 0 \\ 0 & \mathcal{E}_C & 0 \\ 0 & 0 & \mathcal{E}_R \end{bmatrix}, \quad V = \begin{bmatrix} 0 & V_{LC} & 0 \\ V_{CL} & 0 & V_{CR} \\ 0 & V_{RC} & 0 \end{bmatrix}, \qquad (8)$$

and by introducing the diagonal Green's function g which obeys the equation of motion below

$$\left\{ i\frac{d}{dz}\mathbf{1} - \mathcal{E}(z) \right\} g(z;z') = \delta(z;z')\mathbf{1}. \qquad (9)$$

The diagonal g allows us to convert Eq. (7) into a Dyson equation on γ,

$$\mathcal{G}(z;z') = g(z;z') + \int_\gamma d\bar{z}\, g(z;\bar{z}) V(\bar{z}) \mathcal{G}(\bar{z};z'), \qquad (10)$$

provided g obeys the same cyclic relations (5) *and* (6) *as $\mathcal{G}$.* We wish to stress that Eq. (10) is an exact equation *only if* the contour γ includes the forward and backward branches *and* the vertical track. As one can see by inspection, the removal of the vertical track from γ is equivalent to setting $V(z=\tau) = V^0 = 0$ and hence to starting from an initial Hamiltonian $H^0 = \mathcal{E}^0$, with $\mathcal{E}^0 = \mathcal{E}(t < 0)$.

To calculate the time-dependent total current, one needs the lesser component of the Keldysh-Green function. Choosing $z = t_-$ and $z' = t'_+$ in Eq. (10) and using the Langreth theorem,[39,40] we find

$$\mathcal{G}^<(t;t') = g^<(t;t') + \int_0^\infty d\bar{t}\, \mathcal{G}^R(t;\bar{t}) V(\bar{t}) g^<(\bar{t};t')$$

$$+ \int_0^\infty d\bar{t}\, \mathcal{G}^<(t;\bar{t}) V(\bar{t}) g^A(\bar{t};t')$$

$$+ \int_0^{-i\beta} d\bar{\tau}\, \mathcal{G}(t;\bar{\tau}) V(\bar{\tau}) g(\bar{\tau};t'), \qquad (11)$$

where Green's functions with superscript R (A) are retarded (advanced) Green's functions. It is possible to show that Eq. (11) is equivalent to[6]

$$\mathcal{G}^<(t;t') = \mathcal{G}^R(t;0) \mathcal{G}^<(0;0) \mathcal{G}^A(0;t'). \qquad (12)$$

Equation (12), as opposed to Eq. (11), has a simple physical interpretation. The lesser Green's function is completely known once we know how to propagate the one-electron states in time and how these states are populated before the system is driven out of equilibrium. The time evolution is fully described by the retarded or advanced Green's functions $\mathcal{G}^{R,A}$, and the initial equilibrium distribution is fully

described by $\mathcal{G}^<(0;0) = if(H^0)$, where $f(\omega) = 1/[e^{\beta(\omega-\mu)} + 1]$ is the Fermi function.

Equation (12) is valid for noninteracting electrons and for mean-field (Hartree or Hartree-Fock) electrons; it is also valid for Kohn-Sham electrons since in TDDFT the electron-electron interaction is described by an exchange-correlation potential which is local in time. The present work deals with noninteracting electrons (Secs. III and IV) and Kohn-Sham electrons (Sec. V), and hence Eq. (12) can always be used. Due to the nonlocality in time of the correlation self-energy, Eq. (12) is no longer valid beyond the Hartree-Fock approximation of many-body perturbation theory. In the latter case, the exact formula for the lesser Green's function (which fully accounts for transient and correlation effects) can be found in Ref. 6.

III. CURRENT FORMULA FROM NEGF

The total current from region $\alpha = L, C, R$ can be calculated from the time derivative of the total number of particles in α,

$$I_\alpha(t) = -e\frac{d}{dt}\mathrm{Tr}_\alpha[-i\mathcal{G}^<(t;t)], \qquad (13)$$

where Tr_α denotes the trace over a complete set of one-particle states for region α and e is the electron charge. From the equation of motion (7), the change per unit time of the lesser Green's function is proportional to the commutator $[\mathcal{G}^<(t;t), H(t)]$. Projecting the Green's function onto different subregions,

$$\mathcal{G} = \begin{bmatrix} \mathcal{G}_{LL} & \mathcal{G}_{LC} & \mathcal{G}_{LR} \\ \mathcal{G}_{CL} & \mathcal{G}_{CC} & \mathcal{G}_{CR} \\ \mathcal{G}_{RL} & \mathcal{G}_{RC} & \mathcal{G}_{RR} \end{bmatrix}, \qquad (14)$$

it is straightforward to realize that

$$I_\alpha(t) = 2e\,\mathrm{Re}\,\mathrm{Tr}_C[\mathcal{G}_{C\alpha}^<(t;t) V_{\alpha C}(t)], \quad \alpha = L, R. \qquad (15)$$

Equation (15) will be our starting point for the calculation of the long-time limit of $I_\alpha(t)$ for different initial conditions and in the presence of bound states. Equation (15) is valid for both noninteracting and Kohn-Sham electrons. In the latter case, $\mathcal{G}^<$ is the Kohn-Sham Green's function and $I_\alpha(t)$ is the total current of the Kohn-Sham system which, according to the Runge-Gross theorem,[13] is the same as the total current of the real interacting system. In the remainder of this section and in Sec. IV, we specialize to noninteracting electrons. Interacting systems will be considered in Sec. V.

A. Contacting approach

The contacting approach has been originally introduced by Combescot and co-workers in a series of four papers.[1–4] About 20 years after, it has been combined with NEGF to include the effects of time-dependent perturbations and short-range correlations in the scattering region.[5,41] In the contacting approach, regions L and R are in equilibrium at the same temperature and chemical potential and are disconnected from C. The Hamiltonian for negative times is then

$H^0 = \mathcal{E}^0$ and the one-particle eigenstates of the unperturbed (and hence disconnected) system are strictly confined in the left region or in the right region or in the central scattering region. The equilibrium distribution of region C cannot be univocally fixed since C is initially an isolated subsystem. This is equivalent to saying that $\mathcal{E}_C(t<0)=\mathcal{E}_C^0$, is in principle, an arbitrary Hamiltonian.[42] We observe that this ambiguity make the transient current difficult to interpret. To drive a current through the system, one exposes the electrons to a longitudinal electric field, and at the same time switches on the contacts V between C and L/R. In a typical experimental setup, regions L and R are bulk metallic electrodes (see Fig. 1). The dynamical formation of dipole layers at the α-electrode interface screens the potential drop along region α and the total potential turns out to be uniform in the left and right bulks. For this reason, we model the effects of a time-dependent electric field as a uniform shift of the energy levels, i.e., $\mathcal{E}_\alpha(t)=\mathcal{E}_\alpha^0+U_\alpha(t)\mathbf{1}_\alpha$, $\alpha=L,R$ and $\mathbf{1}_\alpha$ the unity matrix in region α.

