

Time-dependent density-functional theory for open systems

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With our proof of the holographic electron density theorem for time-dependent systems, a first-principles method for any open electronic system is established. By introducing the self-energy density functionals for the dissipative interactions between the reduced system and its environment, we develop a time-dependent density-functional theory formalism based on an equation of motion for the Kohn-Sham reduced single-electron density matrix of the reduced system. Two approximate schemes are proposed for the dissipative interactions, the complete second-order approximation and the wide-band limit approximation. A numerical method based on the wide-band limit approximation is subsequently developed and implemented to simulate the steady and transient current through various realistic molecular devices. Simulation results are presented and discussed.

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I. INTRODUCTION

Density-functional theory (DFT) has been widely used as a research tool in condensed matter physics, chemistry, materials science, and nanoscience. The Hohenberg-Kohn theorem¹ lays the foundation of DFT. The Kohn-Sham (KS) formalism² provides a practical solution to calculate the ground-state properties of electronic systems. Runge and Gross extended DFT further to calculate the time-dependent properties and hence the excited state properties of any electronic systems.³ The accuracy of DFT or time-dependent DFT (TDDFT) is determined by the exchange-correlation (XC) functional. If the exact XC functional were known, the KS formalism would have provided the exact ground-state properties, and the Runge-Gross extension, TDDFT, would have yielded the exact time-dependent and excited-states properties. Despite their wide range of applications, DFT and TDDFT have been mostly limited to isolated systems.

Many systems of current research interest are open systems. A molecular electronic device is one such system. Simulations based on DFT have been carried out on such devices.⁴⁻¹³ These simulations focus on steady-state currents under bias voltages. Two types of approaches have been adopted. One is the Lippmann-Schwinger formalism by Lang and co-workers.⁷ The other is the first-principles non-equilibrium Green's function (NEGF) technique.⁸⁻¹³ In both approaches the KS Fock operator is taken as the effective single-electron model Hamiltonian, and the transmission coefficients are calculated within the noninteracting electron model. The investigated systems are not in their ground states, and applying ground-state DFT formalism for such systems is only an approximation.¹⁴ DFT formalisms adapted for current-carrying systems have also been proposed recently, such as Kosov's KS equations with direct current,¹⁵ Kurth *et al.*'s¹⁶ and Zheng *et al.*'s¹⁷ TDDFT formulations, Cui *et al.*'s complete second-order quantum dissipation theory (CS-QDT) formalism¹⁸ and Burke *et al.*'s KS master equation including dissipation to phonons.¹⁹ In this paper, we present a DFT formalism for open electronic systems, and use it to simulate the steady and transient currents through molecular electronic devices. The first-principles formalism

depends only on the electron density function of the reduced system.

This paper is organized as follows. In Sec. II the existence of a first-principles method for any open electronic system is established with the proof of the holographic electron density theorem for time-dependent real physical systems. In Sec. III we describe a TDDFT formalism for open electronic systems based on an equation of motion (EOM) for the reduced single-electron density matrix. By utilizing the holographic electron density theorem, the self-energy functionals with explicit functional dependence on the electron density of the reduced system are introduced, and thus a rigorous and efficient first-principles formalism for the transient dynamics of any open electronic system is established. Two approximate schemes, the complete second-order (CSO) approximation for the dissipative interaction and the wide-band limit (WBL) approximation for the electrodes, are proposed in Sec. III. To demonstrate the applicability of our first-principles formalism, TDDFT calculations are carried out to simulate the transient and steady current through realistic molecular devices. The detailed numerical procedures and results are described in Sec. V. Discussion and summary are given in Sec. VI.

II. HOLOGRAPHIC ELECTRON DENSITY THEOREM

As early as in 1981, Riess and Münch²⁰ discovered the holographic electron density theorem which states that any nonzero volume piece of the ground-state electron density determines the electron density of a molecular system. This is based on the fact that the electron density functions of atomic and molecular eigenfunctions are real analytic away from nuclei. In 1999 Mezey extended the holographic electron density theorem.²¹ And in 2004, Fournais *et al.* proved again the real analyticity of the electron density functions of any atomic or molecular eigenstates.²² Therefore, for a time-independent real physical system made of atoms and molecules, its electron density function is real analytic (except at nuclei) when the system is in its ground state, any of its excited eigenstates, or any state which is a linear combination of a finite number of its eigenstates; and the ground-state

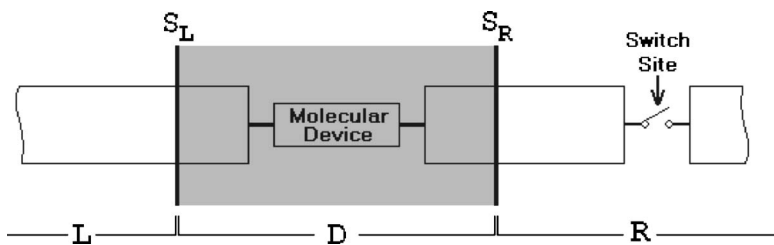


FIG. 1. Schematic representation of the experimental setup for quantum transport through a molecular device.

electron density on any finite subsystem determines completely the electronic properties of the entire system.

As for time-dependent systems, the issue was less clear. Although it seems intuitive that its electron density function is real analytic (except for isolated points in space-time), it becomes quite difficult to prove the analyticity rigorously. Fortunately, we are able to establish a one-to-one correspondence between the electron density function of any finite subsystem and the external potential field which is real analytic in both t space and \mathbf{r} space.²³

Theorem. If the electron density function of a real finite physical system at t_0 , $\rho(\mathbf{r}, t_0)$, is real analytic in \mathbf{r} space, the corresponding wave function is $\Phi(t_0)$, and the system is subjected to a real analytic (in both t space and \mathbf{r} space) external potential field $v(\mathbf{r}, t)$, the time-dependent electron density function on any finite subspace D , $\rho_D(\mathbf{r}, t)$, has a one-to-one correspondence with $v(\mathbf{r}, t)$ and determines uniquely all electronic properties of the entire time-dependent system.

Proof. Let $v(\mathbf{r}, t)$ and $v'(\mathbf{r}, t)$ be two real analytic potentials in both t space and \mathbf{r} space which differ by more than a constant at any time $t \geq t_0$, and their corresponding electron density functions are $\rho(\mathbf{r}, t)$ and $\rho'(\mathbf{r}, t)$, respectively. Therefore, there exists a minimal nonnegative integer k such that the k th order derivative differentiates these two potentials at t_0 :

$$\left. \frac{\partial^k}{\partial t^k} [v(\mathbf{r}, t) - v'(\mathbf{r}, t)] \right|_{t=t_0} \neq \text{const.} \quad (1)$$

Following exactly Eqs. (3)–(6) of Ref. 3, we have

$$\left. \frac{\partial^{k+2}}{\partial t^{k+2}} [\rho(\mathbf{r}, t) - \rho'(\mathbf{r}, t)] \right|_{t=t_0} = -\nabla \cdot \mathbf{u}(\mathbf{r}), \quad (2)$$

where

$$\mathbf{u}(\mathbf{r}) = \rho(\mathbf{r}, t_0) \nabla \left\{ \left. \frac{\partial^k}{\partial t^k} [v(\mathbf{r}, t) - v'(\mathbf{r}, t)] \right|_{t=t_0} \right\}. \quad (3)$$

Due to the analyticity of $\rho(\mathbf{r}, t_0)$, $v(\mathbf{r}, t)$, and $v'(\mathbf{r}, t)$, $\nabla \cdot \mathbf{u}(\mathbf{r})$ is also real analytic in \mathbf{r} space. It has been proven in Ref. 3 that it is impossible to have $\nabla \cdot \mathbf{u}(\mathbf{r}) = 0$ on the entire \mathbf{r} space. Therefore it is also impossible that $\nabla \cdot \mathbf{u}(\mathbf{r}) = 0$ everywhere in D because of analytical continuation of $\nabla \cdot \mathbf{u}(\mathbf{r})$. Note that $\rho_D(\mathbf{r}, t) = \rho(\mathbf{r}, t)$ for $\mathbf{r} \in D$. We have thus

$$\left. \frac{\partial^{k+2}}{\partial t^{k+2}} [\rho_D(\mathbf{r}, t) - \rho'_D(\mathbf{r}, t)] \right|_{t=t_0} \neq 0 \quad (4)$$

for $\mathbf{r} \in D$. This confirms the existence of a one-to-one correspondence between $v(\mathbf{r}, t)$ and $\rho_D(\mathbf{r}, t)$. $\rho_D(\mathbf{r}, t)$ thus deter-

mines uniquely all electronic properties of the entire system. This completes the proof of the theorem.

Note that if $\Phi(t_0)$ is the ground state, any excited eigenstate, or any state being a linear combination of a finite number of eigenstates of a time-independent Hamiltonian, the prerequisite condition in the theorem that the electron density function $\rho(\mathbf{r}, t_0)$ be real analytic is automatically satisfied, as proven in Ref. 22. In particular, if the electron density function at $t=t_0$, $\rho(\mathbf{r}, t_0)$, corresponds to a ground state, it is guaranteed that $\rho_D(\mathbf{r}, t)$ of the subsystem D determines all physical properties of the entire system at any time t , otherwise based on the Runge-Gross theorem,³ the system properties also have a functional dependence on the initial state $\Phi(t_0)$. In our works, we usually start from a ground state, and then switch on external potentials to investigate the dynamic response of the reduced system. Therefore, $\rho_D(\mathbf{r}, t)$ determines uniquely all physical properties of the open electronic systems.

According to the theorem, the electron density function of any subsystem determines all the electronic properties of the entire time-dependent physical system. This proves in principle the existence of a TDDFT formalism for open electronic systems. All one needs to know is the electron density function of the reduced system.

III. FIRST-PRINCIPLES FORMALISM

A. Equation of motion

Figure 1 depicts an open electronic system. Region D is the reduced system of our interests, and the electrodes L and R are the environment. Altogether D , L , and R form the entire system. Taking Fig. 1 as an example, we develop a practical DFT formalism for the open systems. Within the TDDFT formalism, a closed EOM has been derived for the reduced single-electron density matrix $\sigma(t)$ of the entire system:²⁴

$$i\dot{\sigma}(t) = [h(t), \sigma(t)], \quad (5)$$

where $h(t)$ is the KS Fock matrix of the entire system, and the square bracket on the right-hand side (RHS) denotes a commutator. The matrix element of σ is defined as $\sigma_{ij}(t) = \langle a_j^\dagger(t) a_i(t) \rangle$, where $a_i(t)$ and $a_j^\dagger(t)$ are the annihilation and creation operators for atomic orbitals i and j at time t , respectively. Fourier transformed into frequency domain while considering linear response only, Eq. (5) leads to the conventional Casida's equation.²⁵ Expanded in the atomic orbital basis set, the matrix representation of σ can be partitioned as

$$\sigma = \begin{bmatrix} \sigma_L & \sigma_{LD} & \sigma_{LR} \\ \sigma_{DL} & \sigma_D & \sigma_{DR} \\ \sigma_{RL} & \sigma_{RD} & \sigma_R \end{bmatrix}, \quad (6)$$

where σ_L , σ_R , and σ_D represent the diagonal blocks corresponding to the left lead L , the right lead R , and the device region D , respectively; σ_{LD} is the off-diagonal block between L and D ; and σ_{RD} , σ_{LR} , σ_{DL} , σ_{DR} , and σ_{RL} are similarly defined. The KS Fock matrix h can be partitioned in the same way with σ replaced by h in Eq. (6). Thus, the EOM for σ_D can be written as

$$\begin{aligned} i\dot{\sigma}_D &= [h_D, \sigma_D] + \sum_{\alpha=L,R} (h_{D\alpha}\sigma_{\alpha D} - \sigma_{D\alpha}h_{\alpha D}) \\ &= [h_D, \sigma_D] - i \sum_{\alpha=L,R} Q_\alpha, \end{aligned} \quad (7)$$

where Q_L (Q_R) is the dissipation term due to L (R). With the reduced system D and the leads L/R spanned respectively by atomic orbitals $\{l\}$ and single-electron states $\{k_\alpha\}$, Eq. (7) is equivalent to

$$i\dot{\sigma}_{nm} = \sum_{l \in D} (h_{nl}\sigma_{lm} - \sigma_{nl}h_{lm}) - i \sum_{\alpha=L,R} Q_{\alpha,nm}, \quad (8)$$

$$Q_{\alpha,nm} = i \sum_{k_\alpha \in \alpha} (h_{nk_\alpha}\sigma_{k_\alpha m} - \sigma_{nk_\alpha}h_{k_\alpha m}), \quad (9)$$

where m and n correspond to the atomic orbitals in region D ; k_α corresponds to an electronic state in the electrode α ($\alpha = L$ or R). h_{nk_α} is the coupling matrix element between the atomic orbital n and the electronic state k_α . The transient current through the interfaces S_L or S_R (see Fig. 1) can be evaluated as follows:

$$\begin{aligned} J_\alpha(t) &= - \int_\alpha d\mathbf{r} \frac{\partial}{\partial t} \rho(\mathbf{r}, t) = - \sum_{k_\alpha \in \alpha} \frac{d}{dt} \sigma_{k_\alpha k_\alpha}(t) \\ &= i \sum_{l \in D} \sum_{k_\alpha \in \alpha} (h_{k_\alpha l} \sigma_{lk_\alpha} - \sigma_{k_\alpha l} h_{lk_\alpha}) \\ &= - \sum_{l \in D} Q_{\alpha, ll} = - \text{tr}[Q_\alpha(t)]. \end{aligned} \quad (10)$$

Since the dissipation term $Q_\alpha(t)$ is not known *a priori*, Eq. (7) is not self-closed. Therefore, at this stage EOM (7) cannot be solved straightforwardly to obtain the transient dynamics of the reduced system D .

