Quantum master equation scheme of time-dependent density functional theory to time-dependent transport in nanoelectronic devices

Xin-Qi Li*

*State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences,
P. O. Box 912, Beijing 100083, China*

YiJing Yan†

*Department of Chemistry, Hong Kong University of Science and Technology, Kowloon, Hong Kong
(Received 27 August 2006; published 21 February 2007)*

In this work a practical scheme is developed for the first-principles study of time-dependent quantum transport. The basic idea is to combine the transport master equation with the well-known time-dependent density functional theory. The key ingredients of this paper include (i) the partitioning-free initial condition and the consideration of the time-dependent bias voltages which base our treatment on the Runge-Gross existence theorem; (ii) the non-Markovian master equation for the reduced (many-body) central system (i.e., the device); and (iii) the construction of Kohn-Sham master equations for the reduced single-particle density matrix, where a number of auxiliary functions are introduced and their equations of motion (EOMs) are established based on the technique of spectral decomposition. As a result, starting with a well-defined initial state, the time-dependent transport current can be calculated simultaneously along with the propagation of the Kohn-Sham master equation and the EOMs of the auxiliary functions.

DOI: [10.1103/PhysRevB.75.075114](https://doi.org/10.1103/PhysRevB.75.075114)

PACS number(s): 72.10.Bg

I. INTRODUCTION

Quantum transport through nanostructures (e.g., semiconductor quantum dots or organic molecules) would play an essential role in nanoelectronic devices. A rigorous treatment should handle the effect of the electronic structure of the central device as well as the effect of the interface to the external contact. This calls for combining the theory of quantum transport with the first-principles calculation of electronic structures. In recent years, considerable efforts have been focused on density functional theory (DFT) based simulations of such transport devices.¹⁻³ In particular, two types of formalism were involved: one is the Lippmann-Schwinger formalism by Lang and co-workers,⁴ the other is the first-principles nonequilibrium Green's function (NGF) technique.⁵⁻⁹ However, all of these studies were restricted to the steady-state transport under time-independent bias voltages.

On the other hand, time-dependent transport phenomena are of interest in various contexts, such as single-electron pumps and turnstiles, switching-on transient behaviors, and ac response in the applications of high-frequency amplifiers or detectors. Moreover, it would be desirable to be able to model nanoelectronic circuit elements with resistors, capacitors, and inductors. To ascribe appropriate quantum capacitances and inductances for nanocircuits, the study of time-dependent quantum transport is needed. With this motivation, pioneering work has been carried out,¹⁰⁻¹⁵ where the time dependence enters via self-consistent parameters and the entire study was largely based on an oversimplified model description.

Obviously it is desirable to extend this kind of study to the level of first-principles simulation. To this end, a necessary element to be included is seemingly the time-dependent density functional theory¹⁶ (TDDFT), which is a generaliza-

tion of the well-known (ground state) static DFT.^{17,18} Similar to the static DFT, the fundamental variable in TDDFT is no longer the many-body wave function but the density. This time-dependent density is determined by solving an auxiliary set of noninteracting time-dependent Schrödinger equations, say, the Kohn-Sham equations. The nontrivial part of the many-body interaction is contained in the so-called exchange-correlation (XC) potential, for which reasonably good approximations exist. Since the foundation of TDDFT, an enormous amount of progress has been made and the theory has been applied to a large number of problems in physics and chemistry. In particular, even the simplest approximation to the XC potential, i.e., the so-called adiabatic local density approximation, can yield remarkably good results.

Despite the wide range of applications, the TDDFT has been mostly limited to isolated systems. To our knowledge, its application to quantum open systems (e.g., in quantum transport) just began very recently. Conceptually, this transition is seemingly nontrivial. One may understand this point by noting that, in order to apply the TDDFT straightforwardly, even in the context of quantum transport, preliminary efforts have been focused on mapping the open transport system onto a closed one.¹⁹⁻²¹ In Ref. 19, a transport system under the action of a battery, which is in essence an open nonequilibrium problem, was replaced with a closed finite system without a battery. And the transport current, which can persist only for a short time period, stems from the discharging of an initially imbalanced charge distribution. In Refs. 20 and 21, the conventional concept of electrodes (with properly defined chemical potentials) was also avoided. Alternatively, the entire transport system is a finite-length circuit, being subject to a periodic boundary condition. In that treatment, the transport current is driven by an external electric field, and the steady state is achieved by introducing an

electron-phonon scattering mechanism to balance the electric field. The major advantage of these two approaches is to place the entire calculation on the rigorous TDDFT footing. More conventionally, recent interesting efforts also include a combination of the NGF formalism with the TDDFT concept.^{22,23} By carefully eliminating the degrees of freedom of the electrodes, it was shown that the formalism can also be placed on the rigorous TDDFT footing. In the presence of electrodes and (equivalent) chemical potentials, numerical results have been obtained by propagating the wave function at zero temperature.²⁴

In this work, by combining the TDDFT with our recently constructed quantum master equation formalism for quantum transport,^{25–28} we attempt to develop an alternative scheme. The master equation approach to mesoscopic transport can be dated back to the classical rate equation²⁹ and its quantum generalization.³⁰ More recent work based on the master equation approach can be found, for instance, in Refs. 31–34. This approach is of interest not only because of its conceptual difference from the conventional mesoscopic transport theory, e.g., the Landauer-Büttiker theory or the nonequilibrium Green's function technique,^{35,36} but also due to its convenience in applications. More importantly, since the master equation is time dependent, it seems thus a natural framework for the study of time-dependent transport. This is in fact the main motivation for us to combine it with the TDDFT to construct a time-dependent transport scheme at the level of first principles.

In the standard TDDFT, the propagation of the system state is described by the time-dependent Kohn-Sham equation, whose solution is used to calculate the (time-dependent) density and the effective Hamiltonian of the noninteracting Kohn-Sham system. In the context of quantum transport, using the same idea of TDDFT, we first map the entire system (i.e., the central device plus the electrodes) to the noninteracting Kohn-Sham system, then trace out the degrees of freedom of the electrodes. As a consequence, directly related to the time-dependent electron density, we obtain a master equation for the reduced density matrix of the device, which is a counterpart of the well-known Kohn-Sham Schrödinger equation. We notice that this treatment can be exact in principle. That is, the entire system of the device plus electrodes evolves under the influence of a bias voltage, starting from a well-defined initial state. Thus, the requirement of the Runge-Gross existence theorem is satisfied. Of course, as in any other (time-dependent) transport theory, proper approximate consideration is needed for the biased electrodes, which enables us to eliminate the degrees of freedom of the electrodes and obtain a master equation for the reduced state of the central device.

The remainder of the paper is organized as follows. In the next section we first specify the transport setup and some physical considerations, and then outline the main result of the master equation approach to transport. In this work, instead of the Markovian prescription,^{25–28} we would like to adopt the scheme of the non-Markovian master equation for reasons to be specified later in the text. For completeness, a brief derivation for the non-Markovian n -resolved master equation is provided in Appendix A. In Sec. III we combine the TDDFT scheme with the multiparticle-state master equation

obtained in Sec. II. By introducing the single-particle density matrix and a number of auxiliary functions associated with the spectral decomposition, we establish the central result of this work, that is, the Kohn-Sham master equation for the reduced single-particle density matrix, and the propagating equations for the auxiliary functions. These quantities would suffice for the calculation of the transport current. Also, a brief description of the technique of spectral decomposition will be presented in Appendix B. In Sec. IV we describe how the effect of inelastic electron-phonon scattering in the device can be conveniently included into the Kohn-Sham master equation. Finally, a summary and discussions are given in Sec. V.