Using Eq. (11), the time-dependent current of Eq. (15) can be rewritten as[5]

$$I_\alpha(t) = 2e \operatorname{Re} \operatorname{Tr}_C \int_0^\infty d\bar{t}\, [\mathbf{G}^R(t;\bar{t})\mathbf{\Sigma}_\alpha^<(\bar{t};t) + \mathbf{G}^<(t;\bar{t})\mathbf{\Sigma}_\alpha^A(\bar{t};t)],$$
(16)

where we have defined the so-called embedding self-energy

$$\mathbf{\Sigma}_\alpha(z;z') = \mathbf{V}_{C\alpha}(z)\mathbf{g}_{\alpha\alpha}(z;z')\mathbf{V}_{\alpha C}(z'),$$
(17)

and introduced the short-hand notation

$$\mathbf{G}(z;z') \equiv \mathbf{\mathcal{G}}_{CC}(z;z')$$
(18)

for the Green's function projected in region C. In obtaining Eq. (16), we have taken advantage of the fact that $\mathbf{V}(z)$ vanishes on the vertical track (isolated subsystems) and hence the last term in Eq. (11) does not contribute. For the same reason, the embedding self-energy vanishes if z and/or z' lie on the vertical track and the lesser Green's function $\mathbf{G}^<$ appearing in Eq. (16) can then be rewritten as [see Eq. (A1) of Ref. 6]

$$\mathbf{G}^<(t;t') = \int_0^\infty d\bar{t}\, d\bar{t}'\, \mathbf{G}^R(t;\bar{t})\mathbf{\Sigma}^<(\bar{t};\bar{t}')\mathbf{G}^A(\bar{t}';t')$$
$$+ \mathbf{G}^R(t;0)\mathbf{g}_{CC}^<(0;0)\mathbf{G}^A(0;t'),$$
(19)

with $\mathbf{\Sigma}=\sum_{\alpha=L,R}\mathbf{\Sigma}_\alpha$ the total self-energy. In most works on quantum transport, the second term in Eq. (19) is neglected [see, for instance, Eq. (31) of Ref. 41]. This is possible in the limit $t\rightarrow\infty$ and/or $t'\rightarrow\infty$ provided the local density of states (LDOS) D_C in C is a smooth function. However, D_C is not smooth if bound states are present. Bound states render the contacting approach ambiguous because the initial equilibrium of region C affects the behavior of the system also for $t\rightarrow\infty$. Moreover, as it has been recently pointed out,[11] the time-dependent current and one-particle density matrix do not reduce to their equilibrium values when the perturbing electric field is set to zero.

In the next section, we describe the partition-free approach. We will obtain a general expression for $I_\alpha(t)$ which depends explicitly on the initial equilibrium. This expression also allows us to switch easily between the contacting and the partition-free approaches.

B. Partition-free approach

The partition-free approach has been introduced by Cini[12] about a decade after the works of Combescot and co-workers. Here, the system is contacted and in equilibrium at a unique temperature and chemical potential before an external electric field is applied. The initial density matrix of the central region is then uniquely defined and transient phenomena have a direct physical interpretation. Substituting Eq. (12) into Eq. (15) and performing the multiplication between Green's functions, we obtain

$$I_\alpha(t) = 2e \operatorname{Re} \operatorname{Tr}_C[\mathbf{Q}_\alpha(t)], \quad \alpha=L,R,$$
(20)

with

$$\mathbf{Q}_\alpha(t) = \sum_{\gamma\gamma'=L,R} \mathbf{\mathcal{G}}_{C\gamma}^R(t;0)\mathbf{\mathcal{G}}_{\gamma\gamma'}^<(0;0)\mathbf{\mathcal{G}}_{\gamma'\alpha}^A(0;t)\mathbf{V}_{\alpha C}(t)$$
$$+ \sum_{\gamma=L,R} \mathbf{\mathcal{G}}_{C\gamma}^R(t;0)\mathbf{\mathcal{G}}_{\gamma C}^<(0;0)\mathbf{\mathcal{G}}_{C\alpha}^A(0;t)\mathbf{V}_{\alpha C}(t)$$
$$+ \sum_{\gamma'=L,R} \mathbf{\mathcal{G}}_{CC}^R(t;0)\mathbf{\mathcal{G}}_{C\gamma'}^<(0;0)\mathbf{\mathcal{G}}_{\gamma'\alpha}^A(0;t)\mathbf{V}_{\alpha C}(t)$$
$$+ \mathbf{\mathcal{G}}_{CC}^R(t;0)\mathbf{\mathcal{G}}_{CC}^<(0;0)\mathbf{\mathcal{G}}_{C\alpha}^A(0;t)\mathbf{V}_{\alpha C}(t).$$
(21)

Equations (20) and (21) are completely general. In the partition-free approach $\mathbf{\mathcal{G}}^<(0;0)=if(\mathbf{H}^0)=if(\mathcal{E}^0+\mathbf{V}^0)$, while in the contacting approach $\mathbf{\mathcal{G}}^<(0;0)=if(\mathbf{H}^0)=if(\mathcal{E}^0)$ with $\mathcal{E}_C^0$ arbitrary. In Appendix A, we prove that in the contacting approach Eqs. (20) and (21) are equivalent to the current formula in Eq. (16), as it should.

In Ref. 6, we have shown that by exposing the electrons to a constant (in time) electric field, the total current $I_\alpha(t)$ in Eqs. (20) and (21) tends to a steady value $I_\alpha^{(S)}$ given by (for, e.g., $\alpha=L$)

$$I_L^{(S)} = e \int \frac{d\omega}{2\pi}[f(\omega - U_L^\infty) - f(\omega - U_R^\infty)]T(\omega),$$
(22)

with $T(\omega)=\operatorname{Tr}_C[\mathbf{G}^R(\omega)\mathbf{\Gamma}_L(\omega)\mathbf{G}^A(\omega)\mathbf{\Gamma}_R(\omega)]$, $\mathbf{\Gamma}_\alpha(\omega)=-2\times\operatorname{Im}[\mathbf{\Sigma}_\alpha^R(\omega)]$, and $U_\alpha^\infty=\lim_{t\rightarrow\infty}U_\alpha(t)$. We have also shown that the steady value is independent of the history of the applied bias (memory-loss theorem) and of the initial equilibrium distribution of region C (theorem of equivalence). These results were obtained for a smooth LDOS D_C. The presence of bound states requires a generalization of the theory. In the next section, we include bound states in time-dependent quantum transport and investigate how they affect the behavior of $I_\alpha(t)$ for $t\rightarrow\infty$.

IV. INCLUDING BOUND STATES IN QUANTUM TRANSPORT

For simplicity, we consider the case of a sudden switching on of the bias $U_\alpha(t)=\theta(t)U_\alpha^\infty$ in region $\alpha=L,R$ (arbitrary time-dependent biases are considered in the next section).

