Time-dependent density-functional theory for open systems

Xiao Zheng, Fan Wang, Chi Yung Yam, Yan Mo, and GuanHua Chen
Department of Chemistry, The University of Hong Kong, Hong Kong, China
(Dated: June 25, 2021)

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 self-energy density functionals, 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.

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 theorem [1] lays the foundation of DFT. The Kohn-Sham (KS) formalism [2] 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, 5, 6, 7, 8, 9, 10, 11, 12, 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 coworkers [7]. The other is the first-principles nonequilibrium Green’s function (NEGF) technique [8, 9, 10, 11, 12, 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 been also proposed recently, such as Kosov’s KS equations with direct current [13], Kurth et al.’s [16] TDFT formulation, Cui et al.’s complete second-order quantum dissipation theory (CSDT) formalism [18] and Burke et al.’s KS master equation including dissipation to phonons [19]. In this paper, we present a new 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.

As early as in 1981, Riess and Münch [20] 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 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 Fourmais 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 finite number of its eigenstates; and the ground state 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 until recently we [23] were 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 r-space. For time-dependent real physical systems, we have proved the following theorem: [23]

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

According to the Theorem, the electron density function of any subsystem determines all the electronic properties of the entire time-dependent physical system. This
Eq. (1) leads to the conventional Casida’s equation \[ 25 \]. Expanded in the atomic orbital basis set, the matrix representation of \( \sigma \) can be partitioned as

\[
\sigma = \begin{bmatrix}
\sigma_L & \sigma_{LD} & \sigma_{LR} \\
\sigma_{DL} & \sigma_D & \sigma_{DR} \\
\sigma_{RL} & \sigma_{RD} & \sigma_R
\end{bmatrix},
\]

where \( \sigma_L, \sigma_R \) and \( \sigma_D \) represent the diagonal blocks corresponding to the left lead \( L \), the right lead \( R \) and the device region \( D \), respectively; \( \sigma_{LD} \) is the off-diagonal block between \( L \) and \( D \); and \( \sigma_{RD}, \sigma_{LR}, \sigma_{DL}, \sigma_{DR} \) and \( \sigma_{RL} \) are similarly defined. The KS Fock matrix \( h \) can be partitioned in the same way with \( \sigma \) replaced by \( h \) in Eq. (2).

Thus, the EOM for \( \sigma_D \) can be written as

\[
i\dot{\sigma}_D = [h_D, \sigma_D] + \sum_{\alpha=L,R} (h_{D\alpha} \sigma_{\alpha D} - \sigma_{\alpha D} h_{\alpha D}) = [h_D, \sigma_D] - i \sum_{\alpha=L,R} Q_\alpha,
\]

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. (3) is equivalent to:

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

\[
Q_{\alpha,nm} = i \sum_{k_\alpha \in \alpha} (h_{nk_\alpha} \sigma_{k_\alpha,m} - \sigma_{nk_\alpha} h_{k_\alpha,m}),
\]

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

\[
J_\alpha(t) = -\int_\alpha \frac{d}{dt} \rho(r,t)
= -\sum_{k_\alpha \in \alpha} \frac{d}{dt} \sigma_{k_\alpha,k_\alpha}(t)
= i \sum_{l \in D} \sum_{k_\alpha \in \alpha} (h_{k_\alpha l} \sigma_{k_\alpha l} - \sigma_{k_\alpha l} h_{k_\alpha l})
= -\sum_{l \in D} Q_{\alpha,tl} = -\text{tr}[Q_\alpha(t)]. \tag{6}
\]

Since the dissipation term \( Q_\alpha(t) \) is not known \textit{a priori}, Eq. (3) is not self-closed. Therefore, at this stage EOM (3) 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 \( D \); \( \rho_D(r,t) \). \( Q_\alpha \) of Eq. (3) is thus also a functional of \( \rho_D(r,t) \). Therefore, Eq. (3)
can be recast into a formally closed form,
\[ i\dot{\sigma}_D = \left[ h_D[t; \rho_D(r, t)], \sigma_D \right] - i \sum_{\alpha=L,R} Q_\alpha[t; \rho_D(r, t)]. \tag{7} \]

It would thus be much more efficient integrating Eq. (7) than solving Eq. (1), provided that \( Q_\alpha[t; \rho_D(r, t)] \) or its approximation is known. We therefore have a practical formalism for any open electronic systems. Neglecting \( Q_\alpha[t; \rho_D(r, t)] \) from Eq. (7) leads to the conventional TDDFT formulation \[24\] for the isolated reduced system, while \( Q_\alpha[t; \rho_D(r, t)] \) accounts for the dissipative interactions between \( D \) and \( L \) or \( R \). Eq. (7) 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. \[27, 28\] while in our case it is not.

Burke \textit{et al.} extended TDDFT to include electronic systems interacting with phonon baths \[19\], they proved the existence of a one-to-one correspondence between \( \psi(r, t) \) and \( \rho(r, t) \) 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 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 \textit{et al.}. And the only information we need is the electron density of the reduced system. In the frozen DFT approach \[29\] 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 \( Q_\alpha[t; \rho_D(r, t)] \) of Eq. (7).

\[ Q_{\alpha,nm}(t) = \sum_{\ell \in D} \int_{-\infty}^{t} d\tau \left[ G_{\alpha,\ell}^{<}(t, \tau) \Sigma_{\alpha,\ell m}^{a}(\tau, t) + G_{\alpha,\ell}^{>}(t, \tau) \Sigma_{\alpha,\ell m}^{a}(\tau, t) + \text{H.c.} \right], \tag{8} \]

where \( G_{\alpha}^{>}(t, \tau) \) and \( G_{\alpha}^{<}(t, \tau) \) are the retarded and lesser Green’s function of the reduced system \( D \), and \( \Sigma_{\alpha}^{a} \) and \( \Sigma_{\alpha}^{<} \) are the advanced and lesser self-energies due to the lead \( \alpha \) (\( L \) or \( R \)). Combining Eqs. (6) and (8), we obtain

\[ J_{\alpha}(t) = 2\Re \left\{ \int_{-\infty}^{t} d\tau \langle \rho \rangle \left[ G_{\alpha}^{<}(t, \tau) \Sigma_{\alpha}^{a}(\tau, t) + G_{\alpha}^{>}(t, \tau) \Sigma_{\alpha}^{<}(\tau, t) \right] \right\}. \tag{9} \]

Eq. (7) has been derived by Stefanucci and Almbladh \[32\] within the framework of TDDFT under the assumption that the partitioned \[31\] and partition-free \[33\] schemes are equivalent.

It is important to emphasize that Eq. (8) is derived from the initial ground state at \( t = -\infty \) when the device region and the leads are completely isolated, denoted by \( \Phi_{0} \). This corresponds to the partitioned scheme developed by Caroli \textit{et al.} \[34\]. The dissipation term \( Q_\alpha \) can also be derived from the initial ground state at \( t = t_{0} \) when the device region and the leads are fully connected, denoted by \( \Phi_{0} \), as follows (see Appendix A for detailed derivations),

\[ Q_{\alpha,nm}(t) = \left\{ Q_{\alpha,nm}(t_{0}) - \sum_{\ell \in D} \int_{t_{0}}^{t} d\tau \left[ G_{\alpha,\ell}^{<}(t, \tau) \Sigma_{\alpha,\ell m}^{a}(\tau, t) + G_{\alpha,\ell}^{>}(t, \tau) \Sigma_{\alpha,\ell m}^{a}(\tau, t) \right] \right\} + \text{H.c.}, \tag{10} \]

where \( t_{0}^{+} \) is the time immediately after \( t_{0} \), and the first term on the RHS, \( Q_{\alpha,nm}(t_{0}) \), arises due to the initial couplings between the reduced system and the environment. Eq. (10) thus follows the partition-free scheme proposed by Cini \[35\], and its associated Green’s functions and self-energies are defined differently from those in Eq. (8).