II. TRANSPORT MASTER EQUATION

In this section we shall first present the transport model together with some physical considerations about it, and then outline the main result of the transport master equation in many-particle-state Hilbert space, and put its derivation in Appendix A. All of these will form the basis of the TDDFT scheme for quantum transport of the next section.

A. Model considerations

Conventionally, the mesoscopic transport setup can be described by the transfer Hamiltonian

$$H = H_C(a_\mu^\dagger, a_\mu) + \sum_{\alpha=L,R} \sum_{\mu k} \epsilon_{\alpha\mu k} d_{\alpha\mu k}^\dagger d_{\alpha\mu k} + \sum_{\alpha=L,R} \sum_{\mu k} (t_{\alpha\mu k} a_\mu^\dagger d_{\alpha\mu k} + \text{H.c.}). \quad (1)$$

Here H_C is the device Hamiltonian of the central region, which can be rather general, e.g., including electron-electron and electron-phonon interactions, and may be extended to contain a few interface atoms of the electrodes in the context of, e.g., molecular transport devices. The second and third terms describe, respectively, the (left and right) electrodes and the tunneling between them and the central device. Note that in the above Hamiltonian, as widely adopted in transport studies, the electrode electrons are treated as noninteracting after absorbing the interactions into a self-consistent potential. This noninteracting feature of the electrodes is in fact the basis of the Landauer-type theory, which is the cornerstone of quantum transport. Also, the electrode electrons are described in the Bloch-state representation. This choice is largely for the convenience of formulation. To make contact with the first-principles calculation, the local Wannier-state representation will be more appropriate. As will be shown in Sec. III, the conversion between them can be easily implemented via the self-energy matrix.

Since our major concern is the time-dependent and transient behaviors, care should be taken in the choice of initial condition. In practice, two types of initial states were adopted. (i) In the NGF approach to quantum transport, Caroli *et al.*³⁷ considered the two leads as isolated subsystems with different chemical potentials in the remote past. The current starts to flow through the system once the contacts between the device and the leads have been established.

This treatment of partitioning is seemingly a bit fictitious, since in a real experiment the whole system is in thermodynamic equilibrium before an external bias is applied deep inside the electrodes. Later on this scheme was adopted by Meir and Wingreen³⁸ among others to obtain the steady-state current through an interacting central device, and was also applied to time-dependent phenomena.³⁹ (ii) Conceptually differing from the one by Caroli *et al.*, an alternative scheme was suggested by Cini,⁴⁰ in which the central device is contacted and in thermodynamic equilibrium before an external time-dependent disturbance (i.e., the bias voltage) is switched on. This type of initial condition was recently applied by Stefanucci *et al.*^{22,24}

In this work, we involve the Cini initial condition as follows. Initially, before the bias voltage is switched on, we let the central device be in contact with the leads and in thermodynamic equilibrium. As the bias is switched on, the external potential and the disturbance caused by the device region are screened deep inside the electrodes; thus the density inside the electrodes approaches the equilibrium bulk one. This leads to an enormous simplification since the initial-state self-consistency is not disturbed far away from the device. This picture remains valid provided that the driving frequency is smaller than the plasma frequency, which is tens of terahertz in typical doped semiconductors. The bias is established entirely across the device by charge accumulation and depletion near the electrode-device interfaces. The formation of these charge layers then causes a rigid shift of the conduction band of the electrodes, but the population remains unchanged as the initial one. As an equivalent and more convenient description, the above consideration is typically replaced by the statement that the reservoir electrons are always in local thermal equilibrium characterized by the chemical potentials $\mu_{L/R}(t)$ which define the bias voltage $V(t)$ via $eV(t) = \mu_L(t) - \mu_R(t)$. In this way, the initial equilibrium state is violated, and the system starts evolving under the driving of the bias voltage, leading to a time-dependent transport current. In practice, there exist two types of bias voltage: One is the slow time-dependent modulation of the bias voltage, which is appropriate for the study of ac response; the other is the one suddenly switched on, i.e., $eV(t) = (\mu_L - \mu_R)\Theta(t)$, which corresponds to the initial setup for studying the transient behaviors.

Notice that in the above treatment we explicitly keep the chemical potentials (Fermi levels) of the electrodes at instantaneous values determined by the time-dependent bias voltage, and let the electrode reservoirs always in local thermal equilibrium. Physically, this treatment properly takes into account the closed nature of the transport circuit and the rapid relaxation in the electrode reservoirs. In Cini's treatment, two spatially homogeneous and time-dependent *electrical potentials* are added to the electrode Hamiltonians. The use of the initial occupation in the electrodes then corresponds to an initial rigid shift of the Fermi levels. However, in the subsequent evolution it seems unclear how the rapid relaxation in the electrode reservoirs is included, and how the (approximate) local thermal equilibrium of the reservoirs is guaranteed.

B. n -resolved master equation and transport current

The key idea of the quantum master equation approach to transport is to view the device as an open dissipative system, and the electrodes as its environment. Following the standard treatment of quantum dissipation theory, we introduce the reservoir operators $F_\mu = \sum_{\alpha k} t_{\alpha\mu k} d_{\alpha\mu k} \equiv f_{L\mu} + f_{R\mu}$. Accordingly, the tunneling Hamiltonian H' reads $H' = \sum_\mu (a_\mu^\dagger F_\mu + \text{H.c.})$. Let us then consider the entire system evolution starting from the initial state as discussed above, i.e., the central device in a state formed under zero bias in the presence of device-electrode coupling, and the electrodes in local thermal equilibrium states defined by the initial chemical potentials. In the later evolution, we treat H' as a perturbation. Note that this does not mean the partitioning of the device from the electrodes before the bias voltage is switched on.