We also specialize the discussion to a hopping Hamiltonian $V(z) = V^\infty$ that is constant on the forward and backward branch of the contour γ. However, we leave open the possibility of having a different constant value of $V(z) = V^0$ for z on the vertical track (this allows us to deal with different approaches at the same time).

In quantum-transport experiments, the central device is typically connected to macroscopic metallic electrodes. The one-particle eigenstates $|\phi_{k\alpha}\rangle$ of $\mathcal{E}_\alpha^\infty = \mathcal{E}_\alpha(t \to \infty) = \mathcal{E}_\alpha^0 + U_\alpha^\infty \mathbf{1}_\alpha$, $\alpha = L, R$, form a continuum with energy $\varepsilon_{k\alpha}^\infty = \varepsilon_{k\alpha}^0 + U_\alpha^\infty \in W_\alpha$. We define a bound state of the whole *biased* system $L+C+R$ as an eigenstate $|\psi_b\rangle$ of $H^\infty = H(t \to \infty) = \mathcal{E}^\infty + V^\infty$ with energy $\varepsilon_b \notin W_L \cup W_R$. [For one-particle eigenstates of the isolated regions $\mathcal{E}_\alpha$, $\alpha = L, R$, we use the Greek letter ϕ, while for one-particle eigenstates of the connected and biased system H^∞, we use the Greek letter ψ.] Below, we calculate the long-time limit of Q_α in the presence of bound states.

A. Asymptotic kernel Q_α

According to Eq. (21), the long-time limit of the kernel $Q_\alpha(t)$ is known once we know the long-time limit of $\mathcal{G}_{CC}^R(t;0)$, $\mathcal{G}_{C\alpha}^R(t;0)$, and $\mathcal{G}_{C\alpha}^A(0;t) V_{\alpha C}^\infty$, $\mathcal{G}_{\gamma'\alpha}^A(0;t) V_{\alpha C}^\infty$. For any $t > 0$, the retarded Green's function can be written as

$$\mathcal{G}^R(t;0) = -i \exp[-iH^\infty t] \equiv \int \frac{d\omega}{2\pi} \mathcal{G}^R(\omega) e^{-i\omega t} \quad (23)$$

and $\mathcal{G}^A(0;t) = [\mathcal{G}^R(t;0)]^\dagger$. Exploiting the smoothness of the self-energy, we can use the Riemann-Lebesgue theorem to derive the following asymptotic behaviors:

$$\lim_{t \to \infty} \mathcal{G}_{CC}^R(t;0) = -i \sum_b |\psi_{bC}\rangle\langle\psi_{bC}| e^{-i\varepsilon_b t}, \quad (24)$$

$$\lim_{t \to \infty} \mathcal{G}_{C\gamma}^R(t;0) = -i \sum_b |\psi_{bC}\rangle\langle\psi_{bC}| V_{C\gamma}^\infty \frac{e^{-i\varepsilon_b t}}{\varepsilon_b \mathbf{1}_\gamma - \mathcal{E}_\gamma^\infty}$$
$$- i \sum_k G^R(\varepsilon_{k\gamma}^\infty) V_{C\gamma}^\infty |\phi_{k\gamma}\rangle\langle\phi_{k\gamma}| e^{-i\varepsilon_{k\gamma}^\infty t} \quad (25)$$

and

$$\lim_{t \to \infty} \mathcal{G}_{C\alpha}^A(0;t) V_{\alpha C}^\infty = i \sum_b e^{i\varepsilon_b t} |\psi_{bC}\rangle\langle\psi_{bC}| \Sigma_\alpha^A(\varepsilon_b), \quad (26)$$

$$\lim_{t \to \infty} \mathcal{G}_{\gamma'\alpha}^A(0;t) V_{\alpha C}^\infty = i \delta_{\gamma'\alpha} \sum_k e^{i\varepsilon_{k\alpha}^\infty t} |\phi_{k\alpha}\rangle\langle\phi_{k\alpha}| V_{\alpha C}^\infty$$
$$+ i \sum_k e^{i\varepsilon_{k\gamma'}^\infty t} |\phi_{k\gamma'}\rangle$$
$$\times \langle\phi_{k\gamma'}| V_{\gamma'C}^\infty G^A(\varepsilon_{k\gamma'}^\infty) \Sigma_\alpha^A(\varepsilon_{k\gamma'}^\infty)$$
$$+ i \sum_b \frac{e^{i\varepsilon_b t}}{\varepsilon_b \mathbf{1}_{\gamma'} - \mathcal{E}_{\gamma'}^\infty} V_{\gamma'C}^\infty |\psi_{bC}\rangle\langle\psi_{bC}| \Sigma_\alpha^A(\varepsilon_b), \quad (27)$$

where $|\psi_{bC}\rangle$ is the projection of eigenstate $|\psi_b\rangle$ onto region C and $G^{R,A}(\omega) = \mathcal{G}_{CC}^{R,A}(\omega)$.

The above asymptotic results are given in terms of sum over bound states (discrete part) and sum over the continuum

of states of $\mathcal{E}_\alpha$, $\alpha = L, R$ (continuum part). Inserting them into Eq. (21) we obtain a continuum-continuum contribution, $Q_\alpha^{(S)}$, and a discrete-discrete contribution, $Q_\alpha^{(D)}$, as well as cross terms with discrete-continuum contributions. Taking advantage of the smoothness of $G^{R,A}(\omega)$ for $\omega \in W_L \cup W_R$ and exploiting the Riemann-Lebesgue theorem, it is possible to show that all cross terms vanish for $t \to \infty$.

Let us focus on the continuum-continuum part of Q_α [it is straightforward to realize that only the first term in Eq. (21) can contribute to this part]. Expanding $\mathcal{G}^<(0;0)$ in Matsubara modes,

$$\mathcal{G}^<(0;0) = \frac{1}{-i\beta} \sum_n e^{\eta\omega_n} \mathcal{G}^M(\omega_n), \quad \eta \to 0, \quad (28)$$

with $\mathcal{G}^M(\omega_n) = 1/(\omega_n \mathbf{1} - H^0)$ and $\omega_n = \mu + (2n+1)\pi/(-i\beta)$, we can rewrite $\mathcal{G}_{\gamma\gamma'}^<(0;0)$ as

$$\mathcal{G}_{\gamma\gamma'}^<(0;0) = if(\mathcal{E}_\gamma^0)\delta_{\gamma\gamma'}$$
$$+ \frac{1}{-i\beta} \sum_n e^{\eta\omega_n} g_{\gamma\gamma}^M(\omega_n) V_{\gamma C}^0 \mathcal{G}_{CC}^M(\omega_n) V_{C\gamma'}^0 g_{\gamma'\gamma'}^M(\omega_n), \quad (29)$$

with $g_{\gamma\gamma}^M(\omega_n) = 1/(\omega_n \mathbf{1}_\gamma - \mathcal{E}_\gamma^0)$. We observe that in the contacting approach, $V^0 = 0$ (regions L, C, R isolated for negative times) and hence the second term in Eq. (29) vanishes. In this case, the continuum-continuum part is

$$Q_\alpha^{(S)} = i \int \frac{d\omega}{2\pi} f(\omega - U_\alpha^\infty) G^R(\omega) \Gamma_\alpha(\omega) + i \int \frac{d\omega}{2\pi} \sum_\gamma f(\omega - U_\gamma^\infty)$$
$$\times G^R(\omega) \Gamma_\gamma(\omega) G^A(\omega) \Sigma_\alpha^A(\omega), \quad (30)$$

which does *not* depend on time. In Appendix B, we prove that $Q_\alpha^{(S)}$ does not depend on V^0 provided the hopping matrix elements between states in region C and states $|\phi_{k\alpha}\rangle$, $\alpha = L, R$, are smooth functions of k. Thus, the memory of different initial conditions is washed out by the continuum of states and the final result is a steady contribution. Below, we show that this is not the case for the discrete-discrete part $Q_\alpha^{(D)}$.