Based on Gell-Mann and Low theorem \[36\], in most cases \( \Phi_{0} \) can be reached from \( \Phi_{0} \) 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 the device and leads only determines \( \Phi_{0} \) and its corresponding electron density function \( \rho(r, t_{0}) \), and does not influence the dynamic response of the reduced system to external potentials after \( t_{0} \) explicitly. In few cases where the turn-on of the couplings results in an excited eigenstate at \( t_{0} \), Eq. (8) is only an approximation for the \( Q_{\alpha} \) derived from \( \Phi_{0} \) in the partition-free scheme, and in principle we need to resort to Eq. (10).
C. Solution for steady-state current

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

$$G^<_{nm}(t, \tau) = \sum_{p,q \in D} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 G^r_{np}(t_1, t_2) \times \sum_{l} \sum_{l} f^a_l \times \left[ \int_{-\infty}^{\infty} dt_1 e^{-i\epsilon_l^a t_1} G^r_{np}(t_1 - t_2) \right] \Gamma^a_{pq} \times \left[ \int_{-\infty}^{\infty} dt_2 e^{i\epsilon_l^a t_2} G^r_{qm}(t_2 - t) \right]$$

$$= i \int_{-\infty}^{\infty} dt \sum_{l} \sum_{l} f^a_l \times \left[ \int_{-\infty}^{\infty} dt_1 e^{-i\epsilon_l^a t_1} G^r_{np}(t_1 - t_2) \right] \Gamma^a_{pq} \times \left[ \int_{-\infty}^{\infty} dt_2 e^{i\epsilon_l^a t_2} G^r_{qm}(t_2 - t) \right]$$

$$= i \int_{-\infty}^{\infty} dt \sum_{l} \sum_{l} f^a_l \times \left[ \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt \sum_{l} \sum_{l} f^a_l \times \right.$$

where $I$ is an identity matrix, $\delta$ is an infinitesimal positive number, and $f^a_l$ is the occupation number of the single-electron state $l$ of the isolated lead $a$ ($L$ or $R$). The steady-state current can thus be explicitly expressed by combining Eqs. (11) and (13),

$$J_L(\infty) = -J_R(\infty)$$

$$= -\sum_{\alpha \in D} Q_{L,\alpha,\alpha}(\infty)$$

$$= \int_{-\infty}^{\infty} \left[ f^L(\epsilon) - f^R(\epsilon) \right] T(\epsilon) d\epsilon$$

$$= \int_{-\infty}^{\infty} \left[ f^L(\epsilon) - f^R(\epsilon) \right] T(\epsilon) d\epsilon$$

is the density of states (DOS) for the lead $\alpha$ ($L$ or $R$). Eq. (14) appears formally analogous to the Landauer formula $^{38, 39}$ adopted in the conventional DFT-NEGF formalism $^{8, 11}$. 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 TDDFT XC potential for the ground state DFT counterpart in Eq. (14).

D. Self-energy functionals

Due to its convenience for practical implementation, Eq. (8) is adopted in our formalism. The Green’s functions $G^r_{D}$ and $G^<_{D}$ in Eq. (8) can be calculated via the following EOMs if $\Sigma^a$ and $\Sigma^<_{nm}$ are known,

$$\frac{\partial G^<_{nm}(t, \tau)}{\partial t} = \delta(t - \tau) \delta_{nm} + \sum_{l \in D} h_{nl}(t) G^r_{lm}(t, \tau)$$

$$\frac{\partial G^<_{nm}(t, \tau)}{\partial t} = \sum_{l \in D} \int_{-\infty}^{\infty} d\bar{t} \left[ \Sigma^<_{nl}(t, \bar{t}) G^r_{lm}(\bar{t}, \tau) + \Sigma^r_{nl}(t, \bar{t}) \right]$$

$$\times \left[ \Sigma^r_{lm}(\bar{t}, \tau) \right] + \sum_{l \in D} h_{nl}(t) G^r_{lm}(t, \tau),$$

where $\Sigma^r = \sum_{\alpha=L,R} \left( \Sigma^a \right)^\dagger$, $\Sigma^< = \sum_{\alpha=L,R} \Sigma^<_{\alpha}$, and $G^r_{D} = (G^r_{D})^\dagger$. The key quantities for the evaluation of $Q_{\alpha}[t; \rho_D(r, t)]$ are thus the self-energies $\Sigma^a_{\alpha}$ and $\Sigma^<_{\alpha}$. According to our Theorem, $\Sigma^a_{\alpha}$ and $\Sigma^<_{\alpha}$ are in principle functionals of $\rho_D(r, t)$. Therefore, instead of finding $Q_{\alpha}[t; \rho_D(r, t)]$ directly, we need now seek for the density functionals $\Sigma^a_{\alpha}[r, t; \rho_D(r, t)]$ and $\Sigma^<_{\alpha}[r, t; \rho_D(r, t)]$. By their definitions, the self-energy terms have explicit functional dependence on the electron density function of the entire system, $\rho = (\rho_D, \rho_a)$:

$$\Sigma^a_{\alpha}[t; \rho] \equiv i \partial_t \left[ -t \right] h[t; \rho] \exp \left\{ \int_0^t h[x; \rho] dx \right\} \times h[t; \rho]$$

$$\Sigma^<_{\alpha}[t; \rho] \equiv i \partial_t \left[ -t \right] f^a(h_{\alpha}[-\infty; \rho_a]) \exp \left\{ \int_0^t h[x; \rho] dx \right\} \times h[t; \rho],$$

where $\rho_a$ is the electron density function in the lead $\alpha$, $h_{\alpha}$ is the KS Fock matrix of the isolated lead $\alpha$, and $f^a$ is the Fermi distribution function for $\alpha$ ($L$ or $R$). Based on our Theorem, $\rho_a$ are determined uniquely by $\rho_D$ via a certain continuation (CT) operation, i.e.,

$$\rho_D(r, t) \rightarrow \rho_D(r, t) \rightarrow \rho_D(r, t),$$

$$\rho_a(t, r) = \rho_a^CT[r, t; \rho_D(r, t)].$$

We obtain thus the following functionals,

$$\Sigma^a_{\alpha}[r, t] = \Sigma^a_{\alpha}[r, t; \rho_D, \rho_a^CT[\rho_D]]$$

$$\Sigma^<_{\alpha}[r, t] = \Sigma^<_{\alpha}[r, t; \rho_D, \rho_a^CT[\rho_D]].$$
Note that the CT operation is case dependent, and often approximate in practice. For the system depicted in Fig. 1, the CT operation from $\rho_D$ to $\rho_\alpha$ may be approximated by a translation over repeating unit cells if the bulk electrodes are periodic, i.e.,

$$\rho_\alpha(r, t) = \rho_\alpha^{CT}[\rho_D] \approx \rho_D(r + NR, t), \quad (24)$$

where $t = 0$ refers to the initial time when the entire connected system is in its ground state, $R$ is the base vector perpendicular to the interface $S_\alpha$, and $N$ denotes an integer which makes the translated vector $r + NR$ to be inside the reduced system $D$ as well as near the interfaces $S_\alpha$. 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 $S_\alpha$ takes correctly the bulk values.