According to the holographic electron density theorem of time-dependent physical systems, all physical quantities are explicit or implicit functionals of the electron density in the reduced system D , $\rho_D(\mathbf{r}, t)$. Q_α of Eq. (7) is thus also a functional of $\rho_D(\mathbf{r}, t)$. Therefore, Eq. (7) can be recast into a formally closed form,

$$i\dot{\sigma}_D = [h_D[t; \rho_D(\mathbf{r}, t)], \sigma_D] - i \sum_{\alpha=L,R} Q_\alpha[t; \rho_D(\mathbf{r}, t)]. \quad (11)$$

It would thus be much more efficient integrating Eq. (11) than solving Eq. (8), provided that $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ or its approximation is known. We therefore have a practical formalism for any open electronic systems. Neglecting

$Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ from Eq. (11) leads to the conventional TD-DFT formulation²⁴ for the isolated reduced system, while $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ accounts for the dissipative interactions between D and L or R . Equation (11) is the TDDFT EOM for open electronic systems, and is formally analogous to the master equations derived for the system reduced density matrix in conventional QDT.²⁶

Our formalism is similar in its form to one of our early works, in which a dynamic mean-field theory for dissipative interacting many-electron systems was developed.^{27,28} An EOM for the reduced single-electron density matrix was derived to simulate the excitation and nonradiative relaxation of a molecule embedded in a thermal bath. This is in analogy to our case although our environment is actually a fermion bath instead of a boson bath. More importantly, the number of electrons in the reduced system is conserved in Refs. 27 and 28 while in our case it is not.

Burke *et al.* extended TDDFT to include electronic systems interacting with phonon baths,¹⁹ they proved the existence of a one-to-one correspondence between $v(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$ under the condition that the dissipative interactions (denoted by a superoperator \mathcal{C} in Ref. 19) between electrons and phonons are fixed. In our case since the electrons can move in and out of the reduced system, the number of the electrons in the reduced system is not conserved. In addition, the dissipative interactions can be determined in principle by the electron density of the reduced system. We do not need to stipulate that the dissipative interactions with the environment are fixed as Burke *et al.* And the only information we need is the electron density of the reduced system. In the frozen DFT approach²⁹ an additional kinetic energy functional term caused by the environment was introduced to account for the interaction between the system and the environment. This additional term is included in $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ of Eq. (11).

B. The dissipation term Q_α

The challenge now is to express $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$. Based on the Keldysh nonequilibrium Green's function (NEGF) formalism,^{30,31} we have [Appendix A, cf. Eq. (9)]

$$\begin{aligned} Q_{\alpha,nm}(t) &= - \sum_{l \in D} \int_{-\infty}^{\infty} d\tau [G_{nl}^<(t, \tau) \Sigma_{\alpha,lm}^a(\tau, t) \\ &\quad + G_{nl}^r(t, \tau) \Sigma_{\alpha,lm}^<(\tau, t) + \text{H.c.}], \end{aligned} \quad (12)$$

where G_D^r and $G_D^<$ are the retarded and lesser Green's functions of the reduced system, and Σ_α^a and $\Sigma_\alpha^<$ are the advanced and lesser self-energies due to the lead α (L or R), respectively. It is important to emphasize that Eq. (12) is derived from the initial ground state at $t = -\infty$ when the device and leads are completely isolated, denoted by Φ_0 . This corresponds to the partitioned scheme developed by Caroli *et al.*³² The dissipation term Q_α can also be derived from the ground state of the fully connected system at $t = t_0$, denoted by Ψ_0 , as follows (see Appendix B for details),

$$Q_{\alpha, nm}(t) = \left\{ Q_{\alpha, nm}^0(t) - \sum_{l \in D} \int_{t_0^+}^t dt_1 \Gamma_{nl}^r(t, \tau) \Sigma_{\alpha, lm}^<(t, \tau) + G_{nl}^<(t, \tau) \Sigma_{\alpha, lm}^a(\tau, t) \right\} + \text{H.c.}, \quad (13)$$

where t_0^+ is the time immediately after t_0 , and the first term on the RHS, $Q_{\alpha, nm}^0(t)$, arises due to the initial couplings between the reduced system and the environment. Equation (13) thus conforms with the partition-free scheme proposed by Cini,³³ and the relevant Green's functions and self-energies are defined differently from those in Eq. (12), since they are associated with different reference ground states.

Based on Gell-Mann and Low theorem,³⁴ in most cases Ψ_0 can be reached from Φ_0 by adiabatically turning on the couplings between the device and the leads from $t = -\infty$ to t_0 . In these circumstances, the partitioned and partition-free schemes are formally equivalent, since the history of the

couplings between D and L or R only determines Ψ_0 and its corresponding electron density function $\rho(\mathbf{r}, t_0)$, and does not influence the time evolution of the reduced system afterwards. Of course, there might be few exceptional cases where the turn on of the couplings between D and L or R results in only an excited eigenstate at t_0 . In these cases, in principle we need to resort to Eq. (13), while in practice Eq. (12) can be viewed as an approximation to Eq. (13) since it is much more convenient for numerical implementations.

C. Solution for steady-state current

In cases where steady states can be reached, the system-bath coupling, $\Gamma_{nm}^{k\alpha}(t, \tau) \equiv h_{nk_\alpha}(t) h_{k_\alpha m}(\tau)$, becomes asymptotically time independent as $t, \tau \rightarrow +\infty$. The Green's functions and self-energies for the reduced system D rely simply on the difference of the two time variables,³⁵ i.e., $G_D(t, \tau) \sim G_D(t - \tau)$ and $\Sigma(t, \tau) \sim \Sigma(t - \tau)$, and thus we have

$$G_{nm}^<(t, \tau) = \sum_{p, q \in D} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 G_{np}^r(t, t_1) \Sigma_{pq}^<(t_1, t_2) G_{qm}^a(t_2, \tau) = i \sum_{p, q \in D} \sum_{\alpha=L, R} \sum_{l_\alpha \in \alpha} f_{l_\alpha}^\alpha \left[\int_{-\infty}^{\infty} dt_1 e^{-i\epsilon_l^\alpha t_1} G_{np}^r(t - t_1) \right] \Gamma_{pq}^{l_\alpha} \times \left[\int_{-\infty}^{\infty} dt_2 e^{i\epsilon_l^\alpha t_2} G_{qm}^a(t_2 - \tau) \right] = i \sum_{p, q \in D} \sum_{\alpha=L, R} \sum_{l_\alpha \in \alpha} f_{l_\alpha}^\alpha e^{-i\epsilon_l^\alpha(t-\tau)} G_{np}^r(\epsilon_l^\alpha) \Gamma_{pq}^{l_\alpha} G_{qm}^a(\epsilon_l^\alpha), \quad (14)$$

$$G_D^{r,a}(\epsilon) = [\epsilon I - h_D(\infty) - \Sigma^{r,a}(\epsilon)]^{-1}, \quad (15)$$

$$\Sigma_{nm}^{r,a}(\epsilon) = \sum_{\alpha=L, R} \sum_{l \in \alpha} \Gamma_{nm}^{l_\alpha} (\epsilon - \epsilon_l^\alpha \pm i\delta)^{-1}, \quad (16)$$

where I is an identity matrix, δ is an infinitesimal positive number, and f_l^α is the occupation number of the single-electron state l_α of the isolated lead α (L or R). The steady-state current can thus be explicitly expressed by combining Eqs. (14)–(16),

$$J_L(\infty) = -J_R(\infty) = - \sum_{n \in D} Q_{L, nm}(\infty) = 2\pi \left(\sum_{k \in L} f_k^L \sum_{l \in R} \delta(\epsilon_l^R - \epsilon_k^L) \text{tr} [G_D^r(\epsilon_k^L) \Gamma^{lR} G_D^a(\epsilon_k^L) \Gamma^{kL}] - \sum_{l \in R} f_l^R \sum_{k \in L} \delta(\epsilon_k^L - \epsilon_l^R) \text{tr} [G_D^r(\epsilon_l^R) \Gamma^{lR} G_D^a(\epsilon_l^R) \Gamma^{kL}] \right) = \int [f^L(\epsilon) - f^R(\epsilon)] T(\epsilon) d\epsilon, \quad (17)$$

$$T(\epsilon) = 2\pi \eta_L \eta_R \text{tr} [G_D^r(\epsilon) \Gamma^R(\epsilon) G_D^a(\epsilon) \Gamma^L(\epsilon)]. \quad (18)$$

Here $T(\epsilon)$ is the KS transmission coefficient, $f^\alpha(\epsilon)$ is the Fermi distribution function, and $\eta_\alpha(\epsilon) \equiv \sum_{k \in \alpha} \delta(\epsilon - \epsilon_k^\alpha)$ is the density of states (DOS) for the lead α (L or R). Equation (17) appears formally analogous to the Landauer formula^{36,37}

adopted in the conventional DFT-NEGF formalism.^{9,11} However, to obtain the correct steady current, the nonequilibrium effects need to be properly accounted for. This may be accomplished by substituting the asymptotic values of the TD-DFT XC potential for the ground-state DFT counterpart in Eq. (17).

D. Self-energy functionals

Due to its convenience for practical implementation, Eq. (12) is adopted in our formalism. The Green's functions G_D^r and $G_D^<$ in Eq. (12) can be calculated via the following EOMs if Σ_α^a and $\Sigma_\alpha^<$ are known,

$$i \frac{\partial G_{nm}^r(t, \tau)}{\partial t} = \delta(t - \tau) \delta_{nm} + \sum_{l \in D} h_{nl}(t) G_{lm}^r(t, \tau) + \sum_{l \in D} \int_{-\infty}^{\infty} d\bar{t} \Sigma_{nl}^r(t, \bar{t}) G_{lm}^r(\bar{t}, \tau), \quad (19)$$

$$i \frac{\partial G_{nm}^<(t, \tau)}{\partial t} = \sum_{l \in D} \int_{-\infty}^{\infty} d\bar{t} [\Sigma_{nl}^<(t, \bar{t}) G_{lm}^a(\bar{t}, \tau) + \Sigma_{nl}^r(t, \bar{t}) \times G_{lm}^<(\bar{t}, \tau)] + \sum_{l \in D} h_{nl}(t) G_{lm}^<(t, \tau), \quad (20)$$

where $\Sigma^r = \sum_{\alpha=L, R} (\Sigma_\alpha^a)^\dagger$, $\Sigma^< = \sum_{\alpha=L, R} \Sigma_\alpha^<$, and $G_D^a = (G_D^r)^\dagger$. The key quantities for the evaluation of $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ are thus

the self-energies Σ_α^a and $\Sigma_\alpha^<$. According to our theorem, Σ_α^a and $\Sigma_\alpha^<$ are in principle functionals of $\rho_D(\mathbf{r}, t)$. Therefore, instead of finding $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ directly, we need now find the density functionals $\Sigma_\alpha^a[\tau, t; \rho_D(\mathbf{r}, t)]$ and $\Sigma_\alpha^<[\tau, t; \rho_D(\mathbf{r}, t)]$. By definition the self-energies are functionals of the electron density function of the entire system, $\rho = (\rho_D, \rho_\alpha)$:

$$\Sigma_\alpha^a[\tau, t; \rho] \equiv i\vartheta(t-\tau)h[\tau; \rho] \exp\left\{i \int_\tau^t h_\alpha[\bar{t}; \rho_\alpha] d\bar{t}\right\} h[t; \rho], \quad (21)$$

$$\Sigma_\alpha^<[\tau, t; \rho] \equiv ih[\tau; \rho] f^\alpha(h_\alpha[-\infty; \rho_\alpha]) \times \exp\left\{i \int_\tau^t h_\alpha[\bar{t}; \rho_\alpha] d\bar{t}\right\} h[t; \rho], \quad (22)$$

where $\vartheta(t-\tau)$ is the Heaviside step function, ρ_α is the electron density function in lead α , h_α is the Kohn-Sham Fock matrix of the isolated lead α , and f^α is the Fermi distribution function for α (L or R). Based on our theorem, ρ_α are determined uniquely by ρ_D via certain continuation (CT) operation, i.e.,

$$\rho_D(\mathbf{r}, t) \xrightarrow{\text{CT}} \rho_\alpha(\mathbf{r}, t), \quad (23)$$

$$\rho_\alpha(\mathbf{r}, t) = \rho_\alpha^{\text{CT}}[\mathbf{r}, t; \rho_D(\mathbf{r}, t)]. \quad (24)$$

We obtain thus the following functionals,

$$\Sigma_\alpha^a(\tau, t) = \Sigma_\alpha^a[\tau, t; \rho_D, \rho_\alpha^{\text{CT}}[\rho_D]], \quad (25)$$

$$\Sigma_\alpha^<(\tau, t) = \Sigma_\alpha^<[\tau, t; \rho_D, \rho_\alpha^{\text{CT}}[\rho_D]]. \quad (26)$$

Note that the CT operation is case dependent, and often approximate in practice. For the system depicted in Fig. 1, the CT operation from ρ_D to ρ_α may be approximated by a translation over repeating unit cells if the bulk electrodes are periodic, i.e.,

$$\rho_\alpha(\mathbf{r}, t) = \rho_\alpha^{\text{CT}}[\rho_D] \approx \rho_D(\mathbf{r} + N\mathbf{R}, t), \quad (27)$$

where $t=0$ refers to the initial time when the entire connected system is in its ground state, \mathbf{R} is the base vector perpendicular to the interface S_α for the lead α , and N denotes an integer which makes the translated vector $\mathbf{r} + N\mathbf{R}$ to be inside the reduced system D as well as near the interfaces S_α . To ensure the accuracy of such an approximate CT operation, it is vital to include enough portions of electrodes into the region D , so that the electron density function near the interfaces S_α takes correctly the bulk values.