All four terms in Eq. (21) contribute to $Q_\alpha^{(D)}$. After some algebra one finds the following dynamical kernel:

$$Q_\alpha^{(D)}(t) = i \sum_{b,b'} f_{b,b'} |\psi_{bC}\rangle\langle\psi_{b'C}| \Sigma_\alpha^A(\varepsilon_{b'}) e^{-i(\varepsilon_b - \varepsilon_{b'})t}, \quad (31)$$

with

$$f_{b,b'} = \langle\psi_b|f(H^0)|\psi_{b'}\rangle. \quad (32)$$

The coefficient $f_{b,b'}$ is *the matrix element of the equilibrium Fermi function $f(H^0)$ between bound states b, b' of $H(t \to \infty) = H^\infty$.* Equations (31) and (32) have been obtained using the bound-state contributions of the asymptotic behavior in Eqs. (24)–(27) and the relation

$$|\psi_{b\gamma}\rangle = \frac{1}{\varepsilon_b \mathbf{1}_\gamma - \boldsymbol{\mathcal{E}}_\gamma^\infty} V_{\gamma C}^\infty |\psi_{bC}\rangle, \tag{33}$$

with $|\psi_{b\gamma}\rangle$ the projection onto region $\gamma = L, R$ of the full bound state $|\psi_b\rangle$.

In conclusion, we have

$$\lim_{t\to\infty} \boldsymbol{Q}_\alpha(t) = \boldsymbol{Q}_\alpha^{(S)} + \boldsymbol{Q}_\alpha^{(D)}(t). \tag{34}$$

Equation (34) is completely general and is valid provided the Hamiltonian of region $\alpha = L, R$ is uniformly shifted by a constant potential ($\boldsymbol{\mathcal{E}}_\alpha^\infty = \boldsymbol{\mathcal{E}}_\alpha^0 + U_\alpha^\infty \mathbf{1}_\alpha$), and the contacting Hamiltonian $V(t) = V^\infty$ and the Hamiltonian for the central region $\boldsymbol{\mathcal{E}}_C(t) = \boldsymbol{\mathcal{E}}_C^\infty$ are constant in time. We observe that in deriving Eq. (34), no statements about V^0 and $\boldsymbol{\mathcal{E}}_C^0$ have been made; in principle, they might be different from their asymptotic values V^∞ and $\boldsymbol{\mathcal{E}}_C^\infty$.

B. Asymptotic current and one-particle density matrix

The total current in the long-time limit is obtained by substituting Eq. (34) into Eq. (20),

$$\lim_{t\to\infty} I_\alpha(t) = I_\alpha^{(S)} + I_\alpha^{(D)}(t), \tag{35}$$

where $I_\alpha^{(S)}$ is the steady part coming from $\boldsymbol{Q}_\alpha^{(S)}$ and is given in Eq. (22). Taking into account that the imaginary part of $\Sigma_\alpha^A(\omega)$ vanishes for $\omega = \varepsilon_b$, the dynamical part $I_\alpha^{(D)}(t)$ can be written as

$$I_\alpha^{(D)}(t) = 2e \sum_{b,b'} f_{b,b'} \Lambda_{b,b'}^{(\alpha)} \sin[(\varepsilon_b - \varepsilon_{b'})t], \tag{36}$$

with

$$\Lambda_{b,b'}^{(\alpha)} = \mathrm{Tr}_C[|\psi_{bC}\rangle\langle\psi_{b'C}|\Sigma_\alpha^A(\varepsilon_{b'})]. \tag{37}$$

Proceeding along similar lines, one can also prove that the one-particle density matrix $\boldsymbol{\rho}_C(t) = -i\boldsymbol{G}^<(t;t)$ in region C is the sum of steady and dynamical contributions,

$$\lim_{t\to\infty} \boldsymbol{\rho}_C(t) = \boldsymbol{\rho}_C^{(S)} + \boldsymbol{\rho}_C^{(D)}(t), \tag{38}$$

with

$$\boldsymbol{\rho}_C^{(S)} = \int \frac{d\omega}{2\pi} \sum_\gamma f(\omega - U_\gamma^\infty) \boldsymbol{G}^R(\omega) \boldsymbol{\Gamma}_\gamma(\omega) \boldsymbol{G}^A(\omega) \tag{39}$$

and

$$\boldsymbol{\rho}_C^{(D)}(t) = \sum_{b,b'} f_{b,b'} |\psi_{bC}\rangle\langle\psi_{b'C}| e^{-i(\varepsilon_b - \varepsilon_{b'})t}. \tag{40}$$

Equations (32), (36), and (40) and the following discussion (including Sec. V) are the main results of this work.

In the contacting approach ($V^0 = 0$), $\boldsymbol{H}^0 = \boldsymbol{\mathcal{E}}^0$ is a block-diagonal matrix and so is $f(\boldsymbol{\mathcal{E}}^0)$. The coefficients $f_{b,b'}$ can then be rewritten as the sum of three terms,

$$f_{b,b'} = \langle\psi_{bC}|f(\boldsymbol{\mathcal{E}}_C^0)|\psi_{b'C}\rangle + \sum_{\gamma=L,R} \langle\psi_{b\gamma}|f(\boldsymbol{\mathcal{E}}_\gamma^0)|\psi_{b'\gamma}\rangle. \tag{41}$$

The first term in $f_{b,b'}$ depends on the initial equilibrium of the isolated central region and cannot be univocally fixed