Of course, there could be cases that the approximate $\rho_\alpha^{CT}[\rho_D]$ may deviate drastically from their exact values some distance away from the boundary. Usually $\Sigma^>_\alpha$ and $\Sigma^<_\alpha$ depend mostly on the electron density near the boundary where the approximate $\rho_\alpha^{CT}[\rho_D]$ agree best with the correct $\rho_\alpha$. The resulting $\Sigma^>_\alpha[\rho_D, \rho_\alpha^{CT}[\rho_D]]$ and $\Sigma^<_\alpha[\rho_D, \rho_\alpha^{CT}[\rho_D]]$ thus provide reasonable approximations for their exact counterparts. For cases where the self-energies happen to rely heavily on $\rho_\alpha$ far away from $D$, the approximated CT breaks down, and our method fails to be applicable.

Given $\Sigma^>_\alpha[\rho_D]$ and $\Sigma^<_\alpha[\rho_D]$ how do we solve the EOM (17) 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 (17) 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 $t \to -\infty$, $\Delta V^L = \Delta V^R = 0$, and $\Delta V^L(t)$ and $\Delta V^R(t)$ are turned on near $t = 0$. We need thus integrate Eq. (17) 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 $Q_\alpha(t; \rho_D(r, t))$ 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 [37].

### III. TWO APPROXIMATE SCHEMES FOR SELF-ENERGY DENSITY FUNCTIONALS

#### A. Complete second order approximation for dissipative functional

Eqs. (8) and (10) appear quite complicated. To have an unambiguous interpretation of the dissipation term $Q_\alpha$, we further assume the KS Fock matrix $h_D$ is time-independent and treat $G_D^\alpha(t, \tau)$ by means of CS-QDT [26]. Eq. (8) is thus simplified to be (see Appendix C for details)

$$Q_\alpha(t) = i \left\{ [\Sigma^>_\alpha(h_D), \sigma_D]^\dagger + [\Sigma^<_\alpha(h_D), \bar{\sigma}_D]^\dagger \right\}, \quad (25)$$

where $\sigma_D \equiv I - \sigma$ is the reduced single-hole density matrix of the reduced system. On the RHS of Eq. (25) a new commutator has been introduced for arbitrary operators $A$ and $B$:

$$[A, B]^\dagger \equiv AB - B^\dagger A^\dagger. \quad (26)$$

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

$$\tilde{\Sigma}^\leftrightarrow_{\alpha}(h_D) \equiv \int_0^\infty dt e^{ih_D t} \Sigma^\leftrightarrow_{\alpha}(t) \quad = \mp \Gamma_{\alpha}^{(\pm)}(h_D) \pm i\Lambda_{\alpha}^{(\pm)}(h_D), \quad (27)$$

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. (25) can be expanded as

$$Q_\alpha(t) = i \left[ \Gamma_{\alpha}^{(-)}(h_D), \sigma_D \right] + \left\{ \Lambda_{\alpha}^{(-)}(h_D), \sigma_D \right\} - i \left[ \Gamma_{\alpha}^{(+)}(h_D), \bar{\sigma}_D \right] - \left\{ \Lambda_{\alpha}^{(+)}(h_D), \bar{\sigma}_D \right\}. \quad (28)$$

The physical meaning of Eq. (28) 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 $\alpha$, 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 $\alpha$ while contributing to the transient current, respectively. The second term accounts for the electrons leaving the device region, and the third term describes that the holes hop onto the electrodes or the electrons enter the device region from the electrodes.
To simplify the solutions of Eqs. (10)–(17), the WBL approximation may be adopted besides the approximate CT operation (cf. Eq. (24)), 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 line-widths, \( \Delta_\epsilon^\alpha(t, \tau) \), defined by the DOS at \( S_L \) or \( S_R \) times the system-bath couplings, i.e., \( \Delta_\epsilon^\alpha(t, \tau) = \pi \eta_\alpha(\epsilon_k) \Gamma_k(t, \tau) \), are treated as energy independent, i.e., \( \Delta_\epsilon^\alpha(t, \tau) \approx \Delta^\alpha(t, \tau) \approx \Lambda^\alpha \), and (iii) the level shifts of \( L \) or \( R \) are taken as a constant for all energy levels, i.e., \( \Delta_\epsilon^\alpha(t) = \Delta^\alpha(t) = -\Delta V^\alpha(t) \), 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 by

\[
\Sigma^\alpha_{\alpha, nm}(\tau, t) = i\delta(t - \tau)\Lambda^\alpha_{nm}[\rho_D],
\]

\[
\Sigma^{<\alpha}_{\alpha, nm}(\tau, t) = \frac{2i}{\pi} \exp \left\{ i \int_{-\infty}^{\infty} \Delta V^\alpha(\epsilon) d\epsilon \right\} \Lambda^\alpha_{nm}[\rho_D] \times \left[ \int_{-\infty}^{t+} f^\alpha(\epsilon) e^{i\epsilon(t-\tau)} d\epsilon \right],
\]

where \( \Lambda^\alpha_{nm}[\rho_D] = \pi \eta_\alpha(\epsilon_f) \langle h_{nk} [\rho_D, \rho_D(r + NR)] \rangle \times h_{km} [\rho_D, \rho_D(r + NR)] \).

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 band-widths of the leads are five times or larger than the coupling strength between \( D \) and \( L \) or \( R \). The computational details are as follows. The entire system \((L + R + D)\) is initially in its ground state with the chemical potential \( \mu^0 \). External bias voltages are switched on from the time \( t = 0 \), which results in transient current flows through the leads \( L \) and \( R \). The line-widths, \( \Lambda^\alpha \), are treated as energy independent, i.e., \( \Delta_\epsilon^\alpha(t) = \Delta^\alpha(t) = -\Delta V^\alpha(t) \), where \( \Delta V^\alpha(t) \) are the bias voltages applied on \( L \) or \( R \) at time \( t \).
FIG. 4: The calculated transient current through $S_R$ within the WBL scheme. We set $\mu^R = h_D(0) = 0$ for the ground state; and $\Delta e^L(t) = 0$ and $\Delta e^R(t) = \Delta e^R(1 - e^{-t/a})$ after switch-on. The above panels show different cases where (a) $\Delta e^R = 2$ eV, $\Lambda^R = \Delta e^R = 0.1$ eV; (b) $\Delta e^R = 0.2$ eV, $\Lambda^R = \Delta e^R = 0.1$ eV; (c) $\Delta e^R = 10$ eV, $\Lambda^R = \Delta e^R = 0.1$ eV; and (d) $\Delta e^R = 2$ eV, $\Lambda^R = \Delta e^R = 0.04$ eV, respectively.

$\Delta e^R(t) = \Delta e^R(1 - e^{-t/a})$, where $a$ is a positive constant. The real analytic level shift $\Delta e^R(t)$ 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 Fig. 4(a)–(c) it is observed that with the same line-widths $\Lambda^R$, a larger level shift $\Delta e^R$ results in a more fluctuating current, whereas by comparing (a) and (d) we see that under the same $\Delta e^R$, the current decays more rapidly to the steady state value with the larger $\Lambda^R$.