Treating H' perturbatively under the second-order Born approximation,^{28,41,42} and performing the n -resolved electrode states average as shown in Appendix A, we obtain

$$\dot{\rho}^{(n)} = -i\mathcal{L}\rho^{(n)} - \sum_\mu \{[a_\mu^\dagger A_{\rho^{(n)}\mu}^{(-)} + A_{\rho^{(n)}\mu}^{(+)} a_\mu^\dagger - A_{\rho^{(n)}L\mu}^{(-)} a_\mu^\dagger - a_\mu^\dagger A_{\rho^{(n)}L\mu}^{(+)} - A_{\rho^{(n-1)}R\mu}^{(-)} a_\mu^\dagger - a_\mu^\dagger A_{\rho^{(n+1)}R\mu}^{(+)}] + \text{H.c.}\}, \quad (2)$$

where $A_{\rho^{(n)}\mu}^{(\pm)} = \sum_{\alpha=L,R} A_{\rho^{(n)}\alpha\mu}^{(\pm)}$, with

$$A_{\rho^{(n)}\alpha\mu}^{(-)}(t) = \sum_\nu \int_0^t dt' C_{\alpha\nu\mu}^{(-)}(t, t') \mathcal{G}(t, t') [a_\nu \rho^{(n)}(t')],$$

$$A_{\rho^{(n)}\alpha\mu}^{(+)}(t) = \sum_\nu \int_0^t dt' C_{\alpha\nu\mu}^{(+)}(t', t) \mathcal{G}(t, t') [\rho^{(n)}(t') a_\nu]. \quad (3)$$

The bath correlation functions read $C_{\alpha\nu\mu}^{(-)}(t, t') = \langle f_{\alpha\mu}(t) f_{\alpha\nu}^\dagger(t') \rangle$ and $C_{\alpha\nu\mu}^{(+)}(t', t) = \langle f_{\alpha\nu}^\dagger(t') f_{\alpha\mu}(t) \rangle$. Note that here, differing from Ref. 28, we have adopted the non-Markovian (i.e., time nonlocal) form of the master equation.

With the knowledge of $\rho^{(n)}(t)$, one is readily able to compute the various transport properties, such as the transport current and noise spectrum.²⁵⁻²⁸ In this work, we focus on the calculation of transport current. Based on the probability distribution function $P(n, t) \equiv \text{Tr}[\rho^{(n)}(t)]$, inserting Eq. (2) into $I(t) = e \sum_n n \dot{P}(n, t)$ gives rise to

$$I(t) = 2e \sum_\mu \text{Re} \text{Tr} \{ a_\mu^\dagger [A_{\rho^{(n)}\mu}^{(-)}(t) - A_{\rho^{(n)}\mu}^{(+)}(t)] \}. \quad (4)$$

Here, $A_{\rho^{(n)}\mu}^{(\pm)}(t)$ are the same as defined by Eq. (3) with the replacement of $\rho^{(n)}$ by the unconditional density matrix $\rho = \sum_n \rho^{(n)}$. Summing up Eq. (2) over n , we obtain

$$\dot{\rho} = -i\mathcal{L}\rho - \sum_\mu \{[a_\mu^\dagger A_{\rho\mu}^{(-)}(t) - A_{\rho\mu}^{(+)}(t) a_\mu^\dagger] + \text{H.c.}\}, \quad (5)$$

where $A_{\rho\mu}^{(\pm)}(t) = \sum_{\alpha=L,R} A_{\rho\alpha\mu}^{(\pm)}(t)$. In principle, to carry out $A_{\rho\alpha\mu}^{(\pm)}(t)$ in this non-Markovian scheme, one should know $\rho(t')$ for all times $t' \in [0, t)$, which is in fact the non-Markovian nature (i.e., the time nonlocality or memory effect). However, as will be shown in the following, based on the technique of spectral decomposition, we are going to establish the equations of motion (EOMs) of $A_{\rho\alpha\mu}^{(\pm)}(t)$. Then, the com-

bined propagation of $A_{\rho\alpha\mu}^{(\pm)}(t)$ and $\rho(t)$ will give the full time-dependent solution for the transport problem under study. Note that these coupled equations will be time local; their propagation is thus quite straightforward. In contrast, as shown in Ref. 26, if we start with a Markovian scheme for the many-particle-state master equation, the time-local scheme for the reduced single-particle density matrices is seemingly impossible to construct, and the time-nonlocal feature will make the practical propagation quite difficult.

III. TDDFT SCHEME

The transport master equation constructed in the previous section is defined in many-particle Hilbert space. This will restrict its applicability to few-state systems, because the huge dimensions of many-particle Hilbert space for large-scale systems would make the problem intractable. In this section, in the spirit of TDDFT we recast the many-particle interacting system as a Kohn-Sham noninteracting system, and establish the corresponding transport master equation, which is defined in the single-particle-state Hilbert space with dimensions greatly reduced.

A. General considerations

Taking the entire system of electrodes plus device into account and starting with the well-defined initial state as described in Sec. II A, the Runge-Gross theorem implies a one-to-one correspondence between the electron density and the potential function. Then the electron density distribution uniquely determines all the (transport) properties of the system. The significant role of the Runge-Gross existence theorem is to guarantee the construction of a proper noninteracting Kohn-Sham system.

For the electrodes, the Kohn-Sham mapping to a noninteracting system is relatively simple. In practice, the interactions in the electrodes are absorbed into a self-consistent potential, and the electrons in the electrodes are treated as noninteracting. As a matter of fact, the noninteracting feature of the electrodes is the basis of Landauer-type transport theory, which is the cornerstone of quantum transport.

The part of the system that we are going to treat carefully is the (extended) device. Its Kohn-Sham counterpart can be constructed as follows. In principle, if we knew the many-particle density operator $\rho(t)$ of the device, we could introduce the reduced single-particle (RSP) density matrix $\sigma_{\mu\nu}(t) \equiv \text{Tr}[a_\nu^\dagger a_\mu \rho(t)]$. However, rather than solving $\rho(t)$, we should calculate $\sigma_{\mu\nu}(t)$ directly from its equation of motion, which is the central goal of this work. Within the TDDFT framework,¹⁶ we map the device interacting Hamiltonian to the noninteracting Kohn-Sham one as

$$h_{mn}(t) = h_{mn}^0(t) + v_{mn}^{\text{XC}}(t) + \sum_{ij} \sigma_{ij}(t) V_{mnij}. \quad (6)$$

In first-principles calculation the state basis is usually chosen as the local atomic orbitals $\{\phi_m(\mathbf{r}), m=1,2,\dots\}$. Here $h^0(t)$ is the noninteracting Hamiltonian which can be in general time-dependent; V_{mnij} is the two-electron Coulomb integral, $V_{mnij} = \int d\mathbf{r} \int d\mathbf{r}' \phi_m^*(\mathbf{r}) \phi_n(\mathbf{r}) (1/|\mathbf{r}-\mathbf{r}'|) \phi_i^*(\mathbf{r}') \phi_j(\mathbf{r}')$; and

$v_{mn}^{\text{XC}}(t) = \int d\mathbf{r} \phi_m^*(\mathbf{r}) v^{\text{XC}}[n](\mathbf{r}, t) \phi_n(\mathbf{r})$, with $v^{\text{XC}}[n](\mathbf{r}, t)$ the exchange-correlation potential, which is defined by the functional derivative of the exchange-correlation functional A^{XC} . In practice, especially in the time-dependent case, the unknown functional A^{XC} can be approximated by the energy functional E^{XC} , obtained in the Kohn-Sham theory and further with the local density approximation. Note that the density function $n(\mathbf{r}, t)$ appearing in the Kohn-Sham Hamiltonian is related to the RSP density matrix via $n(\mathbf{r}, t) = \sum_{mn} \phi_m(\mathbf{r}) \sigma_{mn}(t) \phi_n^*(\mathbf{r})$. Thus, the entire Kohn-Sham system is described by the noninteracting electrodes, the device Hamiltonian $H(t) = \sum_{mn} h_{mn}(t) a_m^\dagger a_n$, and the coupling between them. Starting with this entire Kohn-Sham Hamiltonian and repeating the derivation in Sec. II B will lead to the same formal result presented there. The only difference is that now the Kohn-Sham Hamiltonian $H(t)$ is noninteracting, which enables us to establish the EOMs for $\sigma_{\mu\nu}(t)$.