Of course, there could be cases that the approximate $\rho_\alpha^{\text{CT}}[\rho_D]$ may deviate drastically from their exact values some distance away from the boundary. Usually Σ_α^a and $\Sigma_\alpha^<$ depend mostly on the electron density near the boundary where the approximate $\rho_\alpha^{\text{CT}}[\rho_D]$ agree best with the correct ρ_α . The resulting $\Sigma_\alpha^a[\rho_D, \rho_\alpha^{\text{CT}}[\rho_D]]$ and $\Sigma_\alpha^<[\rho_D, \rho_\alpha^{\text{CT}}[\rho_D]]$ thus provide reasonable approximations for their exact counterparts. For

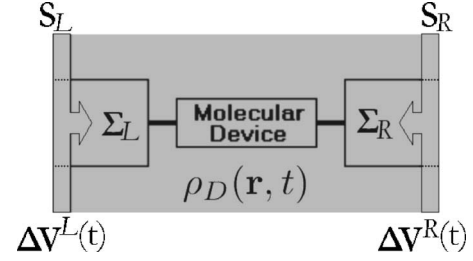


FIG. 2. The molecular device region D is subject to the boundary conditions $\Delta V^L(t)$ and $\Delta V^R(t)$ at the interfaces S_L and S_R . The interactions between the region D and the lead L and R are accounted for by the self-energy functionals Σ_L and Σ_R , respectively.

cases where the self-energies happen to rely heavily on ρ_α far away from D , the approximated CT breaks down, and our method fails to be applicable.

Given $\Sigma_\alpha^a[\rho_D]$ and $\Sigma_\alpha^<[\rho_D]$ how do we solve the EOM (11) in practice? Again take the molecular device shown in Fig. 1 as an example. We focus on the reduced system D as depicted in Fig. 2, and integrate the EOM (11) directly by satisfying the boundary conditions at S_L and S_R . $\Delta V^L(t)$ and $\Delta V^R(t)$ are the bias voltages applied on L and R , respectively, and serve as the boundary conditions at S_L and S_R , respectively. At $t \rightarrow -\infty$, $\Delta V^L = \Delta V^R = 0$, and $\Delta V^L(t)$ and $\Delta V^R(t)$ are turned on near $t=0$. We need thus integrate Eq. (11) together with a Poisson equation for the Coulomb potential inside the device region D subject to the boundary condition determined by the potentials at S_L and S_R . It is important to point out that $Q_\alpha[t; \rho_D(\mathbf{r}, t)]$ is actually a nearly local quantity of the reduced system through the local coupling matrix terms $h_{D\alpha}$ ($\alpha=L$ or R). In this sense, our formalism for open electronic systems is not in conflict with the ‘‘nearsightedness’’ concept of Kohn.³⁸

IV. TWO APPROXIMATE SCHEMES FOR SELF-ENERGY DENSITY FUNCTIONALS

A. Complete second-order approximation for dissipative functional

Equations (12) and (13) appear quite complicated. To have an unambiguous interpretation of the dissipation term Q_α , we further assume the KS Fock matrix h_D is time-independent and treat $G_D^<(t, \tau)$ by means of CS QDT.²⁶ Equation (12) is thus simplified to be (see Appendix C for details)

$$Q_\alpha(t) = i\{[\tilde{\Sigma}_\alpha^>(h_D), \sigma_D]^\dagger + [\tilde{\Sigma}_\alpha^<(h_D), \bar{\sigma}_D]^\dagger\}, \quad (28)$$

where $\bar{\sigma}_D \equiv I - \sigma_D$ is the reduced single-hole density matrix of the reduced system. On the RHS of Eq. (28) a new commutator has been introduced for arbitrary operators A and B :

$$[A, B]^\dagger \equiv AB - B^\dagger A^\dagger. \quad (29)$$

$\tilde{\Sigma}_\alpha^<,>$ are the causality-transformed counterparts of $\Sigma_\alpha^<,>$, with $\Sigma_\alpha^<,>(t, \tau) = \tilde{\Sigma}_\alpha^<,>(t-\tau)$ presumed, i.e.,

$$\tilde{\Sigma}_{\alpha}^{<, >}(h_D) \equiv \int_0^{\infty} dt e^{ih_D t} \Sigma_{\alpha}^{<, >}(t) = \mp \Gamma_{\alpha}^{(\pm)}(h_D) \pm i\Lambda_{\alpha}^{(\pm)}(h_D), \quad (30)$$

where $\Gamma_{\alpha}^{(\pm)}(h_D)$ and $\Lambda_{\alpha}^{(\pm)}(h_D)$ are real symmetric matrices, and associated with each other via the Kramers-Kronig relation.²⁶ Therefore, Eq. (28) can be expanded as

$$Q_{\alpha}(t) = i[\Gamma_{\alpha}^{(-)}(h_D), \sigma_D] + \{\Lambda_{\alpha}^{(-)}(h_D), \sigma_D\} - i[\Gamma_{\alpha}^{(+)}(h_D), \bar{\sigma}_D] - \{\Lambda_{\alpha}^{(+)}(h_D), \bar{\sigma}_D\}. \quad (31)$$

The physical meaning of Eq. (31) is clear and intuitive: the first and third terms on its RHS account for the energy shifting of occupied and virtual orbitals of the reduced system due to the couplings with the lead α , respectively; and the second and fourth terms on its RHS are responsible for the level broadening of occupied and virtual orbitals in D due to the lead α while contributing to the transient current, respectively. The second term accounts for the electrons leaving the device region, and the fourth term describes that the holes hop onto the electrodes or the electrons enter the device region from the electrodes.

B. Solution for transient current with WBL approximation and test on a model system

To simplify the solutions of Eqs. (19) and (20), the WBL approximation^{39,40} may be adopted besides the approximate CT operation [cf. Eq. (27)], which involves the following assumptions for the leads: (i) their bandwidths are assumed to be infinitely large, such that the summation over all the single-electron states in the leads can be replaced by an integration over the entire energy range, i.e., $\sum_{k \in \alpha} \rightarrow \int_{-\infty}^{\infty} d\epsilon \eta_{\alpha}(\epsilon)$, (ii) their linewidths, $\Lambda_k^{\alpha}(t, \tau)$, defined by the DOS at S_L or S_R times the system-bath couplings, i.e., $\Lambda_k^{\alpha}(t, \tau) \equiv \pi \eta_{\alpha}(\epsilon_k^{\alpha}) \Gamma^{k\alpha}(t, \tau)$, are treated as energy independent, i.e., $\Lambda_k^{\alpha}(t, \tau) \approx \Lambda^{\alpha}(t, \tau) \approx \Lambda^{\alpha}$, and (iii) the level shifts of L or R are taken as a constant for all energy levels, i.e., $\Delta \epsilon_k^{\alpha}(t) \approx \Delta \epsilon^{\alpha}(t) = -\Delta V^{\alpha}(t)$, where $\Delta V^{\alpha}(t)$ are the bias voltages applied on L or R at time t .

Within the WBL approximation, the self-energy functionals can be expressed by²³

$$\Sigma_{\alpha, nm}^{\alpha}(\tau, t) = i\delta(t - \tau) \Lambda_{nm}^{\alpha}[\rho_D], \quad (32)$$

$$\begin{aligned} \Sigma_{\alpha, nm}^{<}(\tau, t) &= \frac{2i}{\pi} \exp\left\{i \int_t^{\tau} \Delta V^{\alpha}(\bar{t}) d\bar{t}\right\} \Lambda_{nm}^{\alpha}[\rho_D] \\ &\times \left[\int_{-\infty}^{+\infty} f^{\alpha}(\epsilon) e^{i\epsilon(t-\tau)} d\epsilon \right]. \end{aligned} \quad (33)$$

Here $\Delta V^{\alpha}(\bar{t})$ is the bias voltage applied on the lead α , and $\Lambda^{\alpha}[\rho_D]$ is the linewidth matrix due to lead α ,²³

$$\begin{aligned} \Lambda_{nm}^{\alpha}[\rho_D] &= \pi \eta_{\alpha}(\epsilon_f) \langle h_{nk_f}[\rho_D, \rho_D(\mathbf{r} + N\mathbf{R})] \\ &\times h_{k_f m}[\rho_D, \rho_D(\mathbf{r} + N\mathbf{R})] \rangle, \end{aligned} \quad (34)$$

where $\eta_{\alpha}(\epsilon_f)$ is the density of states for α at its Fermi energy

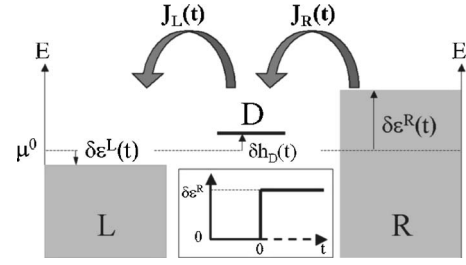


FIG. 3. Model system for the test of the WBL self-energy functionals where a single site spans the device region D . Transient currents through leads L and R , $J_L(t)$ and $J_R(t)$, are simulated. The inset shows the time-dependent level shift of lead R .

ϵ_f , k_f is a surface state of α at ϵ_f , and $\langle \cdots \rangle$ denotes the average over all surface states at ϵ_f . Equations (32)–(34) provide thus the explicit dependence of Σ_{α}^{α} and $\Sigma_{\alpha}^{<}$ on $\rho_D(\mathbf{r}, t)$.

Note that $\Sigma_{\alpha}^{<}[\rho_D]$ depends on the applied voltage $\Delta V^{\alpha}(t)$ explicitly. In principle $\Delta V^{\alpha}(t)$ is a functional of $\rho_D(\mathbf{r}, t)$ as well. $\rho_D(\mathbf{r}, t)$ is unknown and needs to be solved. The potential $v(\mathbf{r})$ in DFT formalism, which includes the potentials from nuclei and external sources, is a functional of electron density $\rho(\mathbf{r})$. In any practical implementation of DFT, $v(\mathbf{r})$ is given and used to solve for $\rho(\mathbf{r})$, instead of determining $v(\mathbf{r})$ from $\rho(\mathbf{r})$. In our formalism $\Delta V^{\alpha}(t)$ is given as a known function and used to determine $\rho_D(\mathbf{r}, t)$ in the same fashion.

Based on Eqs. (32)–(34), the dissipation term within the WBL approximation, Q_{α}^{WBL} , can be obtained readily as follows (see Appendix D for detailed derivations),

$$Q_{\alpha}^{\text{WBL}}(t) = K^{\alpha}(t) + \{\Lambda^{\alpha}[\rho_D], \sigma_D\}. \quad (35)$$

Here the curly bracket on the RHS denotes an anticommutator, and $K^{\alpha}(t)$ is a Hermitian matrix,

$$\begin{aligned} K^{\alpha}(t) &= -\frac{2i}{\pi} \left\{ U^{\alpha}(t) \int_{-\infty}^{\mu^0} \frac{d\epsilon e^{i\epsilon t}}{\epsilon - h_D(0) + i\Lambda} + \int_{-\infty}^{\mu^0} [I - U^{\alpha}(t) e^{i\epsilon t}] \right. \\ &\times \left. \frac{d\epsilon}{\epsilon - h_D(t) + i\Lambda + \Delta \epsilon^{\alpha}(t)} \right\} \Lambda^{\alpha} + \text{H.c.}, \end{aligned} \quad (36)$$

where μ^0 is the chemical potential of the entire system, the overall linewidth $\Lambda = \sum_{\alpha} \Lambda^{\alpha}$, and the effective propagator of the reduced system $U^{\alpha}(t)$ is

$$U^{\alpha}(t) = e^{-i \int_0^t [h_D(\tau) - i\Lambda - \Delta \epsilon^{\alpha}(\tau)] d\tau}. \quad (37)$$

C. Numerical test of wide-band limit approximation

The WBL approximated self-energy functionals are then tested by calculations on a model system which has previously been investigated by Maciejko, Wang, and Guo.⁴⁰ In this model system the device region D consists of a single site spanned by only one atomic orbital (see Fig. 3). Exact transient current driven by a step voltage pulse has been obtained from NEGF simulations,⁴⁰ and the authors concluded that the WBL approximation yields reasonable results provided that the bandwidths of the leads are five times or larger than the coupling strength between D and L or R . The