By transforming its integrand into a diagonal representation, the integration over energy in Eq. (35) can be carried out readily. Therefore, $Q^{\text{WBL}}_\alpha$ are evaluated straightforwardly, which makes the above solution procedures for transient dynamics within the WBL approximation a practical routine for subsequent TDDFT calculations.

IV. TDDFT CALCULATIONS OF TRANSIENT CURRENT THROUGH MOLECULAR DEVICES

A. Numerical procedures

With the EOM (7) and the WBL approximation for the self-energy functionals $\Sigma^a_\alpha[\rho_D]$ 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 a self-developed package LODestar [41].

The ground state properties of the reduced system at $t = 0$ are determined by following the partitioned scheme approach adopted in conventional DFT-NEGF method [8, 9, 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 $\alpha$ ($L$ or $R$), $\frac{\delta}{\delta \mu^\alpha} g^\alpha_0[\mu^\alpha; \rho^\alpha_{\text{CT}}[\rho_D]]$, by applying the translational invariance [42] (cf. Eq. (23)). 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 line-widths $\Lambda^\alpha[\rho_D]$ within the WBL approximation are obtained from $g^\alpha_0$ via

$$
\Lambda^\alpha[\rho_D] = -\Im \left\{ \delta h_{D\alpha} g^\rho_0[\mu^\alpha; \rho^\alpha_{\text{CT}}[\rho_D]] \right\}.
$$

(35)

At $t = 0$ the left-hand side (LHS) of the Eq. (7) vanishes. The EOM (7) reduces thus to a nonlinear equation for $\sigma_D(0)$, and can be solved readily by employing the NEGF approach as follows,

$$
\sigma_D(0) = \frac{2}{\pi} \int_{-\infty}^{0} d\epsilon \, g^{r,0}_D(\epsilon) \Lambda \, g^{a,0}_D(\epsilon),
$$

(36)

where

$$
g^{r,0}_D(\epsilon) = [G^{r,0}_D(\epsilon)]^\dagger = [\epsilon - h_D(0) + i\Lambda]^{-1}.
$$

(37)

Eq. (36) provides the initial condition for the EOM (7).

The molecular device is switched on by a step-like voltage $\Delta V^R(t) = -\Delta e^R(t) = \Delta V^R(1 - e^{-t/a})$ 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 $\Sigma^a_\alpha[\rho_D]$ and $\Sigma^<_\alpha[\rho_D]$ can be evaluated through Eqs. (29)–(30) and (35). The dynamic response of the reduced system is obtained by solving the EOM (7) in time domain within the adiabatic LDA (ALDA) [23] 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.,

$$
\delta h_D(t) = \delta h^H_D(t) + \delta h^\text{XC}_D(t),
$$

(38)

where

$$
\delta h^H_D(t) = \int_D d\tau \, \phi^a_\alpha(\tau) \, \delta v^H(\tau, t) \, \phi_\alpha(\tau).
$$

(39)

Here the Hartree potential $\delta v^H(\tau, t)$ satisfies the following Poisson equation for the device region $D$ subject to
its first-order change due to the switch-on potential: To save computational resources we calculate $v$ where

$$\delta v^H(r, t) = -4 \pi \delta \rho_D(r, t)$$

$$\left. \delta v^H(r, t) \right|_{S_L} = \Delta V^L(t)$$

$$\left. \delta v^H(r, t) \right|_{S_R} = \Delta V^R(t).$$

(40)

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

$$\delta h^{XC}_{ij}(t) = \sum_{m \in D} V^{XC}_{ijmn} \left( \sigma_{mn}(t) - \sigma_{mn}(0) \right),$$

$$V^{XC}_{ijmn} = \int_D d\phi^*_m(r) \phi_n(r) \frac{\delta v^{XC}[r, t; \rho_D]}{\delta \rho_D(r, t)} \times \phi^*_i(r) \phi_j(r),$$

(41)

(42)

where $v^{XC}[r, t; \rho_D]$ is the XC potential. The reduced system is propagated from $t = 0$ following the EOM by the fourth-order Runge-Kutta algorithm 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. The steady currents through $S_L$ and $S_R$ are (a) $-5.9 \, \mu A$ and $5.9 \, \mu A$, (b) $-14.2 \, \mu A$ and $14.2 \, \mu A$, (c) $-18.0 \, \mu A$ and $18.0 \, \mu A$, and (d) $-21.3 \, \mu A$ and $21.3 \, \mu A$, respectively, and thus cancel each other out exactly, as they should. By comparison of panels (a)–(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 line-widths $\Lambda^o$ 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 $10 \sim 15$ fs for applied bias voltages ranging from 0.1 V to 1.0 V. For much higher turn-on voltages the linearized form of $\delta h^{XC}_D(t)$ (Eq. (41)) 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 functions derived from the partitioned scheme (cf. Eq. (8)) is well adapted to a TDDFT formalism.

C. Calculation on a CNT-alkene-CNT 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 totally 290 atoms. The
D. Calculation on an Al-C7-Al system

Another open system adopted in our first-principles calculations is depicted in Fig. [12], 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 geometric 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 totally 115 atoms.

The calculated non-WBL transmission coefficient, \( T(\varepsilon; \Delta V_R = 0) \), is plotted in Fig. [11]. 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, 13], and also the basis set and XC functional adopted are distinctly different. The calculated transient currents driven by step-like 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 \( \sim \) 5 fs for applied voltages ranging from 0.1 V to 0.5 V.

V. DISCUSSION AND SUMMARY

Kurth et al. have proposed a practical TDDFT approach combined with the partition-free scheme [10]. 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 \( r \) and \( t \) spaces, etc.. The performance of their approach has been illustrated by calculations for one-dimensional model systems. Our first-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. [10] 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 [7] 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 \( Q_\alpha(t; \rho_D(\vec{r}, t)) \) 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 QDT [26], the key quantity is the reduced system density matrix, whereas in Eq. [7] the ba-
of electron density only, $E_{XC} = E_{XC}[\rho(r)]$. This is true when the interaction between the electric current and magnetic field is negligible. However, in the presence of a strong magnetic field, $E_{XC} = E_{XC}[\rho(r), j_\alpha(r)]$ or $E_{XC} = E_{XC}[\rho(r), B(r)]$, where $j_\alpha(r)$ is the paramagnetic current density and $B(r)$ is the magnetic field. In such a case, our first-principles formalism needs to be generalized to include $j_\alpha(r)$ or $B(r)$. Of course, $j_\alpha(r)$ or $B(r)$ 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 by introducing the concept of self-energy functionals. In principle the self-energy 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**

Authors would thank Hong Guo, Shubin Liu, Jiang-Hua Lu, Zhigang Shuai, K. M. Tsang, Bing Wang, Jian Wang, Arieh Warshel, Yijing Yan and Weitao Yang for stimulating discussions. Support from the Hong Kong Research Grant Council (HKU 7010/03P) is gratefully acknowledged.