B. Kohn-Sham master equation

In this section, for the Kohn-Sham system, we recast the master equation Eq. (5) into the EOMs of $\sigma_{\mu\nu}(t)$ and a set of auxiliary functions, and reexpress the transport current in terms of them. For brevity, we tentatively restrict our derivation to the special case of constant bias voltage. Generalization to time-dependent voltages is straightforward, and will be discussed in Sec. III D. For constant bias voltage, the correlation functions $C_{\alpha\mu\nu}^{(-)}(t, t')$ and $C_{\alpha\nu\mu}^{(+)}(t', t)$ depend only on the difference of times. By employing the technique of spectral decomposition as described in Appendix B, they can be formally decomposed into the sum of exponential functions

$$\begin{aligned} C_{\alpha\mu\nu}^{(-)}(t, t') &= \sum_k \lambda_{\alpha\mu\nu}^{(-)k} e^{\gamma_{\alpha\mu\nu}^{(-)k}(t-t')}, \\ C_{\alpha\nu\mu}^{(+)}(t', t) &= \sum_k \lambda_{\alpha\nu\mu}^{(+k)} e^{\gamma_{\alpha\nu\mu}^{(+k)}(t-t')}, \end{aligned} \quad (7)$$

where the parameters $\lambda^{(\pm)k}$ and $\gamma^{(\pm)k}$ are uniquely determined by the spectral decomposition. Furthermore, in addition to $\sigma_{\nu\mu}(t)$, we introduce

$$\tilde{\sigma}_{\nu\mu}(t, t') = \text{Tr}\{a_\mu^\dagger \mathcal{G}(t, t') [a_\nu \rho(t')]\}, \quad (8a)$$

$$\bar{\sigma}_{\nu\mu}(t, t') = \text{Tr}\{a_\mu^\dagger \mathcal{G}(t, t') [\rho(t') a_\nu]\}, \quad (8b)$$

and the auxiliary functions

$$A_{\alpha\mu\nu\mu}^{(-)k}(t) = \int_0^t dt' \lambda_{\alpha\mu\nu}^{(-)k} e^{\gamma_{\alpha\mu\nu}^{(-)k}(t-t')} \tilde{\sigma}_{\nu\mu'}(t, t'), \quad (9a)$$

$$A_{\alpha\mu\nu\mu}^{(+k)}(t) = \int_0^t dt' \lambda_{\alpha\nu\mu}^{(+k)} e^{\gamma_{\alpha\nu\mu}^{(+k)}(t-t')} \bar{\sigma}_{\nu\mu'}(t, t'). \quad (9b)$$

Simple algebra leads to the EOMs of $\tilde{\sigma}(t, t')$ and $\bar{\sigma}(t, t')$:

$$\partial_t \tilde{\sigma}_{\nu\mu}(t, t') = i[\tilde{\sigma}(t, t') h(t)]_{\nu\mu}, \quad (10a)$$

$$\partial_t \bar{\sigma}_{\nu\mu}(t, t') = i[\bar{\sigma}(t, t')h(t)]_{\nu\mu}. \quad (10b)$$

Accordingly, the EOMs of $A_{\alpha\mu\nu\mu'}^{(\pm)k}(t)$ can be straightforwardly obtained:

$$\begin{aligned} \partial_t A_{\alpha\mu\nu\mu'}^{(-)k}(t) &= \lambda_{\alpha\mu\nu}^{(-)k} \sigma_{\nu\mu'}(t) + \gamma_{\alpha\mu\nu}^{(-)k} A_{\alpha\mu\nu\mu'}^{(-)k}(t) \\ &+ i \sum_m A_{\alpha\mu\nu m}^{(-)k}(t) h_{m\mu'}(t), \end{aligned} \quad (11a)$$

$$\begin{aligned} \partial_t A_{\alpha\mu\nu\mu'}^{(+k)}(t) &= \lambda_{\alpha\mu\nu}^{(+k)} [\delta_{\nu\mu'} - \sigma_{\nu\mu'}(t)] + \gamma_{\alpha\mu\nu}^{(+k)} A_{\alpha\mu\nu\mu'}^{(+k)}(t) \\ &+ i \sum_m A_{\alpha\mu\nu m}^{(+k)}(t) h_{m\mu'}(t). \end{aligned} \quad (11b)$$

Note that the RSP density matrix $\sigma_{\nu\mu}(t)$ appears in the EOMs of these auxiliary functions. To close the EOMs for the transport problem, we need to derive the EOMs of $\sigma_{\nu\mu}(t)$. Using the identity $\text{Tr}\{a_\mu^\dagger a_\nu \Sigma_{\mu'}[a_\mu^\dagger, A_{\mu'}]\} = \text{Tr}[a_\mu^\dagger A_\nu]$, we easily obtain

$$\dot{\sigma}(t) = -i[h(t), \sigma(t)] - \sum_\alpha [M_\alpha(t) + \text{H.c.}], \quad (12)$$

where the matrix $M_\alpha(t)$ is defined via its elements as

$$[M_\alpha]_{\nu\mu}(t) = \sum_{k\nu'} [A_{\alpha\nu\nu'\mu}^{(-)k}(t) - A_{\alpha\nu\nu'\mu}^{(+k)}(t)].$$

Propagating Eqs. (11) and (12) is numerically straightforward, and the most difficult task arising from the memory kernel in the usual non-Markovian dynamics is avoided. Finally, the transport current is simply related to the auxiliary functions as

$$I(t) = 2e \sum_{k\mu\nu} \text{Re}[A_{R\mu\nu\mu}^{(-)k}(t) - A_{R\mu\nu\mu}^{(+k)}(t)], \quad (13)$$

which is output automatically along the time propagation of the above EOMs.

C. Spectral density function

The treatment in the previous section is based on the spectral decomposition of $\Gamma_{\mu\nu}^\alpha(\epsilon) = 2\pi \sum_k t_{\alpha\mu k}^* t_{\alpha\nu k} \delta(\epsilon - \epsilon_k)$, as shown in Appendix B. Since the spectral decomposition is rooted in a technique of numerical fitting, it is thus in principle suited for an arbitrary shape of the spectral density function $\Gamma_{\mu\nu}^\alpha(\epsilon)$. In particular, it is not limited by the conventional wideband approximation. This advantage makes us able to incorporate the electronic structure of the electrodes which is obtained from other sophisticated methods. One possible way of calculating $\Gamma_{\mu\nu}^\alpha(\epsilon)$ is based on a semiempirical tight-binding model for the electrodes, and using the surface Green's function technique. Some details of this method can be found in Ref. 43. Here we would like only to outline the key idea for completeness.