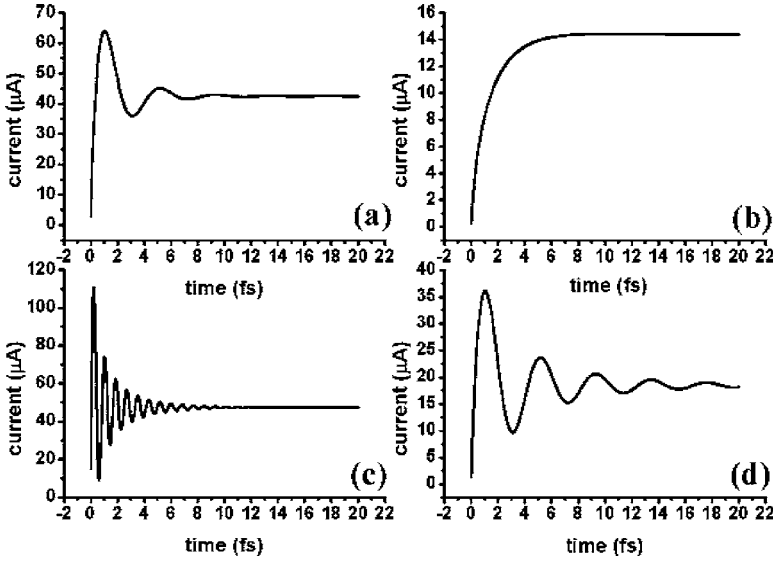


FIG. 4. The calculated transient current through S_R within the WBL scheme. We set $\mu^0 = h_D(0) = 0$ for the ground state; and $\Delta\epsilon^L(t) = 0$ and $\Delta\epsilon^R(t) = \Delta\epsilon^R(1 - e^{-t/a})$ after switch on. The four panels show different cases where (a) $\Delta\epsilon^R = 2$ eV, $\Lambda^L = \Lambda^R = 0.1$ eV; (b) $\Delta\epsilon^R = 0.2$ eV, $\Lambda^L = \Lambda^R = 0.1$ eV; (c) $\Delta\epsilon^R = 10$ eV, $\Lambda^L = \Lambda^R = 0.1$ eV; and (d) $\Delta\epsilon^R = 2$ eV, $\Lambda^L = \Lambda^R = 0.04$ eV, respectively.

computational details are as follows. The entire system ($L + R + D$) is initially in its ground state with the chemical potential μ^0 . External bias voltages are switched on from the time $t=0$, which results in transient current flows through the leads L and R . $\delta h_D(t) \equiv h_D(t) - h_D(0)$, $\Delta\epsilon^L(t)$, and $\Delta\epsilon^R(t)$ are the level shifts of D , L , and R at time t , respectively. In our works we take $\delta h_D(t) = \frac{1}{2}[\Delta\epsilon^L(t) + \Delta\epsilon^R(t)]$, $\Delta\epsilon^L(t) = 0$, and $\Delta\epsilon^R(t) = \Delta\epsilon^R(1 - e^{-t/a})$, where a is a positive constant. The real analytic level shift $\Delta\epsilon^R(t)$ resembles perfectly a step pulse as $a \rightarrow 0^+$ (see the inset of Fig. 3). The calculation results are demonstrated in Fig. 4. We choose exactly the same parameter set as that adopted for Fig. 2 in Ref. 40, and the resulting transient current, represented by Fig. 4(a), excellently reproduces the WBL result in Ref. 40, although the numerical procedures employed are distinctively different. The comparison confirms evidently the accuracy of our formalism. From Figs. 4(a)–4(c), it is observed that with the same linewidths Λ^α , a larger level shift $\Delta\epsilon^R$ results in a more fluctuating current, whereas by comparing Figs. 4(a) and 4(d) we see that under the same $\Delta\epsilon^R$, the current decays more rapidly to the steady-state value with the larger Λ^α .

By transforming its integrand into a diagonal representation, the integration over energy in Eq. (36) can be carried out readily. Therefore, Q_α^{WBL} are evaluated straightforwardly, which makes the above solution procedures for transient dynamics within the WBL approximation a practical routine for subsequent TDDFT calculations.

V. TDDFT CALCULATIONS OF TRANSIENT CURRENT THROUGH MOLECULAR DEVICES

A. Numerical procedures

With the EOM (11) and the WBL approximation for the self-energy functionals $\Sigma_\alpha^a[\rho_D]$ and $\Sigma_\alpha^<[\rho_D]$, it is now straightforward to investigate the transient dynamics of open electronic systems. All our first-principles calculations are carried out with our software package LODESTAR.⁴¹

The ground-state properties of the reduced system at $t=0$ are determined by following the partitioned scheme ap-

proach adopted in conventional DFT-NEGF method.^{8–10,13} Different from the popular periodic-boundary-condition-based approach,^{10,13,42} what we employ is a molecular-cluster-based technique.⁴¹ The ground-state KS Fock matrix of an extended cluster, covering not only the device region D but also portions of leads L and R , is calculated self-consistently by conventional DFT method with local density approximation (LDA) for the XC functional.² Its diagonal blocks corresponding to the leads L and R are then extracted and utilized to evaluate the surface Green's function of isolated lead α (L or R), $g_\alpha^r = g_\alpha^r[\mu^0; \rho_\alpha^{\text{CT}}[\rho_D]]$, by applying the translational invariance⁴³ [cf. Eq. (27)]. In this way the possible misalignment for the chemical potentials of the isolated leads L and R , especially when they are made of different materials, can be avoided so long as the extended cluster is chosen large enough. In an orthogonal atomic orbital basis set, the linewidths $\Lambda^\alpha[\rho_D]$ within the WBL approximation are obtained from g_α^r via

$$\Lambda^\alpha[\rho_D] = -\text{Im}\{h_{D\alpha} g_\alpha^r[\mu^0; \rho_\alpha^{\text{CT}}[\rho_D]] h_{\alpha D}\}. \quad (38)$$

At $t=0$ the left-hand side (LHS) of the Eq. (11) vanishes. The EOM (11) reduces thus to a nonlinear equation for $\sigma_D(0)$, and can be solved readily by employing the NEGF approach as follows:

$$\sigma_D(0) = \frac{2}{\pi} \int_{-\infty}^{\mu^0} d\epsilon G_D^{r,0}(\epsilon) \Lambda G_D^{a,0}(\epsilon), \quad (39)$$

where

$$G_D^{r,0}(\epsilon) = [G_D^{a,0}(\epsilon)]^\dagger = [\epsilon - h_D(0) + i\Lambda]^{-1}. \quad (40)$$

Equation (39) provides the initial condition for the EOM (11).

The molecular device is switched on by a steplike voltage $\Delta V^R(t) = -\Delta\epsilon^R(t) = \Delta V^R(1 - e^{-t/a})$ applied on the right lead with $a \rightarrow 0^+$ (see the inset of Fig. 3), while $\Delta V^L(t) = 0$. The self-energy functionals $\Sigma_\alpha^a[\rho_D]$ and $\Sigma_\alpha^<[\rho_D]$ can be evaluated through Eqs. (32), (33), and (38). The dynamic response of the reduced system is obtained by solving the EOM (11) in

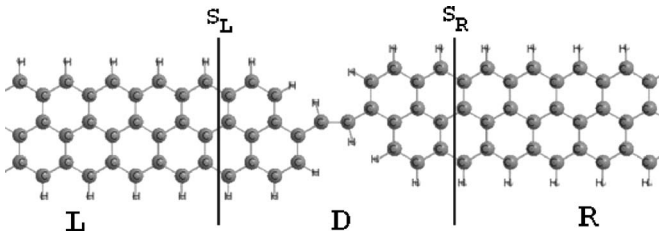


FIG. 5. A graphene-alkene-graphene system adopted in TDDFT calculations.

time domain within the adiabatic local-density approximation (ALDA)²⁵ for the XC functional. The induced KS Fock matrix of the reduced system, $\delta h_D(t) \equiv h_D(t) - h_D(0)$, is comprised of Hartree and XC components,²⁴ i.e.,

$$\delta h_D(t) = \delta h_D^H(t) + \delta h_D^{XC}(t), \quad (41)$$

where

$$\delta h_{ij}^H(t) = \int_D d\mathbf{r} \phi_i^*(\mathbf{r}) \delta v^H(\mathbf{r}, t) \phi_j(\mathbf{r}). \quad (42)$$

Here the Hartree potential $\delta v^H(\mathbf{r}, t)$ satisfies the following Poisson equation for the device region D subject to boundary conditions $\Delta V^\alpha(t)$ at every time t :

$$\begin{aligned} \nabla^2 \delta v^H(\mathbf{r}, t) &= -4\pi \delta \rho_D(\mathbf{r}, t), \\ \delta v^H(\mathbf{r}, t)|_{S_L} &= \Delta V^L(t), \\ \delta v^H(\mathbf{r}, t)|_{S_R} &= \Delta V^R(t). \end{aligned} \quad (43)$$

To save computational resources we calculate $\delta h_D^{XC}(t)$ to its first-order change due to the switch-on potential:

$$\delta h_{ij}^{XC}(t) = \sum_{mn \in D} V_{ijmn}^{XC} [\sigma_{mn}(t) - \sigma_{mn}(0)], \quad (44)$$

$$\begin{aligned} V_{ijmn}^{XC} &= \int_D d\mathbf{r} \phi_m^*(\mathbf{r}) \phi_n(\mathbf{r}) \frac{\delta v^{XC}[\mathbf{r}, t; \rho_D]}{\delta \rho_D(\mathbf{r}, t)} \\ &\quad \times \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}), \end{aligned} \quad (45)$$

where $v^{XC}[\mathbf{r}, t; \rho_D]$ is the XC potential. The reduced system is propagated from $t=0$ following the EOM (11) by the fourth-order Runge-Kutta algorithm⁴⁴ with the time step 0.02 fs. Virtually the same results are yielded by adopting a much smaller time step, which justifies the accuracy of our time-evolution scheme.

B. Calculation on a graphene-alkene-graphene system

A realistic molecular device depicted in Fig. 5 is taken as the open system under investigation. The device region D containing 24 carbon and 12 hydrogen atoms is spanned by the 6-31 Gaussian basis set, i.e., altogether 240 basis functions for the reduced system. The leads are quasi-one-dimensional graphene ribbons with dangling bonds saturated by hydrogen atoms, and the entire system is on a same plane. The extended cluster contains totally 134 atoms.

In Fig. 6 we plot the calculated transient currents through the interfaces S_L and S_R , $J_L(t)$ and $J_R(t)$, under various turn-on voltages. As depicted in Fig. 6, $J_L(t)$ and $J_R(t)$ increase rapidly during the first few fs and then approach gradually towards their steady-state values. This agrees with previous investigations on model systems.^{16,40} The steady currents through S_L and S_R are (a) $-5.9 \mu\text{A}$ and $5.9 \mu\text{A}$, (b) $-14.2 \mu\text{A}$ and $14.2 \mu\text{A}$, (c) $-18.0 \mu\text{A}$ and $18.0 \mu\text{A}$, and (d) $-21.3 \mu\text{A}$ and $21.3 \mu\text{A}$, respectively, and thus cancel each other out exactly, as they should. By comparison of Figs.

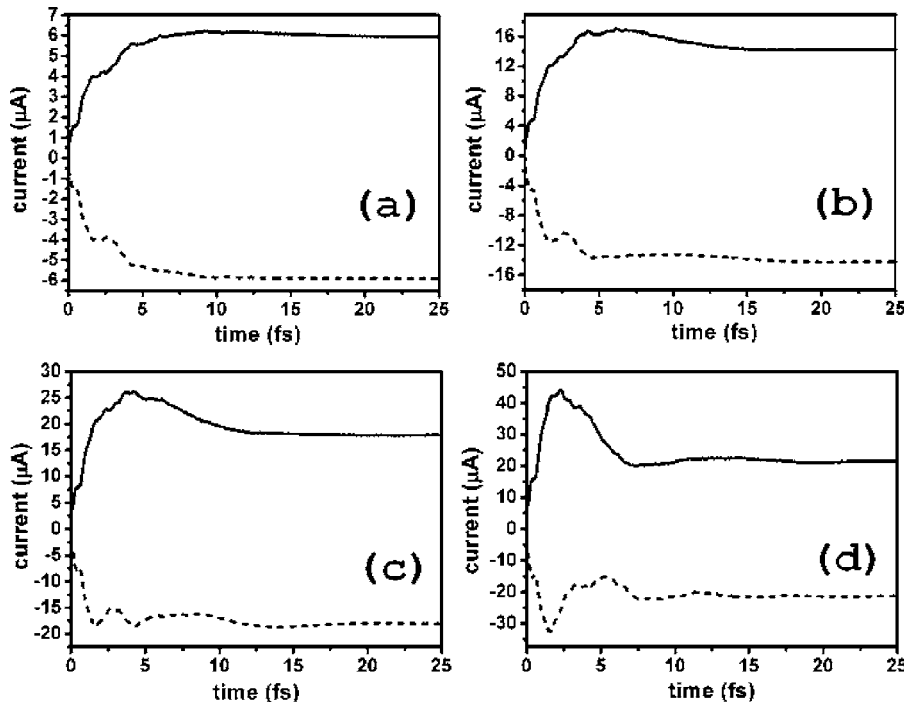


FIG. 6. The solid (dashed) curve represents the transient current through the interface S_R (S_L) of the graphene-alkene-graphene system driven by a steplike voltage applied on the lead R with the amplitude (a) $\Delta V^R = -0.1 \text{ V}$, (b) $\Delta V^R = -0.3 \text{ V}$, (c) $\Delta V^R = -0.5 \text{ V}$, and (d) $\Delta V^R = -1.0 \text{ V}$.

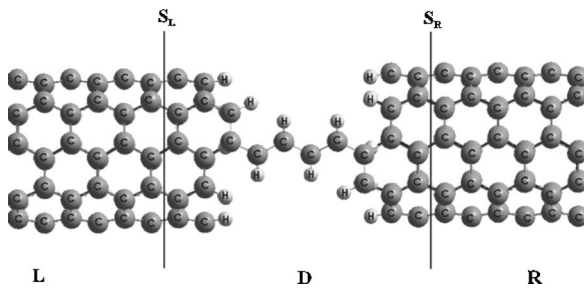


FIG. 7. A CNT-alkene-CNT system adopted in TDDFT calculations.