**APPENDIX A: DERIVATION OF EQ. (8) 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

$$G_{k_\alpha,m}(t,t') \equiv -i \left\langle T_C \left\{ a_{k_\alpha}(t) a^\dagger_m(t') \right\} \rightangle,$$  \hspace{1cm} (A1)

where $T_C$ is the contour-ordering operator along the Keldysh contour \[30, 32\] (see Fig. 12). Its lesser component, $G_\land^{\land}_{k_\alpha,m}(t,t')$, is defined by

$$G_\land^{\land}_{k_\alpha,m}(t,t') \equiv i \langle a^\dagger_m(t') a_{k_\alpha}(t) \rangle.$$  \hspace{1cm} (A2)

The formal NEGF theory has exactly the same structure as that of the time-ordered Green’s function at zero temperature \[32, 48\]. Thus, the Dyson equation for $G_{k_\alpha,m}(t,t')$ can be written as

$$G_{k_\alpha,m}(t,t') = \sum_{l \in D} \int d\tau g_{k_\alpha}(t,\tau) h_{l,\alpha}(\tau) G_{lm}(\tau,t'),$$  \hspace{1cm} (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 $\alpha$ ($L$ or $R$), respectively, and the integration over $\tau$ on the RHS is performed along the entire Keldysh contour (see Fig. [12]).
APPENDIX B: THE DISSIPATION TERM $Q_\alpha$ IN PARTITION-FREE AND PARTITIONED SCHEMES

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

$$H(t) = \sum_{mn\in D} h_{mn}(t) a^\dagger_m a_n + \sum_{k\alpha} \epsilon_{k\alpha}(t) a^\dagger_{k\alpha} a_{k\alpha}$$

$$+ \sum_{m\in D} \sum_{k\alpha} \left[ h_{mk\alpha}(t) a^\dagger_m a_{k\alpha} + \text{H.c.} \right].$$

\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 ($h \equiv 1$):

$$a^\dagger_{m\alpha}(t) = e^{i\int_{t_0}^t H(\tau) d\tau} a^\dagger_m e^{-i\int_{t_0}^t H(\tau) d\tau},$$

$$a_{m\alpha}(t) = e^{i\int_{t_0}^t H(\tau) d\tau} a_m e^{-i\int_{t_0}^t H(\tau) d\tau},$$

$$a^\dagger_{k\alpha}(t) = e^{i\int_{t_0}^t H(\tau) d\tau} a^\dagger_{k\alpha} e^{-i\int_{t_0}^t H(\tau) d\tau},$$

$$a_{k\alpha}(t) = e^{i\int_{t_0}^t H(\tau) d\tau} a_{k\alpha} e^{-i\int_{t_0}^t H(\tau) d\tau},$$

\text{(B2)}

which satisfy their respective EOMs ($\partial_t \equiv \frac{d}{dt}$):

$$\partial_t a^\dagger_{m\alpha}(t) = i \sum_{k\alpha} a^\dagger_{k\alpha}(t) h_{im}(t) + i \sum_{k\alpha} a^\dagger_{k\alpha}(t) h_{mk\alpha}(t),$$

$$\partial_t a_{m\alpha}(t) = -i \sum_{k\alpha} h_{mk\alpha}(t) a_{k\alpha}(t) - i \sum_{k\alpha} h_{im}(t) a_{k\alpha}(t),$$

$$\partial_t a^\dagger_{k\alpha}(t) = i \sum_{i\in D} a^\dagger_{i\alpha}(t) h_{ik\alpha}(t) + i \epsilon_{k\alpha}(t) a^\dagger_{k\alpha}(t),$$

$$\partial_t a_{k\alpha}(t) = -i \sum_{i\in D} h_{i\alpha}(t) a_{k\alpha}(t) - i \epsilon_{k\alpha}(t) a_{k\alpha}(t),$$

\text{(B3)}

with the initial conditions: $a^\dagger_{k\alpha}(t_0) = a^\dagger_{m\alpha}$, $a_{m\alpha}(t_0) = a_{m\alpha}$, $a^\dagger_{k\alpha}(t_0) = a^\dagger_{k\alpha}$, and $a_{k\alpha}(t_0) = a_{k\alpha}$. The retarded, advanced and lesser surface Green’s functions for the isolated lead $\alpha$ ($L$ or $R$) are defined as follows,

$$g^r_{k\alpha}(t, \tau) \equiv \mp i \delta(\pm \tau) \langle \alpha | \{ b_{k\alpha}(t), b^\dagger_{k\alpha}(\tau) \} | \alpha \rangle,$$

$$g^a_{k\alpha}(t, \tau) \equiv i \langle \alpha | b^\dagger_{k\alpha}(t) b_{k\alpha}(\tau) | \alpha \rangle,$$

\text{(B4)}

\text{(B5)}

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

$$H_{\alpha}(t) = \sum_{k\alpha} \epsilon_{k\alpha} a^\dagger_{k\alpha} a_{k\alpha}.$$

\text{(B6)}

The Heisenberg operators in Eqs. \text{(B4)} and \text{(B5)} are defined by

$$b^\dagger_{k\alpha}(t) \equiv e^{i\int_{t_0}^t H_{\alpha}(\tau) d\tau} a^\dagger_{k\alpha} e^{-i\int_{t_0}^t H_{\alpha}(\tau) d\tau},$$

$$b_{k\alpha}(t) \equiv e^{i\int_{t_0}^t H_{\alpha}(\tau) d\tau} a_{k\alpha} e^{-i\int_{t_0}^t H_{\alpha}(\tau) d\tau}.$$

\text{(B7)}
where \( \beta = L \) or \( R \), and \( p_\beta \) denotes a single-electron state in the lead \( \beta \). Hereafter we only solve the Green’s functions for time variables \( t \) and \( \tau \) ranging from \( t_0^+ \) to \( +\infty \).

Taking the first-order time derivatives of \( g_{k_a}(t, \tau) \) and \( \dot{g}_{k_a}(t, \tau) \) leads to
\[
[i\partial_t - \epsilon_{k_a}(t)] \dot{g}_{k_a}(t, \tau) = \delta(t - \tau), \quad (B12)
\]
with the initial conditions for Eq. (B12): \( g_{k_a}(t, \tau)|_{t=\tau^-} = -i \), \( g_{k_a}^\tau(t, \tau)|_{t=\tau^-} = \frac{\tau}{\tau} \), and \( g_{k_a}^\tau(t, \tau)|_{t=\tau^-} = 0 \); and for Eq. (B13): \( g_{k_a}^\tau(t, \tau)|_{t=\tau^-} = 0 \), \( g_{k_a}^\tau(t, \tau)|_{t=\tau^-} = \frac{\tau}{\tau} \), and \( g_{k_a}^\tau(t, \tau)|_{t=\tau^-} = i \), respectively. \( g_{k_a}(t, \tau) \) and \( \dot{g}_{k_a}(t, \tau) \) can thus be utilized to solve partial differential and integro-differential equations. For instance, we have the EOM for \( G^\tau_{k_a,j}(t, \tau) \) as follows,
\[
[i\partial_t - \epsilon_{k_a}(t)] G^\tau_{k_a,j}(t, \tau) = \sum_{m \in D} h_{k_a,m}(t) G^\tau_{m,j}(t, \tau). \quad (B14)
\]

Combining Eqs. (B14) and (B12), we obtain
\[
G^\tau_{k_a,j}(t, \tau) = \sum_{m \in D} \int_{t_0^+}^t dt \dot{g}_{k_a}(t, \tau) h_{k_a,m}(t) G^\tau_{m,j}(t, \tau)
+ i g_{k_a}(t, t_0) G^\tau_{j,j} (t_0^+, \tau). \quad (B15)
\]