(see discussion in Sec III A). To make contact with Ref. 11, we insert a complete set of eigenstates $|\phi_{k\gamma}\rangle$ for region $\gamma = L, R$ in the second term of Eq. (41). We find

$$\langle\psi_{b\gamma}|f(\boldsymbol{\mathcal{E}}_\gamma^0)|\psi_{b'\gamma}\rangle = \sum_k f(\varepsilon_{k\gamma}^0) \frac{\langle\psi_{bC}|V_{C\gamma}^\infty|\phi_{k\gamma}\rangle\langle\phi_{k\gamma}|V_{\gamma C}^\infty|\psi_{b'C}\rangle}{(\varepsilon_b - \varepsilon_{k\gamma}^\infty)(\varepsilon_{b'} - \varepsilon_{k\gamma}^\infty)}$$

$$= \int \frac{d\omega}{2\pi} f(\omega - U_\gamma^\infty) \frac{\langle\psi_{bC}|\boldsymbol{\Gamma}_\gamma(\omega)|\psi_{b'C}\rangle}{(\varepsilon_b - \omega)(\varepsilon_{b'} - \omega)}, \tag{42}$$

which agrees with the result of Dhar and Sen [see Eq. (55) of Ref. 11]. We also observe that $f_{b,b'}$ of Eq. (41) gives rise to oscillatory terms in the total current and one-particle density matrix which do not vanish for $U_\gamma^\infty = 0$, $\gamma = L, R$. Thus, in the *unbiased* system $I_\alpha(t)$ and $\boldsymbol{\rho}_C(t)$ oscillate forever. To solve this problem, Dhar and Sen have proposed a somewhat *ad hoc* procedure which consists in introducing two extra reservoirs with a wide band. The bandwidth should be large enough to allow for the hybridization of the originally localized bound states. Eventually, the coupling to the extra reservoirs is removed and the standard equilibrium result is recovered. However, out of equilibrium this procedure suffers from a serious problem: The nonequilibrium quantities depend on how these extra couplings approach zero.

The partition-free approach is free from all the limitations described above. The initial equilibrium is unambiguous and $\boldsymbol{\mathcal{E}}_C^0$ is simply given by the projection of the physical Hamiltonian onto region C. For the unbiased system, the equilibrium Hamiltonian $\boldsymbol{H}^0$ and the long-time limit Hamiltonian $\boldsymbol{H}^\infty$ are the same. In this case, Eq. (32) implies

$$f_{b,b'} = \delta_{b,b'} f(\varepsilon_b), \tag{43}$$

and the dynamical contribution to the total current vanishes while the dynamical contribution to the one-particle density matrix reduces to the equilibrium contribution of bound states,

$$\boldsymbol{\rho}_C^{(D)} = \sum_b f(\varepsilon_b) |\psi_{bC}\rangle\langle\psi_{bC}|, \tag{44}$$

as it should. Out of equilibrium, both $I_\alpha(t\to\infty)$ and $\boldsymbol{\rho}_C(t\to\infty)$ oscillate around some steady value provided $\boldsymbol{H}^\infty$ has more than one bound-state solution. The amplitudes of the oscillations are calculable expressions and are completely fixed by the original temperature and chemical potential. Nonequilibrium results are well defined.

In Appendix C, we also prove that Eqs. (36) and (40) conserve the total number of particles,

$$\frac{d}{dt} N_C(t) = \frac{1}{e}[I_L(t) + I_R(t)], \tag{45}$$

where

$$N_C(t) = \mathrm{Tr}_C[\boldsymbol{\rho}_C(t)] \tag{46}$$

is the number of particles in region C.

V. IMPLICATIONS FOR TDDFT

One of the main advantage of the partition-free approach over the contacting approach is that the former can be com-

bined with TDDFT.[6–8] In this theory, the time-dependent density of an *interacting* system can be calculated from a fictitious system of *noninteracting* electrons moving under the influence of the Kohn-Sham (KS) potential U. The KS potential is the sum of the external applied potential v_{ext}, the Hartree potential v_H, and the exchange-correlation potential v_{xc}. According to the discussion of Sec. III A, the metallic screening keeps the bulk electrodes in local equilibrium and we can approximate $U=(v_{ext}+v_H+v_{xc})$ with a spatially constant time-dependent shift deep inside region L/R. The one-particle Hamiltonian of TDDFT is then given by Eq. (2) with $\mathcal{E}_\alpha(t)=\mathcal{E}_\alpha^0+U_\alpha(t)\mathbf{1}_\alpha$, $\alpha=L,R$, and $V(t)=V^0$.

Let us expose the electrons to a constant (in time) electric field and let us assume that the system reaches a steady state in the long-time limit. Then, the effective potential of the bulk electrodes and the Hamiltonian of the central region $\mathcal{E}_C$ are stationary in the distant future. We have shown that the steady-state assumption is consistent with the TDDFT equation for the total current provided the density of states in region C is a smooth function.[7] All history and initial-state effects are contained in $v_{xc}(\mathbf{r},t\to\infty)$, meaning that two different time-dependent densities $n(\mathbf{r},t)$ and $n'(\mathbf{r},t)$ may give the same total current. In the adiabatic local-density approximation (ALDA), there is no memory and the exchange-correlation potential depends on the instantaneous density. Hence, $v_{xc}^{ALDA}(\mathbf{r},t\to\infty)$ is completely known once we know $n(\mathbf{r},t\to\infty)$. The latter can be calculated self-consistently from Eq. (39). The ALDA provides a practical scheme to compute the current. However, such a scheme, originally proposed by Lang,[43] is obviously limited to the ALDA. Moreover, owing to the nonlinearity of the problem, there might be multiple steady-state solutions, and the absence of a minimum principle in out-of-equilibrium systems makes impossible to say toward which steady state the electrons actually evolve.

Below, we show that the steady-state assumption is not consistent in the presence of bound states. This result opens up the possibility of having self-consistent oscillatory solutions even for constant biases and may change substantially the standard steady-state picture. Indeed, oscillations of the effective potential in region C give rise to new conductive channels, very much in the spirit of what happens in quantum pumps.

The proof of the above statement proceeds by *reductio ad absurdum*. Let H^∞ be the steady-state Hamiltonian of the fictitious noninteracting system. In Appendix D, we prove that the total current $I_\alpha(t\to\infty)$ and one-particle density matrix $\boldsymbol{\rho}_C(t\to\infty)$ oscillate like in Eqs. (35) and (38) but with new coefficients $f_{b,b'}$. An oscillating density and/or current is not consistent with the steady-state assumption; the effective potential of TDDFT is a functional of the density and hence $H(t)$ cannot be constant in time. We conclude that *a steady current is not compatible with the existence of bound states in the steady Hamiltonian* H^∞.

The new coefficients

$$f_{b,b'} = \langle \psi'_b | f(H^0) | \psi'_{b'} \rangle \tag{47}$$

depend on the history of the bias. Indeed, the state $|\psi'_b\rangle$ is related to the bound state $|\psi_b\rangle$ of H^∞ by a unitary transformation,

$$\begin{bmatrix} |\psi'_{bL}\rangle \\ |\psi'_{bC}\rangle \\ |\psi'_{bR}\rangle \end{bmatrix} = \begin{bmatrix} e^{i\Delta_L^\infty}\mathbf{1}_L & 0 & 0 \\ 0 & M_C & 0 \\ 0 & 0 & e^{i\Delta_R^\infty}\mathbf{1}_R \end{bmatrix} \begin{bmatrix} |\psi_{bL}\rangle \\ |\psi_{bC}\rangle \\ |\psi_{bR}\rangle \end{bmatrix}, \tag{48}$$

with

$$\Delta_\alpha^\infty = \lim_{t\to\infty} \int_0^t d\bar{t}[U_\alpha(\bar{t}) - U_\alpha^\infty], \quad \alpha=L,R, \tag{49}$$

and M_C some unitary "memory matrix" for region C. For constant KS potentials $\Delta_\alpha^\infty=0$ and $M_C=\mathbf{1}_C$ and the coefficients $f_{b,b'}$ reduce to those in Eq. (32).