6(a)–6(d) it is obvious that a larger turn-on voltage results in a more conspicuous overshooting for the transient current. Complex fluctuations are also observed for the time-dependent currents, which are due to the various eigenvalues possessed by the nonnegative definite linewidths Λ^α with their magnitudes ranging from 0 to 4.1 eV, corresponding to various dissipative channels between D and L or R . From Fig. 6, the characteristic switch-on time for the graphene-alkene-graphene system is estimated as about 10–15 fs for applied bias voltages ranging from 0.1 V to 1.0 V. For much higher turn-on voltages the linearized form of $\delta h_D^{XC}(t)$ [Eq. (44)] becomes inadequate, which makes such a TDDFT calculation computationally demanding with our present coding.

It is noted that the reduced system remains in its ground state in absence of an applied bias voltage. This is confirmed by a free propagation for the reduced system. During the course the transient current $J_L(t)$ or $J_R(t)$ vanishes correctly at every time $t > 0$. This thus validates that the WBL approximated self-energy functionals derived from the partitioned

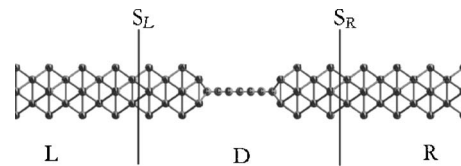


FIG. 9. A linear carbon chain is sandwiched between two Al leads in the (001) direction of bulk Al.

scheme [cf. Eq. (12)] is well adapted to a TDDFT formalism.

C. Calculation on a carbon-nanotubes-alkene-carbon-nanotubes system

The second molecular device we calculate is sketched in Fig. 7, where a linear alkene is connected to semi-infinite single-walled carbon nanotubes (CNT) (5, 5) at its both ends. The device region D consists of 88 carbon and 22 hydrogen atoms, i.e., altogether 836 basis functions for the reduced system. The extended cluster for the ground-state calculation contains 290 atoms in total. The calculated transient currents driven by steplike turn-on voltages $\Delta V^R(t)$ (see the inset of Fig. 3) are plotted in Fig. 8. Here we have set $\Delta V^L=0$. The switch-on time for the CNT-alkene-CNT system is about 10 fs for applied voltages ranging from 0.1 V to 1.0 V.

D. Calculation on an Al-C7-Al system

Another open system adopted in our first-principles calculations is depicted in Fig. 9, where a linear chain of seven carbon atoms is embedded between two semi-infinite Al leads in the (001) direction of bulk Al. The current-voltage characteristics of this Al-C7-Al system with the same geo-

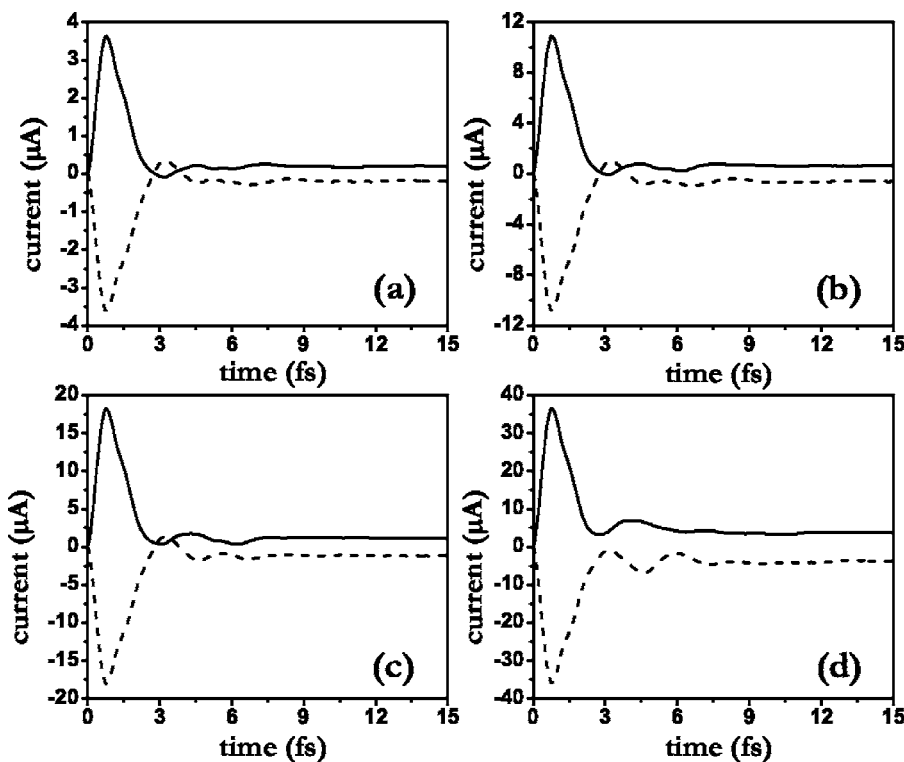


FIG. 8. The solid (dashed) curve represents the transient current through the interface S_R (S_L) of the CNT-alkene-CNT system driven by a steplike voltage applied on the lead R with the amplitude (a) $\Delta V^R=-0.1$ V, (b) $\Delta V^R=-0.3$ V, (c) $\Delta V^R=-0.5$ V, and (d) $\Delta V^R=-1.0$ V.

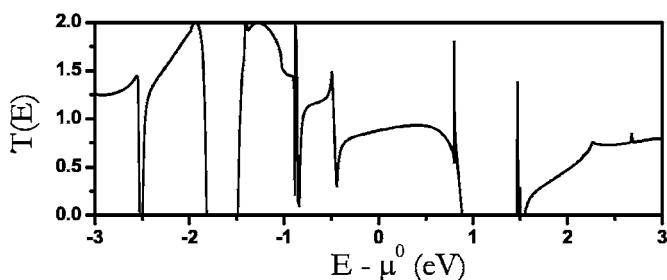


FIG. 10. Non-WBL transmission coefficient $T(\epsilon; \Delta V^R=0 \text{ V})$ of the Al-C7-Al system.

metric configuration has been investigated extensively.^{10,13} In our calculation, the device region D consists of 7 carbon and 18 Al atoms, i.e., altogether 297 basis functions for the reduced system, and the extended cluster for ground state calculation contains 115 atoms in total.

The calculated non-WBL transmission coefficient, $T(\epsilon; \Delta V^R=0 \text{ V})$, is plotted in Fig. 10. The main features of our result agree reasonably with those exhibited in literature.^{10,13} The quantitative discrepancies may be due to the different techniques employed. For instance, a finite molecular cluster is explicitly treated in our calculation, whereas an infinite periodic system is considered in Refs. 10 and 13, and also the basis set and XC functional adopted are distinctively different. The calculated transient currents driven by steplike turn-on voltages $\Delta V^R(t)$ (see the inset of Fig. 3) are plotted in Fig. 11. The switch-on time for the Al-C7-Al system is about 3–5 fs for applied voltages ranging from 0.1 V to 0.5 V.

VI. DISCUSSION AND SUMMARY

Kurth *et al.* have proposed a practical TDDFT approach combined with the partition-free scheme.¹⁶ A number of relevant technical issues have been addressed, for instance, how the intractable propagation of the KS orbitals of an infinitely large system is transformed into the time evolution of KS orbitals in a finite open system subject to correct boundary conditions, how the time-dependent KS equation for the entire system is discretized in both \mathbf{r} and t spaces, etc. The performance of their approach has been illustrated by calculations for one-dimensional model systems. Our first-

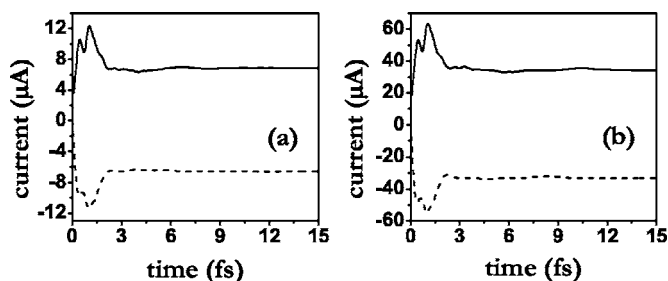


FIG. 11. The solid (dashed) curve represents the transient current through the interface S_R (S_L) of the Al-C7-Al system driven by a steplike voltage applied on the lead R with the amplitude (a) $\Delta V^R=-0.1 \text{ V}$ and (b) $\Delta V^R=-0.5 \text{ V}$.

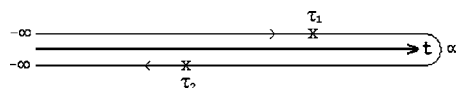


FIG. 12. The Keldysh time contour on which nonequilibrium Green's function theory is constructed. On the contour, the time τ_1 is earlier than τ_2 even though its real-time projection appears larger.

principles formalism for open electronic systems is fundamentally different: (i) In our method the KS reduced single-electron density matrix is used as the basic variable while in Ref. 16 the occupied KS single-electron orbitals are propagated. (ii) The concept of self-energy functional is introduced in our formalism. In principle the self-energy functional depends only on the electron density function of the reduced system, and hence we need only focus on the reduced system of interest without treating explicitly the environment. The influence of the environment enters via boundary conditions and the self-energy functionals. This is not only for quantum transport phenomena, but also for any dynamic process in any open electronic system. In this sense we expect the EOM (11) to be a general recipe for open system problems. (iii) Our EOM is formally analogous to the master equations derived from the conventional QDT.²⁶ From this perspective, well-established methods and techniques of QDT may be employed to improve the evaluations of self-energy functionals and the dissipation term $Q_a[t; \rho_D(\mathbf{r}, t)]$ systematically. For instance, another EOM has recently been proposed by Cui *et al.* based on the CS-QDT with a self-consistent Born approximation (SCBA).¹⁸

In conventional QDT²⁶ the key quantity is the reduced system density matrix, whereas in Eq. (11) the basic variable is the reduced single-electron density matrix, which leads to the drastic reduction of the degrees of freedom in numerical simulation. Linear-scaling methods such as the localized-density-matrix (LDM) method^{24,45} may thus be adopted to further speed up the solution process of Eq. (11). Therefore, Eq. (11) provides an accurate and convenient formalism to investigate the dynamic properties of open systems.

It is worth mentioning that our first-principles method for open systems applies to the same phenomena, properties, or systems as those intended by Hohenberg and Kohn,¹ Kohn and Sham,² and Runge and Gross,³ i.e., where the exchange-correlation energy is a functional of electron density only, $E_{XC}=E_{XC}[\rho(\mathbf{r})]$. This is true when the interaction between the electric current and magnetic field is negligible. However, in the presence of a strong magnetic field, $E_{XC}=E_{XC}[\rho(\mathbf{r}), \mathbf{j}_p(\mathbf{r})]$ or $E_{XC}=E_{XC}[\rho(\mathbf{r}), \mathbf{B}(\mathbf{r})]$, where $\mathbf{j}_p(\mathbf{r})$ is the paramagnetic current density and $\mathbf{B}(\mathbf{r})$ is the magnetic field.⁴⁶ In such a case, our first-principles formalism needs to be generalized to include $\mathbf{j}_p(\mathbf{r})$ or $\mathbf{B}(\mathbf{r})$. Of course, $\mathbf{j}_p(\mathbf{r})$ or $\mathbf{B}(\mathbf{r})$ should be an analytical function in space.

To summarize, we have proven the existence of a first-principles method for time-dependent open electronic systems, and developed a formally closed TDDFT formalism. In principle the functionals depend only on the electron density function of the reduced system. With an efficient WBL approximation for self-energy functionals, we have applied the first-principles formalism to carry out TDDFT calculations for transient current through realistic molecular devices. This

work greatly extends the realm of density-functional theory.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF EQ. (12) WITH THE KELDYSH FORMALISM

In the Keldysh formalism,³⁰ the nonequilibrium single-electron Green's function $G_{k_\alpha m}(t, t')$ is defined by

$$G_{k_\alpha m}(t, t') \equiv -i \langle T_C \{ a_{k_\alpha}(t) a_m^\dagger(t') \} \rangle, \quad (\text{A1})$$

where T_C is the contour-ordering operator along the Keldysh contour^{30,39} (see Fig. 12). Its lesser component, $G_{k_\alpha m}^<(t, t')$, is defined by

$$G_{k_\alpha m}^<(t, t') \equiv i \langle a_m^\dagger(t') a_{k_\alpha}(t) \rangle. \quad (\text{A2})$$

The formal NEGF theory has exactly the same structure as that of the time-ordered Green's function at zero temperature.^{39,47} Thus, the Dyson equation for $G_{k_\alpha m}(t, t')$ can be written as

$$G_{k_\alpha m}(t, t') = \sum_{l \in D} \int_C d\tau g_{k_\alpha}(t, \tau) h_{k_\alpha l}(\tau) G_{lm}(\tau, t'), \quad (\text{A3})$$

where $G_{lm}(\tau, t')$ and $g_{k_\alpha}(t, \tau)$ are the contour-ordered Green's functions for the reduced system D and the isolated semi-infinite lead α (L or R), respectively, and the integration over τ on the RHS is performed along the entire Keldysh contour (see Fig. 12).