With a similar but slightly more tedious treatment for the variable \( \tau \), we arrive at
\[
G^\tau_{k_a,j}(t, \tau) = -i \sum_{m \in D} G^\tau_{k_a,m}(t, t_0^+) G^\tau_{m,j}(t_0, \tau)
- i \sum_{p_\beta \in D} \int_{t_0^+}^\tau dt G^\tau_{k_a,p_\beta}(t, t_0^+)
\times g_{p_\beta}^\tau(t_0, \tau) h_{p_\beta,m}(\tau) G^\tau_{m,j}(\tau, \tau), \quad (B16)
\]
where \( p_\beta \) is short for \( \sum_{\beta=L,R} \sum_{p_\beta \in \beta} \). By taking \( t = t_0^+ \) in Eq. (B16) and then insert it into Eq. (B15), we have
\[
G^\tau_{k_a,j}(t, \tau) = \sum_{m \in D} \int_{t_0^+}^t dt \dot{g}_{k_a}(t, \tau) h_{k_a,m}(\tau) G^\tau_{m,j}(\tau, \tau)
+ i \sum_{m \in D} g_{k_a}^\tau(t_0, t) \sigma_{k_a,m}(t_0^+) G^\tau_{m,j}(t, \tau)
+ i \sum_{p_\beta \in D} \sum_{m \in D} \int_{t_0^+}^\tau dt g_{p_\beta}^\tau(t_0, \tau) \sigma_{k_a,p_\beta}(t_0^+)
\times g_{p_\beta}^\tau(t_0, \tau) h_{p_\beta,m}(\tau) G^\tau_{m,j}(\tau, \tau), \quad (B17)
\]
where the following equalities have been adopted:
\[
\sigma_{k_a,m}(t) = -i G^\tau_{k_a,m}(t, \tau)|_{\tau=t_0^+}, \quad (B18)
\]
\[
\sigma_{k_a,p_\beta}(t) = -i G^\tau_{k_a,p_\beta}(t, \tau)|_{\tau=t_0^+}. \quad (B19)
\]

From Eq. (13) the dissipative term \( Q_\alpha(t) \) is expressed by
\[
Q_{\alpha,i,j}(t) = i \sum_{k \in \alpha} h_{i,k_a}(t) \sigma_{k_a,j}(t) + H.c.
= \sum_{k \in \alpha} h_{i,k_a}(t) G^\tau_{k_a,j}(t, \tau)|_{\tau=t_0^+} + H.c.. \quad (B20)
\]

Combining Eqs. (B17) and (B20), we have thus
\[
Q_{\alpha,i,j}(t) = \left\{ Q^0_{\alpha,i,j}(t) + \sum_{m \in D} \int_{t_0^+}^t dt \Sigma_{\alpha,im}(t, \tau) G^\alpha_{m,j}(\tau, \tau) \right\}
+ \sum_{m \in D} \int_{t_0^+}^t dt \Sigma_{\alpha,im}(t, \tau) G^\alpha_{m,j}(\tau, \tau) + H.c., \quad (B21)
\]
where
\[
Q^0_{\alpha,i,j}(t) = i \sum_{k \in \alpha} \sum_{m \in D} h_{i,k_a}(t) g_{k_a}^\tau(t, t_0) |\sigma_{k_a,m}(t_0^+)\times G^\alpha_{m,j}(t, \tau), \quad (B22)
\]
\[
\Sigma_{\alpha,im}(t, \tau) = i \sum_{k \in \alpha} \sum_{p_\beta \in \beta} h_{i,k_a}(t) g_{k_a}^\tau(t, t_0) |\sigma_{k_a,p_\beta}(t_0^+)\times G^\alpha_{m,j}(t, \tau), \quad (B23)
\]
Low theorem (1951) [36], which basically states that to exactly the same dissipation term electron state $k$, energies previously derived can be simplified as follows, thus the initial time for the Heisenberg creation and annihilation operators defined in Eq. [32] 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 $\Phi_0$, we have

$$
\sigma_{ij}(-\infty) = \sigma_{ij}^0, \quad \sigma_{\alpha j}(-\infty) = 0, \quad \sigma_{\alpha p\beta}(-\infty) = \delta_{\alpha\beta} \delta_{kp} f_{ka}^0,
$$

where $f_{ka}^0$ is the initial occupation number of the single-electron state $k_\alpha$. Thus the Green’s functions and self-energies previously derived can be simplified as follows,

$$
\Sigma_{\alpha,im}(t, \bar{t}) = i \sum_{k_\alpha} f_{ka}^0 \left[ g_{k_\alpha}(t, t_0) g_{p\beta}(t_0, \bar{t}) h_{p,m}(\bar{t}) \right],
$$

where $\Sigma_{\alpha,im}(t, \bar{t})$ is defined as

$$
\Sigma_{\alpha,im}(t, \bar{t}) = i \sum_{k_\alpha} f_{ka}^0 \left[ g_{k_\alpha}(t, t_0) g_{p\beta}(t_0, \bar{t}) h_{p,m}(\bar{t}) \right],
$$

The dissipative term $Q_\alpha(t)$ is thus expressed as

$$
Q_\alpha(t) = \int_{-\infty}^{t} dt \left[ \sum_{\alpha,im}(t, \bar{t}) \right]^a G_{im}^a(\bar{t}, t)
$$

In cases where the KS Fock matrix of the reduced system, $H_r$, is time-independent, the greater and lesser Green’s functions can be approximated by QDT perturbatively to complete second order [24], i.e.,

$$
G_{\alpha}(t, \tau) \approx e^{ih_D(t-\tau)} G_{\alpha}^D(t, \tau) = (-i) e^{ih_D(t-\tau)} \bar{\sigma}_D,
$$

where $\bar{\sigma}_D \equiv 1 - \sigma_D$ is the reduced single-hole density matrix of the reduced system. Assuming the lead Hamiltonian to be time-independent, we have $\Sigma_{\alpha,>}(t, \tau) = \Sigma_{\alpha,>}(t - \tau)$. Hence, Eq. [C5] can be recast into

$$
Q_\alpha(t) = \int_{0}^{\infty} d\tau \sum_{\alpha} \left[ g_{\alpha}(\tau) e^{ih_D\tau} G_{\alpha}^D(t, \tau) + \Sigma_{\alpha,>}(\tau) e^{ih_D\tau} G_{\alpha}^D(t, \tau) + \text{H.c.} \right].
$$

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

$$
\Lambda^{(\pm)}(h_D) = \pm \frac{1}{2} e^{ih_D\tau} \sum_{\alpha} \left[ g_{\alpha}(\tau) e^{ih_D\tau} + e^{-ih_D\tau} \Sigma_{\alpha,>}(\tau) \right],
$$

$$
\Gamma^{(\pm)}(h_D) = \mp \frac{1}{2} e^{ih_D\tau} \sum_{\alpha} \left[ g_{\alpha}(\tau) e^{ih_D\tau} - e^{-ih_D\tau} \Sigma_{\alpha,>}(\tau) \right].
$$
Here the equality $[\Sigma_{\alpha}^{<,>}(\tau,\tau)]^\dagger = -\Sigma_{\alpha}^{<,>}(\tau,\tau)$ has been adopted. With Eqs. (C7)–(C9), Eqs. (25)–(28) are readily recovered. Generally $L^{(\pm)}(\alpha)$ 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, $L^{(\pm)}(h_D)$ and $\Gamma_{\alpha}^{(\pm)}(h_D)$ become real symmetric matrices. With $Q_{\alpha}$ expressed by Eq. (25), the EOM for $\sigma_D$ is reformulated as

$$i\dot{\sigma}_D = [h_D, \sigma_D] + \sum_{\alpha=L,R} [\Sigma_{\alpha}^{<,>}(h_D), \sigma_D]^\dagger + \sum_{\alpha=L,R} [\Sigma_{\alpha}^{<,>}(h_D), \sigma_D]^\dagger. \tag{C10}$$