The above results can be extended to systems of interacting electrons and bosons, such as, e.g., phonons. We consider the system electrons+phonons initially in equilibrium and assume that the electron density is v representable. Then, there must exist a local potential that reproduces the interacting electron density in a noninteracting system of only electrons. Such a potential defines uniquely H^0. Next, we drive the system electrons+phonons out of equilibrium by switching on a longitudinal electric field and we ask the question if the interacting time-dependent electron density can be reproduced in the noninteracting system of only electrons moving under the influence of a time-dependent local potential U. According to the van Leeuwen theorem,[16] the answer is affirmative provided the electron-phonon interaction preserves the continuity equation, which is a very weak condition. Moreover, the local potential U is unique. Again, we can conclude that if the Hamiltonian of the fictitious system globally converges to an asymptotic Hamiltonian H^∞ for $t\to\infty$, the system cannot have more than one bound state.

We also observe that for truly noninteracting electrons, the effective potential is equal to the external potential and does not depend on the density. In this case, the solution of Appendix D is an *exact solution* and Eqs. (36) and (40), with $f_{b,b'}$ given by Eq. (47), can be tested against history-dependent effects in total currents and densities. All history (of the applied bias) and initial-state dependence are contained in the coefficients $f_{b,b'}$.

Finally, we wish to discuss a rather interesting example. Let us imagine to switch on and then off the bias in a system of (i) truly noninteracting electrons and (ii) KS electrons. In system (i), there is no self-consistent evolution since the Hamiltonian is independent of the density. The asymptotic Hamiltonian H^∞ is (trivially) equal to the initial Hamiltonian H^0 and hence the bound states are also eigenstates of H^0. Suppose that the bound-state energies lie in the continuum when the bias is on. Then, switching the bias off would result in a depopulation of the bound states and the asymptotic density matrix $\boldsymbol{\rho}_C(t\to\infty)$ would, in general, differ from its equilibrium value. This expected result is confirmed by the exact solution. The system "remembers" that a bias has been switched on through the memory matrix M_C and the phases Δ_α^∞, $\alpha=L,R$, appearing in Eq. (48). Equation (48) defines new states $\psi'_b \neq \psi_b$ and according to Eq. (47) the coefficients $f_{b,b'}$ are no longer given by $\delta_{b,b'}f(\varepsilon_b)$, as it would be in equilibrium. The situation is totally different in system (ii). The time evolution of interacting electrons in initial nonequi-

librium states has been recently investigated within time-dependent current density functional theory[44,45] (TDCDFT). It has been shown that the inclusion of memory effects[46] in the exchange-correlation vector potential leads to a dissipative KS dynamics,[47–49] and D'Agosta and Vignale have been able to prove[48] that the electron density evolves (unless forbidden by symmetry) toward the ground-state density. Taking into account that the density of the TDDFT KS system, is the same as the density of the TDCDFT KS system we conclude that $H^\infty = H^0$ and, more important, that the memory matrix $M_C = \mathbf{1}_C$ and the phases $\Delta_{\alpha=L,R} = 0 \pmod{2\pi}$, independent of the history of the switching onoff process. Indeed, for these values of M_C and $\Delta_{\alpha=L,R}$, the density matrix is constant in time (and equal to the ground-state density matrix), and hence compatible with the (stationary) ground-state KS Hamiltonian.

VI. CONCLUSIONS

We have generalized the theory developed in Ref. [6] to include bound states in quantum transport. In the partition-free approach, the electrode-device-electrode system is contacted and in equilibrium at a unique temperature and chemical potential (thermodynamic consistency). The electrons are exposed to a time-dependent electric field for positive times. The external potential is local in space and total currents and density can be calculated from a fictitious system of noninteracting electrons, according to the Runge-Gross theorem.

We have shown that for truly noninteracting electrons, the biased system does not evolve toward a steady regime. The total current and density oscillate due to the presence of bound states. The amplitude of the oscillations depends on the initial temperature and chemical potential and on the history of the applied bias. Bound-state oscillations might provide a probe to unveil the past of the system.

In contrast to the contacting approach, in the partition-free approach the initial equilibrium distribution of region C is well defined and all quantities reduce to their equilibrium value by setting the external potential to zero. There is no need of "extra reservoirs" to equilibrate spurious bound-state oscillations.

Our findings might have interesting implications for the fictitious system of TDDFT. In Ref. [7], we have shown that the time-dependent current tends to a steady value provided the Hamiltonian globally converges to a steady Hamiltonian and the density of states in region C is smooth. This result is no longer valid in the presence of bound states. In Sec. V, we have shown that bound electrons in steady-state regimes lead to a contradiction: current and density would oscillate and, as a consequence, the effective potential of TDDFT would oscillate too. Steady quantities are not compatible with the existence of bound states.

According to the above discussion, the effective potential of TDDFT might oscillate upon application of a constant bias. We expect that these oscillations have exponentially small amplitude deep inside the electrodes and are detectable only close to the molecular device. Indeed, for truly noninteracting electrons the amplitude of the density oscillations is proportional to the bound-state wave functions. Therefore,

the KS potential is time dependent in the device region and tends exponentially to a constant (in time) deep inside the electrodes. In this case, one can use a recently proposed practical scheme[8] to investigate bound-state dynamical effects within TDDFT. The scheme is based on the real-time propagation of the occupied KS orbitals and we are currently working at the implementation of the algorithm (which has been tested in one-dimensional model systems with excellent results[8,9]). As for the case of gate voltages in electron pumping, oscillations of the effective potential open new conductive channels. Such an effect is completely left out in static DFT calculations and its possible relevance in molecular transport has yet to be discovered.