Formally, in matrix form, the spectral density function is related to the self-energy matrix Σ^α via

$$\Gamma^\alpha = i(\Sigma^\alpha - \Sigma^{\alpha\dagger}). \quad (14)$$

Further, the self-energy matrix can be calculated by

$$\Sigma = t g t^\dagger, \quad (15)$$

where t is the coupling matrix between the edge atoms of the electrode and the (extended) device, and g is the surface Green's function of the electrode. Recursively, g can be obtained via the following Dyson equation:

$$g^{-1} = g_0^{-1} - \tilde{\Sigma} = g_0^{-1} - \tilde{t} g \tilde{t}^\dagger, \quad (16)$$

where $\tilde{t}$ is the coupling matrix between nearest-neighbor layers in the electrode.

In practice, attention should be paid to the dimensions of the matrices, i.e., there are two types of orbital labels: One is restricted to the device edge orbitals; and the other is over all the device orbitals. From the definition of each matrix, the size of its every dimension can be identified accordingly.

D. Time-dependent voltage

The derivation in Sec. III B corresponds to a time-independent bias voltage. That is, after a constant voltage is switched on, the chemical potentials in the electrodes remain unchanged. This implies that the correlation functions $C_{\alpha\mu\nu}^{(\pm)}(t, t')$ have time-translational invariance during the later evolution. The description under this assumption can be applied to the study of transient behaviors.³⁶

Another important time-dependent setup is applying modification on the bias voltage, such as in the study of the ac response. As we have discussed previously, under proper conditions, the effect of a time-dependent voltage can be approximately described by rigid shifts of the conduction bands of the electrodes, i.e., $\epsilon_{k\alpha}(t) = \epsilon_{k\alpha} + \Delta_\alpha(t)$, keeping the occupation on each state unchanged. Accordingly, the correlation functions read

$$\begin{bmatrix} C_{\alpha\mu\nu}^{(-)}(t, t') \\ C_{\alpha\nu\mu}^{(+)}(t', t) \end{bmatrix} = \begin{bmatrix} \bar{C}_{\alpha\mu\nu}^{(-)}(t - t') \\ \bar{C}_{\alpha\nu\mu}^{(+)}(t - t') \end{bmatrix} \exp\left(-i \int_{t'}^t dt_1 \Delta_\alpha(t_1)\right), \quad (17)$$

where $\bar{C}_{\alpha\mu\nu}^{(\pm)}(t - t')$ are the counterparts in the absence of a time-dependent voltage shift [i.e., $\Delta_\alpha(t) = 0$], and can be obtained by using the surface Green's function technique as described in the previous section.

Replacing the correlation functions in Sec. III B with Eq. (17), all the equations obtained there can be formally re-derived, with only a minor modification in the second terms of the right-hand side of Eq. (11), i.e., $\gamma_{\alpha\mu\nu}^{(\pm)k} \rightarrow \gamma_{\alpha\mu\nu}^{(\pm)k} - i\Delta_\alpha(t)$. The advantage of the proposed TDDFT scheme in Sec. III B is thus prominent, since in other conventional treatments the time-dependent transport is usually regarded as more difficult than its stationary counterpart, owing to the lack of time-translational invariance. However, in our scheme, no extra efforts are needed for a time-dependent voltage in propagating the EOMs of the RSP density matrix $\sigma_{\mu\nu}(t)$ and the auxiliary functions $A_{\alpha\mu\nu}^{(\pm)k}(t)$.

IV. ELECTRON-PHONON INTERACTION

In this section we consider the issue of inelastic scattering in the device. Still within the TDDFT framework, we assume

that the Kohn-Sham subsystem of the device is coupled to a phonon bath ($H_{\text{ph}} = \sum_q \omega_q b_q^\dagger b_q$). In general, the electron-phonon interaction Hamiltonian has the form

$$H_{e\text{-ph}} = \sum_q \sum_{mn} \gamma_{qmn} (b_q^\dagger + b_q) a_m^\dagger a_n \equiv \sum_{q\kappa} (W_{\kappa} f_{q\kappa}^\dagger + W_{\kappa}^\dagger f_{q\kappa}), \quad (18)$$

where for brevity we introduce $W_{\kappa} \equiv W_{mn} = a_m^\dagger a_n$, and $f_{q\kappa}$ is defined accordingly. Here and in the remainder of this section, we adopt the electronic eigenstate basis of the device Kohn-Sham Hamiltonian before the bias voltage is applied. This choice has the advantage of making the electronic-state transition due to phonon scattering clearly defined.

Formally, the many-electron-state master equation for the device can be expressed as

$$\dot{\rho} = -i\mathcal{L}\rho - \mathcal{R}_e\rho - \mathcal{R}_{\text{ph}}\rho. \quad (19)$$

In this equation, the term $\mathcal{R}_e\rho$ describes the electrode effect on the device, and $\mathcal{R}_{\text{ph}}\rho$ stems from the effect of the electron-phonon interaction. In the previous sections, we have focused on the term $\mathcal{R}_e\rho$, by performing a non-Markovian treatment at the level of the second-order Born approximation. For $\mathcal{R}_{\text{ph}}\rho$, one can in principle perform the same treatment, by also applying the spectral decomposition technique for the phonon bath. Nevertheless, for simplicity we would like to treat the electron-phonon interaction under the Markovian approximation as usual. Following Ref. 42, we have

$$\mathcal{R}_{\text{ph}}\rho = \frac{1}{2} \sum_{\kappa} \{ [W_{\kappa}^\dagger, \tilde{W}_{\kappa}^{(-)}\rho - \rho\tilde{W}_{\kappa}^{(+)}] + \text{H.c.} \}. \quad (20)$$

At the transition energy $\omega_{\kappa} \equiv |\epsilon_m - \epsilon_n|$, the operators $\tilde{W}_{\kappa}^{(\pm)}$ read $\tilde{W}_{\kappa}^{(\pm)} = \tilde{\Gamma}_{\kappa}^{(\pm)} W_{\kappa}$, where $\tilde{\Gamma}_{\kappa}^{(\pm)}$ are defined by $\tilde{\Gamma}_{\kappa}^{(+)} = g(\omega_{\kappa}) |\gamma_{\kappa}|^2 (\bar{n}_{\omega_{\kappa}} + 1)$ and $\tilde{\Gamma}_{\kappa}^{(-)} = g(\omega_{\kappa}) |\gamma_{\kappa}|^2 \bar{n}_{\omega_{\kappa}}$, respectively. Here $g(\omega)$ is the density of states of the phonon modes, and $\bar{n}_{\omega}$ is the corresponding phonon occupation number. Also, we would like to mention that to arrive at Eq. (20), we have inserted the device Kohn-Sham Hamiltonian at the initial equilibrium state, but not the time-dependent one associated with the later evolution, into the dissipation terms. This is the well-known approximation in studying dissipative systems under external-field driving. This treatment reduces Eq. (20) to the Lindblad form.