$G_{lm}^r(\tau, t')$, $G_{lm}^a(\tau, t')$, and $G_{lm}^<(\tau, t')$ denote the retarded, advanced, and lesser components of $G_{lm}(\tau, t')$, respectively. Their definitions are as follows:

$$G_{lm}^r(\tau, t') \equiv -i \vartheta(\tau - t') \langle \{ a_l(\tau), a_m^\dagger(t') \} \rangle, \quad (\text{A4})$$

$$G_{lm}^a(\tau, t') \equiv i \vartheta(t' - \tau) \langle \{ a_l(\tau), a_m^\dagger(t') \} \rangle, \quad (\text{A5})$$

$$G_{lm}^<(\tau, t') \equiv i \langle a_m^\dagger(t') a_l(\tau) \rangle, \quad (\text{A6})$$

where $\vartheta(\tau - t')$ is the Heaviside step function, and the expectation values $\langle \cdots \rangle$ are taken at the ground state of the entire system at $t = -\infty$, i.e., when the reduced system and the environment are completely decoupled. $G_{lm}^r(\tau, t')$ and $G_{lm}^<(\tau, t')$ are to be calculated via their EOMs (19) and (20). The related self-energies $\Sigma_\alpha^a(t, \tau)$ and $\Sigma_\alpha^<(t, \tau)$ are evaluated through

$$\Sigma_{\alpha, ln}^a(t, \tau) = \sum_{k_\alpha \in \alpha} h_{lk_\alpha}(t) g_{k_\alpha}^a(t, \tau) h_{k_\alpha n}(\tau), \quad (\text{A7})$$

$$\Sigma_{\alpha, ln}^<(t, \tau) = \sum_{k_\alpha \in \alpha} h_{lk_\alpha}(t) g_{k_\alpha}^<(t, \tau) h_{k_\alpha n}(\tau), \quad (\text{A8})$$

for $\alpha = L$ or R . Here $g_{k_\alpha}^a(t, \tau)$ and $g_{k_\alpha}^<(t, \tau)$ are the advanced and lesser surface Green's functions for the isolated lead α (L or R).³⁹

Applying the analytical continuation rules of Langreth,³¹ we have

$$\begin{aligned} G_{mk_\alpha}^<(t', t) &\equiv i \langle a_{k_\alpha}^\dagger(t) a_m(t') \rangle \\ &= - [G_{k_\alpha m}^<(t, t')]^* = \sum_{l \in D} \int_{-\infty}^{\infty} d\tau h_{lk_\alpha}(\tau) \\ &\quad \times [g_{k_\alpha}^<(\tau, t) G_{ml}^r(t', \tau) + g_{k_\alpha}^a(\tau, t) G_{ml}^<(t', \tau)] \end{aligned} \quad (\text{A9})$$

by adopting the following equalities:

$$\begin{aligned} G_{ml}^r(t', \tau) &= [G_{lm}^a(\tau, t')]^*, \\ G_{ml}^<(t', \tau) &= - [G_{lm}^<(\tau, t')]^*, \\ g_{k_\alpha}^a(\tau, t) &= [g_{k_\alpha}^r(t, \tau)]^*, \\ g_{k_\alpha}^<(\tau, t) &= - [g_{k_\alpha}^<(t, \tau)]^*. \end{aligned} \quad (\text{A10})$$

Note that $\sigma_{mk_\alpha}(t)$ is precisely the lesser Green's function of identical time variables, i.e.,

$$\sigma_{mk_\alpha}(t) = -i G_{mk_\alpha}^<(t, t')|_{t'=t}. \quad (\text{A11})$$

By inserting Eqs. (A9) and (A11) into Eq. (9), Eq. (12) can be recovered straightforwardly.

APPENDIX B: THE DISSIPATION TERM Q_α IN PARTITION-FREE SCHEME AND PARTITIONED SCHEME

For brevity, $\Sigma_{\alpha=L,R} \Sigma_{k_\alpha \in \alpha}$ will be shortened to Σ_{k_α} . The Hamiltonian of the entire noninteracting KS system is

$$\begin{aligned} H(t) &= \sum_{mn \in D} h_{mn}(t) a_m^\dagger a_n + \sum_{k_\alpha} \epsilon_{k_\alpha}(t) a_{k_\alpha}^\dagger a_{k_\alpha} \\ &\quad + \sum_{m \in D} \sum_{k_\alpha} [h_{mk_\alpha}(t) a_m^\dagger a_{k_\alpha} + \text{H.c.}]. \end{aligned} \quad (\text{B1})$$

Initially (at $t = t_0$) the entire KS system is in its ground state $\Psi(t_0)$ (denoted by $|0\rangle$ hereafter), i.e., $H(t_0)\Psi(t_0) = E_0\Psi(t_0)$. We define the following Heisenberg creation and annihilation operators ($\hbar \equiv 1$):

$$\begin{aligned} a_m^\dagger(t) &\equiv e^{i\int_{t_0}^t H(\tau) d\tau} a_m^\dagger e^{-i\int_{t_0}^t H(\tau) d\tau}, \\ a_m(t) &\equiv e^{i\int_{t_0}^t H(\tau) d\tau} a_m e^{-i\int_{t_0}^t H(\tau) d\tau}, \\ a_{k_\alpha}^\dagger(t) &\equiv e^{i\int_{t_0}^t H(\tau) d\tau} a_{k_\alpha}^\dagger e^{-i\int_{t_0}^t H(\tau) d\tau}, \\ a_{k_\alpha}(t) &\equiv e^{i\int_{t_0}^t H(\tau) d\tau} a_{k_\alpha} e^{-i\int_{t_0}^t H(\tau) d\tau}, \end{aligned} \quad (\text{B2})$$

which satisfy their respective EOMs ($\partial_t \equiv \frac{\partial}{\partial t}$):

$$\begin{aligned}
 \partial_t a_m^\dagger(t) &= i \sum_{i \in D} a_i^\dagger(t) h_{im}(t) + i \sum_{k_\alpha} a_{k_\alpha}^\dagger(t) h_{k_\alpha m}(t), \\
 \partial_t a_m(t) &= -i \sum_{i \in D} h_{mi}(t) a_i(t) - i \sum_{k_\alpha} h_{mk_\alpha}(t) a_{k_\alpha}(t), \\
 \partial_t a_{k_\alpha}^\dagger(t) &= i \sum_{i \in D} a_i^\dagger(t) h_{ik_\alpha}(t) + i \epsilon_{k_\alpha}(t) a_{k_\alpha}^\dagger(t), \\
 \partial_t a_{k_\alpha}(t) &= -i \sum_{i \in D} h_{k_\alpha i}(t) a_i(t) - i \epsilon_{k_\alpha}(t) a_{k_\alpha}(t), \quad (\text{B3})
 \end{aligned}$$

with the initial conditions: $a_m^\dagger(t_0) = a_m^\dagger$, $a_m(t_0) = a_m$, $a_{k_\alpha}^\dagger(t_0) = a_{k_\alpha}^\dagger$, and $a_{k_\alpha}(t_0) = a_{k_\alpha}$.

The retarded, advanced, and lesser surface Green's functions for the isolated lead α (L or R) are defined as follows:

$$g_{k_\alpha}^{r,a}(t, \tau) \equiv \mp i \vartheta(\pm t \mp \tau) \langle \alpha | \{ b_{k_\alpha}^\dagger(t), b_{k_\alpha}^\dagger(\tau) \} | \alpha \rangle, \quad (\text{B4})$$

$$g_{k_\alpha}^<(t, \tau) \equiv i \langle \alpha | b_{k_\alpha}^\dagger(\tau) b_{k_\alpha}(t) | \alpha \rangle, \quad (\text{B5})$$

where the curly bracket on the RHS of Eq. (B4) denotes an anticommutator, and $|\alpha\rangle$ is the ground state wave function corresponding to the initial lead Hamiltonian $H_\alpha(t_0)$,

$$H_\alpha(t) = \sum_{k \in \alpha} \epsilon_{k_\alpha}(t) a_{k_\alpha}^\dagger a_{k_\alpha}. \quad (\text{B6})$$

The Heisenberg operators in Eqs. (B4) and (B5) are defined by

$$\begin{aligned}
 b_{k_\alpha}^\dagger(t) &\equiv e^{i \int_{t_0}^t H_\alpha(\tau) d\tau} a_{k_\alpha}^\dagger e^{-i \int_{t_0}^t H_\alpha(\tau) d\tau}, \\
 b_{k_\alpha}(t) &\equiv e^{i \int_{t_0}^t H_\alpha(\tau) d\tau} a_{k_\alpha} e^{-i \int_{t_0}^t H_\alpha(\tau) d\tau}. \quad (\text{B7})
 \end{aligned}$$

We then define the retarded, advanced, and lesser Green's functions of the entire KS system via their matrix elements as

$$G_{ij}^{r,a}(t, \tau) \equiv \mp i \vartheta(\pm t \mp \tau) \langle 0 | \{ a_i(t), a_j^\dagger(\tau) \} | 0 \rangle, \quad (\text{B8})$$

$$G_{k_\alpha j}^<(t, \tau) \equiv i \langle 0 | a_j^\dagger(\tau) a_{k_\alpha}(t) | 0 \rangle, \quad (\text{B9})$$

$$G_{k_\alpha p_\beta}^<(t, \tau) \equiv i \langle 0 | a_{p_\beta}^\dagger(\tau) a_{k_\alpha}(t) | 0 \rangle, \quad (\text{B10})$$

$$G_{ij}^<(t, \tau) \equiv i \langle 0 | a_j^\dagger(\tau) a_i(t) | 0 \rangle, \quad (\text{B11})$$

where $\beta = L$ or R , and p_β denotes a single-electron state in the lead β . Hereafter we only solve the Green's functions for time variables t and τ ranging from t_0^+ to $+\infty$. Taking the first-order time derivatives of $g_{k_\alpha}^r(t, \tau)$ and $g_{k_\alpha}^a(t, \tau)$ leads to

$$[i \partial_t - \epsilon_{k_\alpha}(t)] g_{k_\alpha}^r(t, \tau) = \delta(t - \tau), \quad (\text{B12})$$

$$- [i \partial_\tau + \epsilon_{k_\alpha}(\tau)] g_{k_\alpha}^a(t, \tau) = \delta(t - \tau), \quad (\text{B13})$$

with the initial conditions for Eq. (B12): $g_{k_\alpha}^r(t, \tau)|_{t=\tau^+} = -i$, $g_{k_\alpha}^r(t, \tau)|_{t=\tau^-} = -\frac{i}{2}$, and $g_{k_\alpha}^r(t, \tau)|_{t=\tau} = 0$; and for Eq. (B13): $g_{k_\alpha}^a(t, \tau)|_{\tau=t} = 0$, $g_{k_\alpha}^a(t, \tau)|_{\tau=t} = \frac{i}{2}$, and $g_{k_\alpha}^a(t, \tau)|_{\tau=t^+} = i$, re-

spectively. $g_{k_\alpha}^r(t, \tau)$ and $g_{k_\alpha}^a(t, \tau)$ can thus be utilized to solve partial differential and integrodifferential equations. For instance, we have the EOM for $G_{k_\alpha j}^<(t, \tau)$ as

$$[i \partial_t - \epsilon_{k_\alpha}(t)] G_{k_\alpha j}^<(t, \tau) = \sum_{m \in D} h_{k_\alpha m}(t) G_{mj}^<(t, \tau). \quad (\text{B14})$$

Combining Eqs. (B12) and (B14), we obtain

$$\begin{aligned}
 G_{k_\alpha j}^<(t, \tau) &= \sum_{m \in D} \int_{t_0^+}^t d\bar{t} g_{k_\alpha}^r(t, \bar{t}) h_{k_\alpha m}(\bar{t}) G_{mj}^<(\bar{t}, \tau) \\
 &\quad + i g_{k_\alpha}^r(t, t_0) G_{k_\alpha j}^<(t_0^+, \tau). \quad (\text{B15})
 \end{aligned}$$

With a similar but slightly more tedious treatment for the time variable τ , we arrive at

$$\begin{aligned}
 G_{k_\alpha j}^<(t, \tau) &= -i \sum_{m \in D} G_{k_\alpha m}^<(t, t_0^+) G_{mj}^a(t_0, \tau) \\
 &\quad - i \sum_{p_\beta} \sum_{m \in D} \int_{t_0^+}^\tau d\bar{t} G_{k_\alpha p_\beta}^<(t, t_0^+) \\
 &\quad \times g_{p_\beta}^a(t_0, \bar{t}) h_{p_\beta m}(\bar{t}) G_{mj}^a(\bar{t}, \tau), \quad (\text{B16})
 \end{aligned}$$

where Σ_{p_β} is short for $\Sigma_{\beta=L, R} \Sigma_{p \in \beta}$. By taking $t = t_0^+$ in Eq. (B16) and then inserting it into Eq. (B15), we have

$$\begin{aligned}
 G_{k_\alpha j}^<(t, \tau) &= \sum_{m \in D} \int_{t_0^+}^t d\bar{t} g_{k_\alpha}^r(t, \bar{t}) h_{k_\alpha m}(\bar{t}) G_{mj}^<(\bar{t}, \tau) \\
 &\quad + i \sum_{m \in D} g_{k_\alpha}^r(t, t_0) \sigma_{k_\alpha m}(t_0^+) G_{mj}^a(t_0, \tau) \\
 &\quad + i \sum_{p_\beta} \sum_{m \in D} \int_{t_0^+}^\tau d\bar{t} g_{k_\alpha}^r(t, t_0) \sigma_{k_\alpha p_\beta}(t_0^+) \\
 &\quad \times g_{p_\beta}^a(t_0, \bar{t}) h_{p_\beta m}(\bar{t}) G_{mj}^a(\bar{t}, \tau), \quad (\text{B17})
 \end{aligned}$$

where the following equalities have been adopted:

$$\sigma_{k_\alpha m}(t) = -i G_{k_\alpha m}^<(t, \tau)|_{\tau=t}, \quad (\text{B18})$$

$$\sigma_{k_\alpha p_\beta}(t) = -i G_{k_\alpha p_\beta}^<(t, \tau)|_{\tau=t}. \quad (\text{B19})$$