Eq. (C10) resembles closely Eq. (8) in Ref. [13], which is developed from CS-QDT with the Markovian approximation. The correlation functions of the leads used in Ref. [12], $C^{(\pm)}(t,\tau)$, are related to the self-energies adopted in our work as follows,

$$\Sigma_{\alpha}^{<,>}(t,\tau) = \pm i C^{(\pm)}(t,\tau). \tag{C11}$$

Following the SCBA scheme proposed in Ref. [13], higher order effects due to interactions between the reduced system and the environment can be partially accounted for by substituting in Eq. (C5) an effective propagator of the reduced system, $e^{ih_D^{eff}(t-\tau)}$, 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 $\tilde{\Sigma}_{\alpha}^{<,>}(h_D^{eff})$ instead of $\Sigma_{\alpha}^{<,>}(h_D)$ in Eq. (C10).

**APPENDIX D: WIDE-BAND LIMIT SCHEME FOR THE DISSIPATION TERM $Q_{\alpha}$.**

With the WBL approximation, the advanced self-energy becomes local in time [32],

$$\Sigma_{\alpha,nn}^{\alpha}(\tau,\tau) = \sum_{k_a \in \alpha} h_{nk_a}(\tau) h_{k_a,m}(\tau) g_{k_a}^{\alpha}(\tau,\tau)$$

$$= \sum_{k_a \in \alpha} h_{nk_a}(\tau) h_{k_a,m}(\tau)$$

$$+ \left[ i \theta(t-\tau) e^{i\epsilon_{k_a}(t-\tau)} e^{i f_{\alpha}^i(t-\tau)} \Delta^{\alpha}(t) d\tilde{t} \right]$$

$$= i \theta(t-\tau) e^{i f_{\alpha}^i(t-\tau)} \Delta^{\alpha}(t) d\tilde{t}$$

$$\times \left\{ \int_{-\infty}^{+\infty} e^{i\epsilon_{k_a}(t-\tau)} d\tilde{t} \right\} \Lambda_{nn}^{\alpha}$$

$$= i \theta(t-\tau) \Lambda_{nn}^{\alpha}. \tag{D1}$$

Here the Dirac Delta function on the RHS effectively removes the tricky off-diagonal elements of $G_{\alpha D}(t,\tau)$ from the NEGF formulation for $Q_{\alpha}$ (cf. Eq. (5)). The third equality of Eq. (D1) involves the following approximation for the line-widths within the WBL approximation,

$$\Lambda_{\alpha,nn}^{\alpha}(t,\tau) \equiv \pi h q_{\alpha}^{\alpha}(\epsilon_{k_a}^{\alpha}) h_{nk_a}(\tau) h_{k_a,m}(\tau)$$

$$\approx \Lambda_{nn}^{\alpha}(t,\tau) \approx \Lambda_{nn}^{\alpha}. \tag{D2}$$

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

$$\Sigma_{\alpha,nn}^{<,>}^{\alpha}(\tau,\tau) = \sum_{k_a \in \alpha} h_{nk_a}(\tau) h_{k_a,m}(\tau) g_{k_a}^{\alpha}(\tau,\tau)$$

$$= \sum_{k_a \in \alpha} h_{nk_a}(\tau) h_{k_a,m}(\tau)$$

$$\times \left[ i f_{\alpha}^i(t-\tau) e^{i\epsilon_{k_a}(t-\tau)} e^{i f_{\alpha}^i(t-\tau)} \Delta^{\alpha}(t) d\tilde{t} \right]$$

$$= \frac{2i}{\pi} e^{i f_{\alpha}^i(t-\tau)} \Delta^{\alpha}(t) d\tilde{t} \Lambda_{nn}^{\alpha}$$

$$\times \left\{ \int_{-\infty}^{+\infty} f_{\alpha}^i(t-\tau) d\tilde{t} \right\}, \tag{D3}$$

$$G_{\alpha}^{r,nm}(t,\tau) = -i \theta(t-\tau) \sum_{l \in D} U_{nl}^{(-)}(t) U_{lm}^{(+)}(\tau). \tag{D4}$$

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

$$\Sigma_{\alpha,nn}^{<,>}(\tau,\tau) = \sum_{k_a \in \alpha} h_{nk_a}(\tau) h_{k_a,m}(\tau) g_{k_a}^{\alpha}(\tau,\tau)$$

$$= \sum_{k_a \in \alpha} h_{nk_a}(\tau) h_{k_a,m}(\tau)$$

$$\times \left[ i \theta(t-\tau) e^{i\epsilon_{k_a}(t-\tau)} e^{i f_{\alpha}^i(t-\tau)} \Delta^{\alpha}(t) d\tilde{t} \right]$$

$$= \frac{2i}{\pi} e^{i f_{\alpha}^i(t-\tau)} \Delta^{\alpha}(t) d\tilde{t} \Lambda_{nn}^{\alpha}$$

$$\times \left\{ \int_{-\infty}^{+\infty} f_{\alpha}^i(t-\tau) d\tilde{t} \right\}, \tag{D5}$$

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

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

$$U^{(\pm)}(t) = \exp \left\{ \pm i \int_{0}^{t} h_D(\tau) d\tau \pm \Lambda t \right\}, \tag{D7}$$

where $\Lambda = \sum_{\alpha=L,R} \Lambda_{\alpha}^\alpha$. By inserting Eqs. (D1)–(D6) into Eq. (5), the dissipation term $Q_{\alpha}$ is simplified to be

$$Q_{\alpha}^{WBL}(t) = K_{\alpha}(t) + \{ \Lambda_{\alpha}, \sigma_D(t) \}, \tag{D8}$$

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

$$K_{\alpha}(t) = P_{\alpha}(t) + [P_{\alpha}(t)]^\dagger. \tag{D9}$$

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

\[
P^{\alpha}(t) \equiv -\int_{-\infty}^{+\infty} d\tau G^\text{D}_\alpha(t,\tau)\Sigma^\leq(\tau,t)
= P^{(-)}_\alpha(t) + P^{(+)}_\alpha(t), \tag{D10}
\]