To incorporate the effect of electron-phonon interaction into the Kohn-Sham master equation (12), we need to recast $\mathcal{R}_{\text{ph}}\rho$ in a RSP density matrix form. Simple algebra gives

$$\begin{aligned} \text{Tr} \left\{ a_{\mu}^\dagger a_n \sum_{\kappa} [W_{\kappa}^\dagger, \tilde{W}_{\kappa}^{(-)}\rho - \rho\tilde{W}_{\kappa}^{(+)}] \right\} &\approx \sigma_{\nu\mu} \sum_n [\tilde{\Gamma}_{n\nu}^{(-)} + \tilde{\Gamma}_{\mu n}^{(+)}] \bar{\sigma}_{nm} \\ &- \bar{\sigma}_{\nu\mu} \sum_n [\tilde{\Gamma}_{n\nu}^{(+)} + \tilde{\Gamma}_{\mu n}^{(-)}] \sigma_{nm}. \end{aligned} \quad (21)$$

In the derivation of this result, a Wick-type factorization such as $\langle a_{\mu}^\dagger a_n W_{n\nu} \rangle \approx \sigma_{\nu\mu} \bar{\sigma}_{nm}$ is assumed. We would like to note that Eq. (21) coincides precisely with the central result derived by Gebauer and Car in an alternative transport approach.²¹ After simple basis transformation (i.e., from

eigenstates to local atomic orbitals), inserting Eq. (21) into the Kohn-Sham master equation (12) leads to an elegant scheme which can also account for the electron-phonon scattering in the time-dependent transport process. We stress that this is another significant advantage of the proposed transport approach.

V. CONCLUSION AND DISCUSSION

To summarize, based on the quantum master equation approach, we have constructed a practical scheme for the first-principles study of time-dependent quantum transport. The basic idea is to combine the transport master equation with the well-known time-dependent density functional theory. By utilizing a partitioning-free initial condition, the scheme is reliably based on the Runge-Gross theorem. Then, with the help of spectral decomposition, a closed set of equations for the RSP density matrices is obtained. Time propagation of this set of equations will directly output the time-dependent transport current.

It is of interest to note that it is the non-Markovian (but not the Markovian) master equation that allows us to construct the closed set of equations for the RSP density matrices, based on the spectral decomposition technique. In Ref. 26, without using the spectral decomposition and in the framework of the Markovian master equation, we established an alternative form of TDDFT based master equation for the RSP density matrix. However, in that scheme, the numerical propagation seems inefficient, because of the nonlocal effect of time integration. On the contrary, the numerical implementation of the present scheme should be efficient and straightforward. Moreover, it will be very flexible for the parametrization of highly structured spectral densities, which takes the description far beyond the Markovian approximation. Systematic applications and numerical implementations of the proposed scheme are in progress and will appear in the forthcoming publications.

Finally, we remark that the major approximation involved in the master equation is the second-order Born approximation for the tunnel Hamiltonian. This is a standard and well-justified approximation, which makes the resultant master equation good enough in a large number of dissipative systems (e.g., in quantum optics). Also, our recent work clearly showed its satisfactory accuracy in quantum transport.²⁵⁻²⁸ In this context, we may roughly claim that its accuracy is at least at the level of sequential transport. Noticeably, in a first-principles study, other numerical errors will completely cover up the inaccuracy of sequential transport. Therefore, the proposed TDDFT master equation scheme should be an attracting theoretical tool for the first-principles study of time-dependent transport.

ACKNOWLEDGMENTS

Support from the National Natural Science Foundation of China (Grants No. 90503013 and No. 60425412), the Major State Basic Research Project No. G001CB3095 of China, and the Research Grants Council of the Hong Kong Government is gratefully acknowledged.

APPENDIX A: n -RESOLVED MASTER EQUATION

In this appendix we present the derivation of the non-Markovian form of the n -resolved master equation. In almost the same spirit as Ref. 25, let us regard $H' = \sum_{\mu} (a_{\mu}^{\dagger} F_{\mu} + \text{H.c.})$ as a coupling of the system of interest to a dissipative environment. Treating H' as a perturbation and up to the second order, a formal equation for the reduced density matrix is obtained as⁴¹

$$\dot{\rho}(t) = -i\mathcal{L}\rho(t) - \int_0^t d\tau \mathcal{L}'(\tau) \mathcal{G}(t, \tau) \mathcal{L}'(\tau) \rho(\tau). \quad (\text{A1})$$

Here the Liouvillian superoperators are defined as $\mathcal{L}(\cdots) \equiv [H_S, (\cdots)]$, $\mathcal{L}'(\cdots) \equiv [H', (\cdots)]$, and $\mathcal{G}(t, \tau)(\cdots) \equiv G(t, \tau) \times (\cdots) G^{\dagger}(t, \tau)$ with $G(t, \tau)$ the usual propagator (Green's function) associated with the central system (device) Hamiltonian H_S . The reduced density matrix $\rho(t) = \text{Tr}_B[\rho_T(t)]$, and $\langle(\cdots)\rangle = \text{Tr}_B[(\cdots)\rho_B]$ with ρ_B the density matrix of the electrode reservoirs.

The trace in Eq. (A1) is over all the electrode degrees of freedom, leading thus to the equation of motion of the unconditional reduced density matrix of the central system. However, more information is contained if we keep track of the record of electron numbers arrived at the collector (right electrode). We therefore classify the Hilbert space of the electrodes as follows. First, we define the subspace in the absence of any electron arrived at the collector as $B^{(0)}$, which is spanned by the product of all many-particle states of the two isolated reservoirs, formally denoted as $B^{(0)} \equiv \text{span}\{|\Psi_L\rangle \otimes |\Psi_R\rangle\}$. Then we introduce the Hilbert subspace $B^{(n)}$ ($n=1, 2, \dots$), corresponding to n electrons arrived at the collector. The entire Hilbert space of the two electrodes is $B = \bigoplus_n B^{(n)}$.

With the above classification of the reservoir states, the average over states in the entire Hilbert space B in Eq. (2) is replaced with states in the subspace $B^{(n)}$, leading to a conditional master equation

$$\dot{\rho}^{(n)}(t) = -i\mathcal{L}\rho^{(n)}(t) - \int_0^t d\tau \text{Tr}_{B^{(n)}}[\mathcal{L}'(\tau) \mathcal{G}(t, \tau) \times \mathcal{L}'(\tau) \rho_T(\tau)]. \quad (\text{A2})$$

Here $\rho^{(n)}(t) = \text{Tr}_{B^{(n)}}[\rho_T(t)]$, which is the reduced density matrix of the system conditioned by the number of electrons arrived at the collector until time t . Now we transform the Liouvillian operator product in Eq. (A2) into the conventional Hilbert form:

$$\begin{aligned} \mathcal{L}'(\tau) \mathcal{G}(t, \tau) \mathcal{L}'(\tau) \rho_T(\tau) &= [H'(\tau) G(t, \tau) H'(\tau) \rho_T(\tau) G^{\dagger}(t, \tau) \\ &\quad - G(t, \tau) H'(\tau) \rho_T(\tau) G^{\dagger}(t, \tau) H'(\tau)] \\ &\quad + \text{H.c.} \equiv [I - II] + \text{H.c.} \end{aligned} \quad (\text{A3})$$