From Eq. (9) the dissipative term $Q_\alpha(t)$ is expressed by

$$\begin{aligned}
 Q_{\alpha, ij}(t) &= i \sum_{k \in \alpha} h_{ik_\alpha}(t) \sigma_{k_\alpha j}(t) + \text{H.c.} \\
 &= \sum_{k \in \alpha} h_{ik_\alpha}(t) G_{k_\alpha j}^<(t, \tau)|_{\tau=t} + \text{H.c.} \quad (\text{B20})
 \end{aligned}$$

Combining Eqs. (B17) and (B20), we have thus

$$\begin{aligned}
 Q_{\alpha, ij}(t) &= \left\{ Q_{\alpha, ij}^0(t) + \sum_{m \in D} \int_{t_0^+}^t d\bar{t} \Sigma_{\alpha, im}^<(t, \bar{t}) G_{mj}^a(\bar{t}, t) \right. \\
 &\quad \left. + \sum_{m \in D} \int_{t_0^+}^t d\bar{t} \Sigma_{\alpha, im}^r(t, \bar{t}) G_{mj}^<(\bar{t}, t) \right\} + \text{H.c.}, \quad (\text{B21})
 \end{aligned}$$

where

$$Q_{\alpha,ij}^0(t) \equiv i \sum_{k \in \alpha} \sum_{m \in D} h_{ik_\alpha}(t) g_{k_\alpha}^r(t, t_0) \sigma_{k_\alpha m}(t_0^+) G_{mj}^a(t_0, t), \quad (\text{B22})$$

$$\begin{aligned} \Sigma_{\alpha,im}^<(t, \bar{t}) &\equiv i \sum_{k \in \alpha} \sum_{p \in \beta} h_{ik_\alpha}(t) g_{k_\alpha}^r(t, t_0) \sigma_{k_\alpha p \beta}(t_0^+) \\ &\times g_{p\beta}^a(t_0, \bar{t}) h_{p\beta m}(\bar{t}), \end{aligned} \quad (\text{B23})$$

$$\Sigma_{\alpha,im}^r(t, \bar{t}) \equiv \sum_{k \in \alpha} h_{ik_\alpha}(t) g_{k_\alpha}^r(t, \bar{t}) h_{k_\alpha m}(\bar{t}), \quad (\text{B24})$$

where $\Sigma_\alpha^<$ and Σ_α^r are the lesser and retarded self-energies of the device region, respectively. Note that by definitions $G_D^r = [G_D^a]^\dagger$, $G_D^< = -[G_D^<]^\dagger$, $\Sigma_\alpha^a = [\Sigma_\alpha^r]^\dagger$, and $\Sigma_\alpha^< = -[\Sigma_\alpha^<]^\dagger$. Therefore, it is trivial to validate Eq. (B21) is equivalent to Eq. (13).

It is important to emphasize that $\Psi(t_0^+)$ may be different from $\Psi(t_0)$, so that the corresponding reduced single-electron density matrix $\sigma(t_0^+)$ may also differ from $\sigma(t_0)$. This would happen if $\int_{t_0}^+ H(\tau) d\tau \neq 0$, for instance, in the cases where the external field involves a delta function switched on at t_0 . However, for real physical systems, the applied external field is real analytic in time. In this circumstance, $\int_{t_0}^+ H(\tau) d\tau = 0$, $\Psi(t_0^+) = \Psi(t_0)$, and $\sigma(t_0^+) = \sigma(t_0)$.

The above derivations follow rigorously the partition-free scheme, since the initial state $\Psi(t_0)$ can be the ground state of the fully connected entire system including the device region and the leads. As for the partitioned scheme, we need to introduce another reference state Φ_0 , which is the ground state of Hamiltonian \tilde{H} ,

$$\tilde{H} \equiv \sum_{mn \in D} h_{mn}(t_0) a_m^\dagger a_n + \sum_{k_\alpha} \epsilon_{k_\alpha}(t_0) a_{k_\alpha}^\dagger a_{k_\alpha}. \quad (\text{B25})$$

Since \tilde{H} does not contain any coupling terms between D and L or R , Φ_0 depicts the scenario that the device region and the leads are isolated from each other. Hence there is no electron populated across the boundary S_L and S_R , i.e., $\tilde{\sigma}_{D\alpha} = 0$ and $\tilde{\sigma}_{LR} = 0$. We now assume $\Psi(t_0)$ can be reached by a time propagation of the entire system starting from the state Φ_0 , i.e.,

$$\Psi(t_0) = e^{-i \int_{-\infty}^{t_0} H(\tau) d\tau} \Phi_0. \quad (\text{B26})$$

At $t = -\infty$, $H(-\infty) = \tilde{H}$ and $\sigma(-\infty) = \tilde{\sigma}$. In this sense, the initial time for the Heisenberg creation and annihilation operators defined in Eq. (B2) becomes $-\infty$ instead of t_0 , and the above derivations for the various Green's functions remain valid. Note that for the decoupled ground state Φ_0 , we have

$$\sigma_{ij}(-\infty) = \sigma_{ij}^0, \quad (\text{B27})$$

$$\sigma_{k_\alpha j}(-\infty) = 0, \quad (\text{B28})$$

$$\sigma_{k_\alpha p \beta}(-\infty) = \delta_{\alpha\beta} \delta_{kp} f_{k_\alpha}^0, \quad (\text{B29})$$

where $f_{k_\alpha}^0$ is the initial occupation number of the single-electron state k_α . Thus the Green's functions and self-

energies previously derived can be simplified as follows:

$$\begin{aligned} \Sigma_{\alpha,im}^<(t, \bar{t}) &= i \sum_{k \in \alpha} f_{k_\alpha}^0 h_{ik_\alpha}(t) g_{k_\alpha}^r(t, t_0) g_{p\beta}^a(t_0, \bar{t}) h_{p\beta m}(\bar{t}), \\ &= \sum_{k \in \alpha} h_{ik_\alpha}(t) g_{k_\alpha}^<(t, \bar{t}) h_{k_\alpha m}(\bar{t}), \end{aligned} \quad (\text{B30})$$

$$\begin{aligned} G_{k_\alpha j}^<(t, \tau) &= \sum_{m \in D} \left\{ \int_{-\infty}^{\tau} d\bar{t} g_{k_\alpha}^<(t, \bar{t}) h_{k_\alpha m}(\bar{t}) G_{mj}^a(\bar{t}, \tau) \right. \\ &\left. + \int_{-\infty}^t d\bar{t} g_{k_\alpha}^r(t, \bar{t}) h_{k_\alpha m}(\bar{t}) G_{mj}^<(\bar{t}, \tau) \right\}, \end{aligned} \quad (\text{B31})$$

$$\begin{aligned} G_{ij}^<(t, \tau) &= i \sum_{mn \in D} G_{im}^r(t, -\infty) \sigma_{mn}^0 G_{nj}^a(-\infty, \tau) \\ &+ \sum_{mn \in D} \int_{-\infty}^t dt_1 \int_{-\infty}^{\tau} dt_2 G_{im}^r(t, t_1) \\ &\times \Sigma_{mn}^<(t_1, t_2) G_{nj}^a(t_2, \tau). \end{aligned} \quad (\text{B32})$$

The dissipative term Q_α is thus expressed as

$$\begin{aligned} Q_{\alpha,ij}(t) &= \sum_{m \in D} \int_{-\infty}^t d\bar{t} [\Sigma_{\alpha,im}^<(t, \bar{t}) G_{mj}^a(\bar{t}, t) \\ &+ \Sigma_{\alpha,im}^r(t, \bar{t}) G_{mj}^<(\bar{t}, t) + \text{H.c.}]. \end{aligned} \quad (\text{B33})$$

Equations (B30)–(B33) recover exactly Eq. (12) derived from the Keldysh NEGF formalism.³⁰ Therefore, we conclude that as long as the relation (B26) holds, the partition-free and the partitioned schemes of NEGF yield exactly the same dissipation term $Q_\alpha(t)$ for $t \geq t_0$.

In fact, Eq. (B26) is proved by Gell-Mann and Low theorem (1951),³⁴ which basically states that $\Psi(t_0)$ can be reached from Φ_0 by adiabatically turning on the coupling terms between D and L or R from $t = -\infty$ to t_0 . The resulting $\Psi(t_0)$ is an eigenstate of the Hamiltonian $H(t_0)$ and in most cases is the ground state.

APPENDIX C: DERIVATION OF EQ. (28)

The greater Green's function for the reduced system, $G_{ij}^>(t, \tau)$, is defined as

$$G_{ij}^>(t, \tau) \equiv -i \langle a_i(t) a_j^\dagger(\tau) \rangle. \quad (\text{C1})$$

The advanced Green's function of the reduced system can thus be expressed as

$$G_D^a(t, \tau) = -\vartheta(\tau - t) [G_D^>(t, \tau) - G_D^<(t, \tau)]. \quad (\text{C2})$$

Similarly the retarded and advanced self-energies can be associated with the greater and lesser self-energies as

$$\Sigma_\alpha^{r,a}(t, \tau) = \pm \vartheta(\pm t \mp \tau) [\Sigma_\alpha^>(t, \tau) - \Sigma_\alpha^<(t, \tau)], \quad (\text{C3})$$

where the greater self-energy $\Sigma_\alpha^>(t, \tau)$ is defined as

$$\begin{aligned}\Sigma_{\alpha,ij}^{\gt}(t,\tau) &\equiv \sum_{k \in \alpha} h_{ik_{\alpha}}(t) g_{k_{\alpha}}^{\gt}(t,\tau) h_{k_{\alpha}j}(\tau) \\ &= -i \sum_{k \in \alpha} h_{ik_{\alpha}}(t) h_{k_{\alpha}j}(\tau) \times \langle \alpha | b_{k_{\alpha}}(\tau) b_{k_{\alpha}}^{\dagger}(t) | \alpha \rangle.\end{aligned}\quad (\text{C4})$$

Equation (12) is thus equivalent to

$$Q_{\alpha}(t) = \int_{-\infty}^t d\tau [\Sigma_{\alpha}^{\gt}(t,\tau) G_D^{\lt}(\tau,t) - \Sigma_{\alpha}^{\lt}(t,\tau) G_D^{\gt}(\tau,t)] + \text{H.c.}\quad (\text{C5})$$

In cases where the KS Fock matrix of the reduced system, h_D , is time-independent, the greater and lesser Green's functions can be approximated by QDT perturbatively to complete second order,²⁶ i.e.,

$$\begin{aligned}G_D^{\gt}(\tau,t) &\approx e^{ih_D(t-\tau)} G_D^{\gt}(t,t) = (-i) e^{ih_D(t-\tau)} \bar{\sigma}_D, \\ G_D^{\lt}(\tau,t) &\approx e^{ih_D(t-\tau)} G_D^{\lt}(t,t) = i e^{ih_D(t-\tau)} \sigma_D,\end{aligned}\quad (\text{C6})$$

where $\bar{\sigma}_D \equiv I - \sigma_D$ is the reduced single-hole density matrix of the reduced system. Assuming the lead Hamiltonian to be time independent, we have $\Sigma_{\alpha}^{\lt,\gt}(t,\tau) = \Sigma_{\alpha}^{\lt,\gt}(t-\tau)$. Hence, Eq. (C5) can be recast into

$$\begin{aligned}Q_{\alpha}(t) &= \int_0^{\infty} d\tau \Sigma_{\alpha}^{\lt}(\tau) e^{ih_D\tau} G_D^{\gt}(t,t) + \int_0^{\infty} d\tau \Sigma_{\alpha}^{\gt}(\tau) e^{ih_D\tau} G_D^{\lt}(t,t) \\ &+ \text{H.c.}\end{aligned}\quad (\text{C7})$$

To evaluate the causality transforms involved in Eq. (C7), we define

$$\Lambda_{\alpha}^{(\pm)}(h_D) \equiv \pm \frac{1}{2i} \int_0^{\infty} d\tau [\Sigma_{\alpha}^{\lt,\gt}(\tau) e^{ih_D\tau} + e^{-ih_D\tau} \Sigma_{\alpha}^{\lt,\gt}(-\tau)],\quad (\text{C8})$$

$$\Gamma_{\alpha}^{(\pm)}(h_D) \equiv \mp \frac{1}{2} \int_0^{\infty} d\tau [\Sigma_{\alpha}^{\lt,\gt}(\tau) e^{ih_D\tau} - e^{-ih_D\tau} \Sigma_{\alpha}^{\lt,\gt}(-\tau)].\quad (\text{C9})$$

Here the equality $[\Sigma_{\alpha}^{\lt,\gt}(\tau)]^{\dagger} = -\Sigma_{\alpha}^{\lt,\gt}(-\tau)$ has been adopted. With Eqs. (C7)–(C9), Eqs. (28)–(31) are readily recovered. Generally $\Lambda_{\alpha}^{(\pm)}(h_D)$ and $\Gamma_{\alpha}^{(\pm)}(h_D)$ are Hermitian matrices, and associated with each other via the Kramers-Kronig relation.²⁶ In particular, when the KS Fock matrix h is real, $\Lambda_{\alpha}^{(\pm)}(h_D)$ and $\Gamma_{\alpha}^{(\pm)}(h_D)$ become real symmetric matrices. With Q_{α} expressed by Eq. (28), the EOM for σ_D is reformulated as

$$i\dot{\sigma}_D = [h_D, \sigma_D] + \sum_{\alpha=L,R} [\tilde{\Sigma}_{\alpha}^{\gt}(h_D), \sigma_D]^{\dagger} + \sum_{\alpha=L,R} [\tilde{\Sigma}_{\alpha}^{\lt}(h_D), \bar{\sigma}_D]^{\dagger}.\quad (\text{C10})$$

Equation (C10) resembles closely Eq. (8) in Ref. 18, which is developed from CS-QDT with the Markovian approximation. The correlation functions of the leads used in Ref. 18, $C_{\alpha}^{(\pm)}(t,\tau)$, are related to the self-energies adopted in our work as follows,

$$\Sigma_{\alpha}^{\lt,\gt}(t,\tau) = \pm i C_{\alpha}^{(\pm)}(t,\tau).\quad (\text{C11})$$

Following the SCBA scheme proposed in Ref. 18, higher-order effects due to interactions between the reduced system and the environment can be partially accounted for by substituting in Eq. (C6) an effective propagator of the reduced system, $e^{ih_D^{\text{eff}}(t-\tau)}$, for the propagator of the isolated reduced system, $e^{ih_D(t-\tau)}$, where h_D^{eff} is some effective KS Fock matrix of the reduced system. This results in self-energy terms $\tilde{\Sigma}_{\alpha}^{\lt,\gt}(h_D^{\text{eff}})$ instead of $\tilde{\Sigma}_{\alpha}^{\lt,\gt}(h_D)$ in Eq. (C10).