APPENDIX A: EQUIVALENCE BETWEEN CURRENT FORMULAS IN THE CONTACTING APPROACH

In the contacting approach, regions L, C, R are isolated for negative times and hence $\mathcal{G}_{\gamma C}^{<}(0;0) = \mathcal{G}_{C\gamma'}^{<}(0;0) = 0$, $\mathcal{G}_{\gamma\gamma'}^{<}(0;0) = \delta_{\gamma\gamma'} g_{\gamma\gamma}^{<}(0;0)$, and $\mathcal{G}_{CC}^{<}(0;0) = g_{CC}^{<}(0;0)$. The kernel $Q_\alpha(t)$ simplifies to

$$Q_\alpha(t) = \sum_\gamma \mathcal{G}_{C\gamma}^{R}(t;0) g_{\gamma\gamma}^{<}(0;0) \mathcal{G}_{\gamma\alpha}^{A}(0;t) V_{\alpha C}(t)$$

$$+ \mathcal{G}_{CC}^{R}(t;0) g_{CC}^{<}(0;0) \mathcal{G}_{C\alpha}^{A}(0;t) V_{\alpha C}(t). \quad \text{(A1)}$$

Extracting the retarded and advanced component of the Keldysh-Green function from the Dyson equation (10), we can express $\mathcal{G}_{C\gamma}^{R}$ in terms of $\mathcal{G}_{CC}^{R} = G^R$, and $\mathcal{G}_{\gamma\alpha}^{A}$, $\mathcal{G}_{C\alpha}^{A}$ in terms of $\mathcal{G}_{CC}^{A} = G^A$. Equation (A1) can then be rewritten as

$$Q_\alpha(t) = \int G^R(t;\bar{t}) \Sigma^{<}(\bar{t};\bar{t}') G^A(\bar{t}';\bar{t}'') \Sigma_\alpha^{A}(\bar{t}'';t)$$

$$+ G^R(t;0) g_{CC}^{<}(0;0) \int G^A(0;\bar{t}) \Sigma_\alpha^{A}(\bar{t};t)$$

$$+ \int G^R(t;\bar{t}) \Sigma_\alpha^{<}(\bar{t};t), \quad \text{(A2)}$$

where the integrals (between 0 and ∞) are over barred time variables. Taking into account Eq. (19), it is straightforward to realize that Eq. (16) is actually equivalent to Eqs. (20) and (21).

APPENDIX B: INDEPENDENCE OF V^0 IN $Q_\alpha^{(S)}$

The continuum-continuum contribution to $Q_\alpha(t)$ can be written as $Q_\alpha^{(S)} + \delta Q_\alpha$. The steady value $Q_\alpha^{(S)}$ originates from the first term on the right-hand side of Eq. (29) and is inde-

pendent of V^0. The extra term δQ_α accounts for the possible effects of a nonvanishing coupling V^0 in the remote past. Here, we prove that δQ_α vanishes in the long-time limit. From Eq. (29), we find

$$\delta Q_\alpha = \frac{1}{-i\beta} \sum_n e^{\eta \omega_n} \delta Q_\alpha(\omega_n), \tag{B1}$$

with

$$\delta Q_\alpha(\omega_n) = \sum_\gamma \int \frac{d\omega}{2\pi} \frac{G^R(\omega) S_\gamma(\omega)}{\omega_n - \omega + U_\gamma^\infty} e^{-i\omega t} G^M(\omega_n) \sum_{\gamma'}$$

$$\times \int \frac{d\omega'}{2\pi} S_{\gamma'}^\dagger(\omega') \frac{\delta_{\alpha\gamma'} + G^A(\omega') \Sigma_\alpha^A(\omega')}{\omega_n - \omega' + U_\alpha^\infty} e^{-i\omega' t}. \tag{B2}$$

The matrix $S_\gamma(\omega)$ is defined according to

$$S_\gamma(\omega) = \sum_k 2\pi \delta(\omega - \varepsilon_{k\gamma}^\infty) V_{C\gamma}^\infty |\phi_{k\gamma}\rangle\langle\phi_{k\gamma}| V_{\gamma C}^0 \tag{B3}$$

and is a smooth function of ω provided the matrix elements of V^0 between states in region C and states $|\phi_{k\gamma}\rangle$, $\gamma = L, R$ are smooth functions of k. Also, $S_\gamma(\omega) = 0$ for $\omega \notin W_L \cup W_R$ and hence the products $S_\gamma G^R$ and $S_{\gamma'}^\dagger G^A$ are smooth functions. At finite temperature, the Matsubara frequencies have a finite imaginary part and the denominators in Eq. (B2) are well behaved. Exploiting the Riemann-Lebesgue theorem, we conclude that both integrals in Eq. (B2) vanish for $t \to \infty$, meaning that $\delta Q_\alpha = 0$.

APPENDIX C: CONSERVATION OF THE PARTICLE NUMBER

The time derivative of the number of particles in region C can be easily calculated from Eq. (40),

$$\frac{d}{dt} N_C(t) = -\sum_{b,b'} (\varepsilon_b - \varepsilon_{b'}) f_{b,b'} S_{b,b'} \sin[(\varepsilon_b - \varepsilon_{b'})t], \tag{C1}$$

with $S_{b,b'}$ the overlap between bound states b, b' in C,

$$S_{b,b'} = \mathrm{Tr}_C[|\psi_{bC}\rangle\langle\psi_{b'C}|]. \tag{C2}$$

Let us now consider the expression for the total current. The sum $I_L^{(S)} + I_R^{(S)}$ of steady contributions vanishes. Taking into account that $f_{b,b'}$ is symmetric under the exchange of b and b', and that the real part of the advanced self-energy is a Hermitian matrix, we can safely replace $\Lambda_{b,b'}^{(\alpha)}$ with

$$\Lambda_{b,b'}^{(\alpha)} = \frac{1}{2} \mathrm{Tr}_C\left[|\psi_{bC}\rangle\langle\psi_{b'C}| \left(\Sigma_\alpha^A(\varepsilon_{b'}) - \Sigma_\alpha^A(\varepsilon_b)\right)\right] \tag{C3}$$

in the expression for the dynamical contribution to $I_\alpha(t)$. The difference between self-energies at different bound-state energies is

$$\Sigma_\alpha^A(\varepsilon_{b'}) - \Sigma_\alpha^A(\varepsilon_b) = V_{C\alpha}^\infty \frac{(\varepsilon_b - \varepsilon_{b'})}{[\varepsilon_{b'} \mathbf{1}_\alpha - \boldsymbol{\mathcal{E}}_\alpha^\infty][\varepsilon_b \mathbf{1}_\alpha - \boldsymbol{\mathcal{E}}_\alpha^\infty]} V_{\alpha C}^\infty, \tag{C4}$$

and hence Eq. (C3) becomes

$$\Lambda_{b,b'}^{(\alpha)} = \frac{(\varepsilon_b - \varepsilon_{b'})}{2} \mathrm{Tr}_\alpha[|\psi_{b\alpha}\rangle\langle\psi_{b'\alpha}|], \tag{C5}$$

where we have used Eq. (33). Exploiting the orthonormality relation

$$\sum_{\alpha=L,C,R} \mathrm{Tr}_\alpha[|\psi_{b\alpha}\rangle\langle\psi_{b'\alpha}|] = \delta_{b,b'}, \tag{C6}$$

we find

$$\sum_{\alpha=L,R} \Lambda_{b,b'}^{(\alpha)} = -\frac{(\varepsilon_b - \varepsilon_{b'})}{2} S_{b,b'}. \tag{C7}$$

It is now straightforward to realize that the sum $I_L^{(D)} + I_R^{(D)}$ of dynamical contributions is equal to the change per unit time of the number of particle in region C [which is given in Eq. (C1)].