To proceed, two physical considerations are further taken into account as follows. (i) Instead of the conventional Born approximation for the entire density matrix $\rho_T(\tau) \approx \rho(\tau) \otimes \rho_B$, we propose the ansatz $\rho_T(\tau) \approx \sum_n \rho^{(n)}(\tau) \otimes \rho_B^{(n)}$, where $\rho_B^{(n)}$ is the density operator of the electron reservoirs associated with n electrons arrived at the collector. With this ansatz

for the density operator, tracing over the subspace $B^{(n)}$ yields

$$\begin{aligned} \text{Tr}_{B^{(n)}}[I] &= \sum_{\mu, \nu} \{ \text{Tr}_B[F_{\mu}^{\dagger}(t) F_{\nu}(\tau) \rho_B^{(n)}] [a_{\mu} G(t, \tau) a_{\nu}^{\dagger} \rho^{(n)}(\tau) G^{\dagger}(t, \tau)] \\ &\quad + \text{Tr}_B[F_{\mu}(\tau) F_{\nu}^{\dagger}(t) \rho_B^{(n)}] [a_{\mu}^{\dagger} G(t, \tau) a_{\nu} \rho^{(n)}(\tau) G^{\dagger}(t, \tau)] \}, \end{aligned} \quad (\text{A4a})$$

$$\begin{aligned} \text{Tr}_{B^{(n)}}[II] &= \sum_{\mu, \nu} \{ \text{Tr}_B[f_{L\nu}^{\dagger}(\tau) \rho_B^{(n)} f_{L\mu}(t)] [G(t, \tau) a_{\nu} \rho^{(n)}(\tau) \\ &\quad \times G^{\dagger}(t, \tau) a_{\mu}^{\dagger}] + \text{Tr}_B[f_{L\nu}(\tau) \rho_B^{(n)} f_{L\mu}^{\dagger}(t)] \\ &\quad \times [G(t, \tau) a_{\nu}^{\dagger} \rho^{(n)}(\tau) G^{\dagger}(t, \tau) a_{\mu}] \\ &\quad + \text{Tr}_B[f_{R\nu}^{\dagger}(\tau) \rho_B^{(n-1)} f_{R\mu}(t)] \times [G(t, \tau) a_{\nu} \rho^{(n-1)}(\tau) \\ &\quad \times G^{\dagger}(t, \tau) a_{\mu}^{\dagger}] + \text{Tr}_B[f_{R\nu}(\tau) \rho_B^{(n-1)} f_{R\mu}^{\dagger}(t)] \\ &\quad \times [G(t, \tau) a_{\nu}^{\dagger} \rho^{(n-1)}(\tau) G^{\dagger}(t, \tau) a_{\mu}] \}. \end{aligned} \quad (\text{A4b})$$

Here we have utilized the orthogonality between states in different subspaces, which in fact leads to the term selection from the entire density operator ρ_T . (ii) Due to the closed nature of the transport circuit, the extra electrons arrived at the collector will flow back into the emitter (left reservoir) via the external circuit. Also, the rapid relaxation processes in the reservoirs will quickly bring the reservoirs to the local thermal equilibrium state determined by the chemical potentials. As a consequence, after the procedure (i.e., the state selection) done in Eq. (A4a), the electron reservoir density matrices $\rho_B^{(n)}$ and $\rho_B^{(n\pm 1)}$ should be replaced by $\rho_B^{(0)}$, i.e., the local thermal equilibrium reservoir state. Then, the non-Markovian n -resolved master equation Eq. (2) is obtained.

APPENDIX B: SPECTRAL DECOMPOSITION

In this appendix we show how to express the correlation functions $C_{\alpha\mu\nu}^{(-)}(t, t') = \langle f_{\alpha\mu}(t) f_{\alpha\nu}^{\dagger}(t') \rangle$ and $C_{\alpha\mu\nu}^{(+)}(t', t) = \langle f_{\alpha\nu}^{\dagger}(t') f_{\alpha\mu}(t) \rangle$ in terms of the sum of exponential functions, via the technique of spectral decomposition. For constant bias voltage, let us reexpress, for instance, $C_{\alpha\mu\nu}^{(+)}(t', t)$ as

$$\begin{aligned} C_{\alpha\mu\nu}^{(+)}(t', t) &= \sum_k t_{\alpha\nu k}^* t_{\alpha\mu k} e^{-i\epsilon_k(t-t')} n_{\alpha}(\epsilon_k) \\ &= \int \frac{d\epsilon}{2\pi} \Gamma_{\nu\mu}^{\alpha}(\epsilon) n_{\alpha}(\epsilon) e^{-i\epsilon(t-t')}, \end{aligned} \quad (\text{B1})$$

where $\Gamma_{\nu\mu}^{\alpha}(\epsilon) = 2\pi \sum_k t_{\alpha\nu k}^* t_{\alpha\mu k} \delta(\epsilon - \epsilon_k)$ is the spectral density function of the α th electrode, which can be obtained by the surface Green's function technique as described in Sec. III C.

To express $C_{\alpha\mu\nu}^{(+)}(t', t)$ as a sum of exponential functions, let us parametrize the spectral density as follows:

$$\Gamma_{\nu\mu}^{\alpha}(\epsilon) = \sum_{k=1}^m \frac{p_{\alpha\nu\mu}^k}{(\epsilon - \Omega_{\alpha\nu\mu}^k)^2 + (\Gamma_{\alpha\nu\mu}^k)^2}. \quad (\text{B2})$$

By employing the theorem of residues, the integral result of Eq. (B1) reads

$$C_{\alpha\nu\mu}^{(+)}(t', t) = \sum_{k=1}^m \frac{P_{\alpha\nu\mu}^k}{2\Gamma_{\alpha\nu\mu}^k} n_{\alpha}(\tilde{\Omega}_{\alpha\nu\mu}^k) e^{-i\tilde{\Omega}_{\alpha\nu\mu}^k(t-t')} + \frac{i}{\beta} \sum_{n=0}^{\infty} \Gamma_{\nu\mu}^{\alpha}(\epsilon_n) e^{-i\epsilon_n(t-t')}, \quad (\text{B3})$$

where $\tilde{\Omega}_{\alpha\nu\mu}^k = \tilde{\Omega}_{\alpha\nu\mu}^k - i\Gamma_{\alpha\nu\mu}^k$ and $\epsilon_n = \epsilon_F - i(2n+1)\pi/\beta$. Similarly, the correlation function $C_{\alpha\nu\mu}^{(-)}(t, t')$ can be decomposed. Then, these two functions can be formally reexpressed as Eq. (7).