APPENDIX D: WIDE-BAND LIMIT SCHEME FOR THE DISSIPATION TERM Q_{α}

With the WBL approximation, the advanced self-energy becomes local in time,³⁹

$$\begin{aligned}\Sigma_{\alpha,nm}^{\alpha}(\tau,t) &= \sum_{k_{\alpha} \in \alpha} h_{nk_{\alpha}}(\tau) h_{k_{\alpha}m}(t) g_{k_{\alpha}}^{\alpha}(\tau,t) = \sum_{k_{\alpha} \in \alpha} h_{nk_{\alpha}}(\tau) h_{k_{\alpha}m}(t) \\ &\times [i\vartheta(t-\tau) e^{i\epsilon_k^{\alpha}(t-\tau)} e^{i\int_{\tau}^t \Delta\epsilon^{\alpha}(\bar{t}) d\bar{t}}] = \frac{i}{\pi} \vartheta(t \\ &- \tau) e^{i\int_{\tau}^t \Delta\epsilon^{\alpha}(\bar{t}) d\bar{t}} \times \left\{ \int_{-\infty}^{+\infty} e^{i\epsilon(t-\tau)} d\epsilon \right\} \Lambda_{nm}^{\alpha} \\ &= i\delta(t-\tau) \Lambda_{nm}^{\alpha}.\end{aligned}\quad (\text{D1})$$

Here the Dirac delta function on the RHS effectively removes the tricky off-diagonal elements of $G_D^{\lt}(t,\tau)$ from the NEGF formulation for Q_{α} [cf. Eq. (12)]. The third equality of Eq. (D1) involves the following approximation for the linewidths within the WBL approximation,

$$\Lambda_{k,nm}^{\alpha}(t,\tau) \equiv \pi \eta_{\alpha}(\epsilon_k^{\alpha}) h_{nk_{\alpha}}(t) h_{k_{\alpha}m}(\tau) \approx \Lambda_{nm}^{\alpha}(t,\tau) \approx \Lambda_{nm}^{\alpha}.\quad (\text{D2})$$

At time $t=0$ the entire fully connected system ($D+L+R$) is in its ground state with the chemical potential μ^0 . Afterwards the external potential is switched on, resulting in homogeneous time-dependent level shifts $\Delta\epsilon^{\alpha}(t)$ for the lead α (L or R). Hence, for $t,\tau > 0$ we have

$$\begin{aligned}\Sigma_{\alpha,nm}^{\lt}(\tau,t) &= \sum_{k_{\alpha} \in \alpha} h_{nk_{\alpha}}(\tau) h_{k_{\alpha}m}(t) g_{k_{\alpha}}^{\lt}(\tau,t) = \sum_{k_{\alpha} \in \alpha} h_{nk_{\alpha}}(\tau) h_{k_{\alpha}m}(t) \\ &\times [i f^{\alpha}(\epsilon_k^{\alpha}) e^{i\epsilon_k^{\alpha}(t-\tau)} e^{i\int_{\tau}^t \Delta\epsilon^{\alpha}(\bar{t}) d\bar{t}}] = \frac{2i}{\pi} e^{i\int_{\tau}^t \Delta\epsilon^{\alpha}(\bar{t}) d\bar{t}} \Lambda_{nm}^{\alpha} \\ &\times \left\{ \int_{-\infty}^{+\infty} f^{\alpha}(\epsilon) e^{i\epsilon(t-\tau)} d\epsilon \right\},\end{aligned}\quad (\text{D3})$$

$$G_{nm}^{\lt}(t,\tau) = -i\vartheta(t-\tau) \sum_{l \in D} U_{nl}^{(-)}(t) U_{lm}^{(+)}(\tau),\quad (\text{D4})$$

while for $\tau < 0$ and $t > 0$, the counterparts of Eqs. (D3) and (D4) are as follows,

$$\begin{aligned} \Sigma_{\alpha, nm}^{\leftarrow}(\tau, t) &= \sum_{k_{\alpha} \in \alpha} h_{nk_{\alpha}}(\tau) h_{k_{\alpha} m}(t) \mathcal{G}_{k_{\alpha}}^{\leftarrow}(\tau, t) = \sum_{k_{\alpha} \in \alpha} h_{nk_{\alpha}}(\tau) h_{k_{\alpha} m}(t) \\ &\times [i f^{\alpha}(\epsilon_k^{\alpha}) e^{i\epsilon_k^{\alpha}(t-\tau)} e^{i \int_0^t \Delta \epsilon^{\alpha}(\bar{\tau}) d\bar{\tau}}] = \frac{2i}{\pi} e^{i \int_0^t \Delta \epsilon^{\alpha}(\bar{\tau}) d\bar{\tau}} \Lambda_{nm}^{\alpha} \\ &\times \left\{ \int_{-\infty}^{+\infty} f^{\alpha}(\epsilon) e^{i\epsilon(t-\tau)} d\epsilon \right\}, \end{aligned} \quad (\text{D5})$$

$$G_{nm}^r(t, \tau) = \sum_{l \in D} U_{nl}^{(-)}(t) G_{lm}^r(0, \tau). \quad (\text{D6})$$

Here the effective propagators for the reduced system, $U^{(\pm)}(t)$, are defined as

$$U^{(\pm)}(t) = \exp \left\{ \pm i \int_0^t h_D(\tau) d\tau \pm \Lambda t \right\}, \quad (\text{D7})$$

where $\Lambda = \sum_{\alpha=L,R} \Lambda^{\alpha}$. By inserting Eqs. (D1)–(D6) into Eq. (12), the dissipation term Q_{α} is simplified to be

$$Q_{\alpha}^{\text{WBL}}(t) = K^{\alpha}(t) + \{ \Lambda^{\alpha}, \sigma_D(t) \}, \quad (\text{D8})$$

where the curly bracket on the RHS denotes an anticommutator and $K^{\alpha}(t)$ is a Hermitian matrix,

$$K^{\alpha}(t) = P^{\alpha}(t) + [P^{\alpha}(t)]^{\dagger}. \quad (\text{D9})$$

Here $P^{\alpha}(t)$ involves an integration over the entire real t axis, which is then decomposed into positive and negative parts, denoted by $P_{\alpha}^{(+)}(t)$ and $P_{\alpha}^{(-)}(t)$, respectively. We thus have

$$P^{\alpha}(t) \equiv - \int_{-\infty}^{+\infty} d\tau G_D^r(t, \tau) \Sigma_{\alpha}^{\leftarrow}(\tau, t) = P_{\alpha}^{(-)}(t) + P_{\alpha}^{(+)}(t). \quad (\text{D10})$$

$P_{\alpha}^{(-)}(t)$ and $P_{\alpha}^{(+)}(t)$ are evaluated via

$$\begin{aligned} P_{\alpha}^{(-)}(t) &\equiv - \int_{-\infty}^0 d\tau G_D^r(t, \tau) \Sigma_{\alpha}^{\leftarrow}(\tau, t) = \\ &- \frac{2i}{\pi} \exp \left\{ i \int_0^t \Delta \epsilon^{\alpha}(\tau) d\tau \right\} U^{(-)}(t) \\ &\times \left\{ \int_{-\infty}^{\mu^0} \frac{d\epsilon e^{i\epsilon t}}{\epsilon - h_D(0) + i\Lambda} \right\} \Lambda^{\alpha}, \end{aligned} \quad (\text{D11})$$

and

$$P_{\alpha}^{(+)}(t) \equiv - \frac{2}{\pi} \int_{-\infty}^{\mu^0} d\epsilon W_{\alpha}^{(-)}(\epsilon, t) \int_0^t d\tau W_{\alpha}^{(+)}(\epsilon, \tau) \Lambda^{\alpha}, \quad (\text{D12})$$

respectively, where

$$W_{\alpha}^{\pm}(\epsilon, t) = e^{\pm i \int_0^t d\tau [h_D(\tau) - i\Lambda - \Delta \epsilon^{\alpha}(\tau) - \epsilon]}. \quad (\text{D13})$$

However, the evaluations of Eqs. (D12) and (D13) are found extremely time consuming since at every time t one needs to propagate $W_{\alpha}^{\pm}(\epsilon, t)$ for every individual ϵ inside the lead en-

ergy spectrum. It is thus inevitable to have a simpler approximate form for $P_{\alpha}^{(+)}(t)$ with satisfactory accuracy retained. Note that Eq. (D12) can be reformulated as

$$P_{\alpha}^{(+)}(t) = - \frac{2}{\pi} \int_{-\infty}^{\mu^0} d\epsilon \int_0^t d\tau e^{-i \int_{\tau}^t [h_D(\bar{\tau}) - i\Lambda - \Delta \epsilon^{\alpha}(\bar{\tau}) - \epsilon] d\bar{\tau}} \Lambda^{\alpha}. \quad (\text{D14})$$

For cases where steady states can be ultimately reached, $\Delta \epsilon^{\alpha}(t)$ and $h_D(t)$ become asymptotically constant as time $t \rightarrow +\infty$, i.e., $\Delta \epsilon^{\alpha}(t) \rightarrow \Delta \epsilon^{\alpha}(\infty)$ and $h_D(t) \rightarrow h_D(\infty)$. Therefore, the steady state $P_{\alpha}^{(+)}(\infty)$ can be approximated by substituting $\Delta \epsilon^{\alpha}(\infty)$ and $h_D(\infty)$ for $\Delta \epsilon^{\alpha}(t)$ and $h_D(t)$ in Eq. (D14), respectively.

$$\begin{aligned} P_{\alpha}^{(+)}(\infty) &\approx - \frac{2}{\pi} \int_{-\infty}^{\mu^0} d\epsilon \int_0^t d\tau e^{-i [h_D(\infty) - i\Lambda - \Delta \epsilon^{\alpha}(\infty) - \epsilon](t-\tau)} \Lambda^{\alpha} \\ &= - \frac{2i}{\pi} \int_{-\infty}^{\mu^0} \{ I - e^{-i [h_D(\infty) - i\Lambda - \Delta \epsilon^{\alpha}(\infty) - \epsilon] \tau} \} \\ &\times \frac{d\epsilon}{\epsilon - h_D(\infty) + i\Lambda + \Delta \epsilon^{\alpha}(\infty)} \Lambda^{\alpha}. \end{aligned} \quad (\text{D15})$$

It is obvious from Eq. (D14) that

$$P_{\alpha}^{(+)}(0) = 0. \quad (\text{D16})$$

Thus $P_{\alpha}^{(+)}(t)$ for any time t between 0 and $+\infty$ can be approximately expressed by adiabatically connecting Eq. (D15) with Eq. (D16) as follows,

$$\begin{aligned} P_{\alpha}^{(+)}(t) &\approx - \frac{2i}{\pi} \int_{-\infty}^{\mu^0} \{ I - e^{-i \int_0^t [h_D(\tau) - i\Lambda - \Delta \epsilon^{\alpha}(\tau) - \epsilon] d\tau} \} \\ &\times \frac{d\epsilon}{\epsilon - h_D(t) + i\Lambda + \Delta \epsilon^{\alpha}(t)} \Lambda^{\alpha}. \end{aligned} \quad (\text{D17})$$

Both Eqs. (D14) and (D17) lead to the correct $P^{\alpha}(\infty)$ for steady states,

$$P^{\alpha}(\infty) = - \frac{2i}{\pi} \int_{-\infty}^{\mu^0} d\epsilon \frac{1}{\epsilon - h_D(\infty) + i\Lambda + \Delta \epsilon^{\alpha}(\infty)} \Lambda^{\alpha}. \quad (\text{D18})$$

If the external applied voltage assumes a steplike form, for instance, $\Delta V^{\alpha}(t) = -\Delta \epsilon^{\alpha}(t) = \Delta V^{\alpha}(1 - e^{-t/a})$ with $a \rightarrow 0^+$, and $h_D(t)$ is not affected by the fluctuation of $\sigma_D(t)$, Eq. (D17) would recover exactly Eq. (D14). In other cases, Eq. (D17) provides an accurate and efficient approximation for Eq. (D14), so long as $\Delta V^{\alpha}(t)$ do not vary dramatically in time. Since the integration over energy in Eq. (D17) can be performed readily by transforming the integrand into a diagonal representation, Eq. (D17) is evaluated much faster than Eq. (D14). Due to its efficiency and accuracy, Eq. (D17) is then combined with Eqs. (D8)–(D11) to calculate the dissipation term Q_{α}^{WBL} , and thus recovers Eq. (36) of Sec. IV B.

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