\( P^{(-)}_\alpha(t) \) and \( P^{(+)}_\alpha(t) \) are evaluated via

\[
P^{(-)}_\alpha(t) \equiv -\int_{-\infty}^{0} d\tau G^\text{D}_\alpha(t,\tau)\Sigma^\leq(\tau,t)
= -\frac{2i}{\pi} \exp\left\{ i \int_{0}^{t} \Delta \epsilon^\alpha(\tau) d\tau \right\} U^{(-)}(t)
\times \left\{ \int_{-\infty}^{0} \frac{d \epsilon \exp(i\epsilon t)}{\epsilon - h_D(0) + i\Lambda + \Delta \epsilon^\alpha(\infty)} \right\} \Lambda^\alpha, \tag{D11}
\]

and

\[
P^{(+)}_\alpha(t) \equiv -\frac{2}{\pi} \int_{0}^{\infty} d\epsilon W^{(-)}_\alpha(\epsilon,t)
\times \int_{0}^{t} d\tau W^{(+)}_\alpha(\epsilon,\tau) \Lambda^\alpha, \tag{D12}
\]

respectively, where

\[
W^{\pm}_\alpha(\epsilon,t) = \epsilon \pm i \int_{0}^{t} d\tau [h_D(\tau) - i\Lambda - \Delta \epsilon^\alpha(\tau) - \epsilon]. \tag{D13}
\]

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

\[
P^{(+)}_\alpha(t) = -\frac{2}{\pi} \int_{-\infty}^{0} d\epsilon \int_{0}^{t} d\tau \times \epsilon \exp^{-i \int_{0}^{t} [h_D(\tau) - i\Lambda - \Delta \epsilon^\alpha(\tau) - \epsilon] d\tau} \Lambda^\alpha. \tag{D14}
\]

For cases where steady states can be ultimately reached, \( \Delta \epsilon^\alpha(\tau) \) and \( h_D(\tau) \) become asymptotically constant as time \( t \to +\infty \), i.e., \( \Delta \epsilon^\alpha(\tau) \to \Delta \epsilon^\alpha(\infty) \) and \( h_D(\tau) \to h_D(\infty) \). 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.

\[
P^{(+)}_\alpha(\infty) \approx -\frac{2}{\pi} \int_{-\infty}^{0} d\epsilon \int_{0}^{t} d\tau \times \exp^{-i [h_D(\infty) - i\Lambda - \Delta \epsilon^\alpha(\infty) - \epsilon] t} \Lambda^\alpha
= -\frac{2i}{\pi} \int_{-\infty}^{0} d\epsilon \left\{ I - \exp^{-i [h_D(\infty) - i\Lambda - \Delta \epsilon^\alpha(\infty) - \epsilon] t} \right\}
\times \frac{d \epsilon}{\epsilon - h_D(\infty) + i\Lambda + \Delta \epsilon^\alpha(\infty)} \Lambda^\alpha. \tag{D15}
\]

It is obvious from Eq. (D14) that

\[
P^{(+)}_\alpha(0) = 0. \tag{D16}
\]

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

\[
P^{(+)}_\alpha(t) \approx -\frac{2i}{\pi} \int_{-\infty}^{0} d\epsilon \left\{ I - \exp^{-i \int_{0}^{t} [h_D(\tau) - i\Lambda - \Delta \epsilon^\alpha(\tau) - \epsilon] d\tau} \right\}
\times \frac{d \epsilon}{\epsilon - h_D(\infty) + i\Lambda + \Delta \epsilon^\alpha(\infty)} \Lambda^\alpha. \tag{D17}
\]

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

\[
P^{\alpha}(\infty) = -\frac{2i}{\pi} \int_{-\infty}^{0} d\epsilon \frac{1}{\epsilon - h_D(\infty) + i\Lambda + \Delta \epsilon^\alpha(\infty)} \Lambda^\alpha. \tag{D18}
\]

If the external applied voltage assumes a step-like form, for instance, \( \Delta V^{\alpha}(t) = -\Delta \epsilon^\alpha(t) = \Delta V^{\alpha}(1 - e^{-t/\alpha}) \) with \( a \to 0^+ \), 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 \( Q^{\text{WBL}}_\alpha \), and thus recovers Eq. (33) of Sec. III B.

[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B 864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. 140, A 1133 (1965).
[3] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
[4] N. D. Lang and Ph. Avouris, Phys. Rev. Lett. 84, 358 (2000).
[5] J. Heurich, J. C. Cuevas, W. Wenzel and G. Schön, Phys. Rev. Lett. 88, 256803 (2002).
[6] C.-K. Wang and Y. Luo, J. Chem. Phys. 119, 4923 (2003).
[7] N. D. Lang, Phys. Rev. B 52, 5355 (1995).
[8] Y. Xue, S. Datta and M. A. Ratner, J. Chem. Phys. 115, 4292 (2001).
[9] J. Taylor, H. Guo and J. Wang, Phys. Rev. B 63, 245407 (2001).
[10] S.-H. Ke, H. U. Baranger and W. Yang, Phys. Rev. B. 70, 085410 (2004).
[11] S.-H. Ke, H. U. Baranger and W. Yang, J. Am. Chem. Soc. 126, 15897 (2004).
[12] W.-Q. Deng, R. P. Muller and W. A. Goddard III, J. Am. Chem. Soc. 126, 13563 (2004).
[13] M. Brandbyge et al., Phys. Rev. B 65, 165401 (2002).
[14] Y. Xue, S. Datta and M. A. Ratner, Chem. Phys. 281, 151 (2002); Phys. Rev. B 72, 035308 (2005).
[15] D. S. Kosov, J. Chem. Phys. 119, 2541 (2006).
[16] S.-H. Ke, H. U. Baranger and W. Yang, Phys. Rev. B. 50, 5528 (1994).
[17] G. Stefanucci and C.-O. Almbladh, Europhys. Lett. 67 (1), 14 (2004).
[18] C. Caroli, R. Combescot, P. Nozieres and D. Saint-James, J. Phys. C 4, 916 (1971); C. Caroli, R. Combescot, D. Lederer, P. Nozieres and D. Saint-James, J. Phys. C 4, 2598 (1971).
[19] M. Cini, Phys. Rev. B 22, 5887 (1980).
[20] M. Gell-Mann and F. Low, Phys. Rev. 84, 350 (1951).
[21] W. Kohn, Phys. Rev. Lett. 76, 3168 (1996).
[22] Y. Yan, Phys. Rev. A 70, 085324 (2006).
[23] W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, Numerical Recipes in C, Cambridge University Press (1988).
[24] A. M. Rao et al., Science 275, 187 (1997); X. Blase et al., Phys. Rev. Lett. 72, 1878 (1994); R. A. Jishi, J. Bragin and L. Lou, Phys. Rev. B 59, 9862 (1999).
[25] S. Yokojima and G.H. Chen, Chem. Phys. Lett. 292, 379 (1998); Phys. Rev. B 59, 7259 (1999); S. Yokojima and G.H. Chen, Chem. Phys. Lett. 300, 540-544 (1999); S. Yokojima, D.H. Zhou and G.H. Chen, Chem. Phys. Lett. 302, 495-498 (1999); W.Z. Liang, S. Yokojima, D.H. Zhou and G.H. Chen, J. Phys. Chem. A 104, 2445 (2000); W.Z. Liang, S. Yokojima and G.H. Chen, J. Chem. Phys. 110, 1844 (1999); W.Z. Liang, S. Yokojima, M.F. Ng, G.H. Chen and G. He, J. Am. Chem. Soc. 123, 9830 (2001).
[26] G. Vignale and M. Rasolt, Phys. Rev. Lett. 59, 2360 (1987); C. J. Grayce and R. A. Harris, Phys. Rev. A 50, 3089 (1994).
[27] G. D. Mahan, Many-particle Physics, Kluwer Academic/Plenum Publishers, New York (2000).