About the spectral decomposition, a few remarks are made as follows. (i) This spectral decomposition technique has been successfully applied to non-Markovian dissipative systems⁴⁴ and to the quantum transport through molecular wires very recently.³⁴ The most prominent advantage of this technique is its flexibility. That is, it is extremely well suited for the parametrization of highly structured spectral densities, leading to long and oscillatory correlation functions, thus taking the description far beyond the Markovian approximation. In the context of quantum transport, this decomposition technique avoids the usual wideband approximation, and can handle arbitrary band structures which may be obtained even by first-principles calculation. (ii) In reality, we might find different sets of parameters that can approxi-

mate a given spectral density to the same degree of accuracy. Nevertheless, this will not lead to a different dynamical behavior, since the dynamics is determined by the spectral density itself. (iii) Not all types of spectral densities need the numerical decomposition of the spectral densities. For instance, for the Drude spectral density $J(\omega) = \eta\omega/[\omega^2 + (\omega/\omega_d)^2]$, or other spectral densities with simple poles, there is no approximation other than the finite number of Matsubara terms involved. In practice, the number of fitting terms depends on the shape of spectral density. For example, for the Ohmic spectral density with exponential cutoff $J(\omega) = \eta\omega e^{-\omega/\omega_c}$, only three terms are accurate enough to parametrize the spectral density. However, for another spectral density of the form $J(\omega) = \eta\omega^2/(2\omega_c^3) e^{-\omega/\omega_c}$, nine terms were necessary for an accurate fit.⁴⁴ (iv) For finite temperatures, the contributions of the high Matsubara frequencies will be small, so that for practical purposes the summation over the Matsubara frequencies can be truncated at some value. Hence, this decomposition will be most profitable for high temperatures, when only a few Matsubara frequencies contribute. For very low temperatures, we may alternatively parametrize the combined spectral density, say, $\tilde{\Gamma}_{\nu\mu}^{\alpha}(\epsilon) = \Gamma_{\nu\mu}^{\alpha}(\epsilon) n_{\alpha}(\epsilon)$, in terms of the Lorentzian spectral function Eq. (B2).

*Electronic address: xqli@red.semi.ac.cn

†Electronic address: yan@ust.hk

- ¹N. D. Lang and Ph. Avouris, Phys. Rev. Lett. **84**, 358 (2000).
- ²J. Heurich, J. C. Cuevas, W. Wenzel, and G. Schön, Phys. Rev. Lett. **88**, 256803 (2002).
- ³C.-K. Wang and Y. Luo, J. Chem. Phys. **119**, 4923 (2003).
- ⁴N. D. Lang, Phys. Rev. B **52**, 5335 (1995).
- ⁵J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 245407 (2001).
- ⁶S.-H. Ke, H. U. Baranger, and W. Yang, J. Am. Chem. Soc. **126**, 15897 (2004).
- ⁷W.-Q. Deng, R. P. Muller, and W. A. Goddard III, J. Am. Chem. Soc. **126**, 13563 (2004).
- ⁸M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).
- ⁹Y. Xue, S. Datta, and M. A. Ratner, J. Chem. Phys. **115**, 4292 (2001).
- ¹⁰L. Y. Chen and C. S. Ting, Phys. Rev. B **43**, 2097 (1991).
- ¹¹D. C. Langreth and P. Nordlander, Phys. Rev. B **43**, 2541 (1991).
- ¹²H. M. Pastawski, Phys. Rev. B **46**, 4053 (1992).
- ¹³T. Ivanov, D. Marvakov, V. Valtchinov, and L. T. Wille, Phys. Rev. B **48**, 4679 (1993); T. Ivanov, *ibid.* **52**, 2838 (1995).
- ¹⁴N. S. Wingreen, A. P. Jauho, and Y. Meir, Phys. Rev. B **48**, 8487 (1993); A. P. Jauho, N. S. Wingreen, and Y. Meir, *ibid.* **50**, 5528 (1994); C. A. Stafford and N. S. Wingreen, Phys. Rev. Lett. **76**, 1916 (1996).
- ¹⁵C. Bruder and H. Schoeller, Phys. Rev. Lett. **72**, 1076 (1994); M. H. Hettler and H. Schoeller, *ibid.* **74**, 4907 (1995).
- ¹⁶E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- ¹⁷P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ¹⁸W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

- ¹⁹M. Di Ventra and T. N. Todorov, J. Phys.: Condens. Matter **16**, 8025 (2004); N. Bushong, N. Sai, and M. Di Ventra, Nano Lett. **5**, 2569 (2005).
- ²⁰K. Burke, R. Car, and R. Gebauer, Phys. Rev. Lett. **94**, 146803 (2005).
- ²¹R. Gebauer and R. Car, Int. J. Quantum Chem. **101**, 564 (2005).
- ²²G. Stefanucci and C.-O. Almbladh, Europhys. Lett. **67**, 14 (2004).
- ²³X. Zheng and G. H. Chen (unpublished).
- ²⁴S. Kurth, G. Stefanucci, C.-O. Almbladh, A. Rubio, and E. K. U. Gross, Phys. Rev. B **72**, 035308 (2005).
- ²⁵X. Q. Li, J. Luo, Y. G. Yang, P. Cui, and Y. J. Yan, Phys. Rev. B **71**, 205304 (2005).
- ²⁶P. Cui, X. Q. Li, J. S. Shao, and Y. J. Yan, Phys. Lett. A **357**, 449 (2006).
- ²⁷J. Y. Luo, X. Q. Li, and Y. J. Yan, cond-mat/0603163 (unpublished).
- ²⁸X. Q. Li, P. Cui, and Y. J. Yan, Phys. Rev. Lett. **94**, 066803 (2005).
- ²⁹L. I. Glazman and K. A. Matveev, JETP Lett. **48**, 445 (1988); D. V. Averin and A. N. Korotkov, Sov. Phys. JETP **70**, 937 (1990); C. W. J. Beenakker, Phys. Rev. B **44**, 1646 (1991); Yu. V. Nazarov, Physica B **189**, 57 (1993); S. A. Gurvitz, H. J. Lipkin, and Ya. S. Prager, Phys. Lett. A **212**, 91 (1996).
- ³⁰S. A. Gurvitz and Ya. S. Prager, Phys. Rev. B **53**, 15932 (1996).
- ³¹V. N. Golovach and D. Loss, Phys. Rev. B **69**, 245327 (2004); J. Lehmann and D. Loss, *ibid.* **73**, 045328 (2006).
- ³²F. Marquardt and C. Bruder, Phys. Rev. B **68**, 195305 (2003).
- ³³T. Novotny, A. Donarini, C. Flindt, and A.-P. Jauho, Phys. Rev. Lett. **92**, 248302 (2004).

- ³⁴S. Welack, M. Schreiber, and U. Kleinekathöfer, J. Chem. Phys. **124**, 044712 (2006).
- ³⁵S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, New York, 1995).
- ³⁶H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer-Verlag, Berlin, 1996).
- ³⁷C. Caroli *et al.*, J. Phys. C **4**, 916 (1971); **4**, 2598 (1971).
- ³⁸Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).
- ³⁹Ned S. Wingreen, A.-P. Jauho, and Y. Meir, Phys. Rev. B **48**, 8487 (1993); A.-P. Jauho, N. S. Wingreen, and Y. Meir, *ibid.* **50**, 5528 (1994); H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductor* (Springer-Verlag, Berlin, 1998).
- ⁴⁰M. Cini, Phys. Rev. B **22**, 5887 (1980).
- ⁴¹Y. J. Yan, Phys. Rev. A **58**, 2721 (1998).
- ⁴²R. Xu, Y. J. Yan, and X. Q. Li, Phys. Rev. A **65**, 023807 (2002).
- ⁴³E. Zahid, M. Paulsson, and S. Datta, in *Advanced Semiconductors and Organic Nano-Techniques*, edited by H. Morkoc (Academic Press, San Diego, 2003).
- ⁴⁴C. Meier and D. J. Tannor, J. Chem. Phys. **111**, 3365 (1999); U. Kleinekathöfer, *ibid.* **121**, 2505 (2004).