APPENDIX D: LONG-TIME LIMIT OF TDDFT

We have already shown in Sec. IV that for a sudden switching on, $H(t>0) = H^\infty$, $\forall t > 0$, the total current and one-particle density matrix oscillate in the long-time limit. Let us denote with a bar ($\bar{g}$, $\bar{\mathcal{G}}$, and $\bar{\Sigma}$) Green's functions and self-energies corresponding to this case. The asymptotic expressions of $\bar{\mathcal{G}}_{CC}^R(t;0)$, $\bar{\mathcal{G}}_{C\gamma}^R(t;0)$ and $\bar{\mathcal{G}}_{C\alpha}^A(0;t) V_{\alpha C}^0$, $\bar{\mathcal{G}}_{\gamma'\alpha}^A(0;t) V_{\alpha C}^0$ are given in Eqs. (24)–(27). Below, we will find a relation between the asymptotic behavior of $\mathcal{G}$ and $\bar{\mathcal{G}}$, with $\mathcal{G}$ the Green's function of the TDDFT Hamiltonian.

For arbitrary time-dependent potentials in region $\alpha = L, R$, the retarded self-energy can be expressed in terms of $\bar{\Sigma}^R$ as

$$\Sigma_\alpha^R(t;t') = e^{-i\Delta_\alpha(t)} \bar{\Sigma}_\alpha^R(t;t') e^{i\Delta_\alpha(t')}, \tag{D1}$$

with

$$\Delta_\alpha(t) = \int_0^t d\bar{t}[U_\alpha(t) - U_\alpha^\infty]. \tag{D2}$$

The quantity $\Delta_\alpha(t)$ depends on the history of the applied bias. We assume $U_\alpha(t)$ to approach U_α^∞ rapidly enough that $\Delta_\alpha(t)$ converges to some value Δ_α^∞ for $t \to \infty$. Then,

$$\lim_{t,t' \to \infty} \Sigma_\alpha^R(t;t') = \bar{\Sigma}_\alpha^R(t;t'). \tag{D3}$$

The above identity allows us to fix the asymptotic behavior of the Green's function in region C. From the equation of motion, we have

$$\left\{ i\frac{d}{dt}\mathbf{1}_C - \boldsymbol{\mathcal{E}}_C(t) \right\} \boldsymbol{\mathcal{G}}_{CC}^R(t;0) - \int d\bar{t}\boldsymbol{\Sigma}_\alpha^R(t;\bar{t})\boldsymbol{\mathcal{G}}_{CC}^R(\bar{t};0) = \delta(t).$$

(D4)

For large t, we can replace $\boldsymbol{\mathcal{E}}_C(t)$ with its asymptotic value $\boldsymbol{\mathcal{E}}_C^\infty$. Moreover, taking into account that the self-energy vanishes when the separation between its time arguments goes to infinity, we can replace $\boldsymbol{\Sigma}_\alpha^R(t;\bar{t})$ with $\overline{\boldsymbol{\Sigma}}_\alpha^R(t;\bar{t})$, in accordance with Eq. (D3). Then, Eq. (D4) reduces to the equation obeyed by $\overline{\boldsymbol{\mathcal{G}}}_{CC}^R(t\rightarrow\infty;0)$, meaning that

$$\lim_{t\rightarrow\infty} \boldsymbol{\mathcal{G}}_{CC}^R(t;0) = \lim_{t\rightarrow\infty} \overline{\boldsymbol{\mathcal{G}}}_{CC}^R(t;0)\boldsymbol{M}_C^\dagger,$$

(D5)

where $\boldsymbol{M}_C^\dagger$ is some unitary matrix that accounts for the history of the applied bias (memory effects). From Eq. (D5) and the equation of motion for $\boldsymbol{\mathcal{G}}_{C\alpha}^A(0;t)$, one can also prove that

$$\lim_{t\rightarrow\infty} \boldsymbol{\mathcal{G}}_{C\alpha}^A(0;t)\boldsymbol{V}_{\alpha C}^0 = \lim_{t\rightarrow\infty} \boldsymbol{M}_C \overline{\boldsymbol{\mathcal{G}}}_{C\alpha}^A(0;t)\boldsymbol{V}_{\alpha C}^0.$$

(D6)

Also the asymptotic behavior of $\boldsymbol{\mathcal{G}}_{C\gamma}^R$ can be calculated from the equation of motion. We have

$$\left\{ i\frac{d}{dt}\mathbf{1}_C - \boldsymbol{\mathcal{E}}_C(t) \right\} \boldsymbol{\mathcal{G}}_{C\gamma}^R(t;0) - \boldsymbol{V}_{C\gamma}^0 \boldsymbol{g}_{\gamma\gamma}^R(t;0)$$

$$- \int d\bar{t}\boldsymbol{\Sigma}_\alpha^R(t;\bar{t})\boldsymbol{\mathcal{G}}_{C\gamma}^R(\bar{t};0) = 0.$$

(D7)

Taking the limit $t\rightarrow\infty$ and exploiting the relation $\boldsymbol{g}_{\gamma\gamma}^R(t\rightarrow\infty;0) = e^{-i\Delta_\gamma^\infty}\overline{\boldsymbol{g}}_{\gamma\gamma}^R(t\rightarrow\infty;0)$, we obtain

$$\lim_{t\rightarrow\infty} \boldsymbol{\mathcal{G}}_{C\gamma}^R(t;0) = e^{-i\Delta_\gamma^\infty} \lim_{t\rightarrow\infty} \overline{\boldsymbol{\mathcal{G}}}_{C\gamma}^R(t;0).$$

(D8)

In a similar way, one can prove that

$$\lim_{t\rightarrow\infty} \boldsymbol{\mathcal{G}}_{\gamma'\alpha}^A(0;t)\boldsymbol{V}_{\alpha C}^0 = e^{i\Delta_{\gamma'}^\infty} \lim_{t\rightarrow\infty} \overline{\boldsymbol{\mathcal{G}}}_{\gamma'\alpha}^A(0;t)\boldsymbol{V}_{\alpha C}^0.$$

(D9)

Substituting these results [Eqs. (D5) and (D6) and Eqs. (D8) and (D9)] in Eqs. (20) and (21), one can calculate the asymptotic behavior of the time-dependent total current. Proceeding along the same line which leads to Eq. (35), one can show that $I_\alpha(t)$ is again given by the sum of the steady-state value $I_\alpha^{(S)}$ of Eq. (22) and the dynamical contribution $I_\alpha^{(D)}(t)$ of Eq. (36). However, the coefficients $f_{b,b'}$ are in general different from those in Eq. (32). After some algebra, one readily finds that the new coefficients $f_{b,b'}$ can be expressed as in Eqs. (47) and (48).

The time-dependent one-particle density matrix also has the same analytic form of Eqs. (38)–(40) but with the same new coefficients $f_{b,b'}$ of Eqs. (47) and (48).

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