Chapter 20
First-Principles Method for Open Electronic Systems

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We prove the existence of the exact density-functional theory formalism for open electronic systems, and develop subsequently an exact time-dependent density-functional theory (TDDFT) formulation for the dynamic response. The TDDFT formulation depends in principle only on the electron density of the reduced system. Based on the nonequilibrium Green's function technique, it is expressed in the form of the equation of motion for the reduced single-electron density matrix, and this provides thus an efficient numerical approach to calculate the dynamic properties of open electronic systems. In the steady-state limit, the conventional first-principles nonequilibrium Green's function formulation for the current is recovered.

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 (1964) lays the foundation of DFT. The Kohn-Sham formalism (1965) provides the practical solution to calculate the ground state properties of electronic systems. Runge and Gross extended further DFT to calculate the time-dependent properties and hence the excited state properties of any electronic systems (Runge and Gross, 1984). The accuracy of DFT or TDDFT is determined by the exchange-correlation functional. If the exact exchange-correlation functional were known, the Kohn-Sham formalism would have provided the exact ground state properties, and the Runge-Gross extension, TDDFT, would have yielded the exact properties of excited states. Despite of their wide range of applications, DFT and TDDFT have been mostly limited to closed systems.

Fundamental progress has been made in the field of molecular electronics recently. DFT-based simulations on quantum transport through individual molecules attached to electrodes offer guidance for the design of practical devices (Lang and Avouris, 2000; Heurich et al., 2002; Wang and Luo, 2003). These simulations focus on the steady-state currents under the bias voltages. Two types of approaches have been adopted. One is the Lippmann-Schwinger formalism by Lang and coworkers (Lang, 1995). The other is the first-principles nonequilibrium Green's function technique (Taylor et al., 2001; Ke et al., 2004; Deng et al., 2004; Brandbyge et al., 2002; Xue et al., 2001). In both approaches the Kohn-Sham

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Fock operator is taken as the effective single-electron model Hamiltonian, and the transmission coefficients are calculated within the noninteracting electron model. It is thus not clear whether the two approaches are rigorous. Recently Stefanucci and Almbladh (2004) derived an exact expression for time-dependent current in the framework of TDDFT. In the steady-current limit, their expression leads to the conventional first-principles nonequilibrium Green's function formalism if the TDDFT exchange-correlation functional is adopted. However, they did not provide a feasible numerical formulation for simulating the transient response of molecular electronic devices. In this communication, we present a rigorous first-principles formulation to calculate the dynamic properties of open electronic systems. We prove first a theorem that the electron density distribution of the reduced system determines all physical properties or processes of the entire system. The theorem lays down the foundation of the first-principles method for open systems. We present then the equation of motion (EOM) for nonequilibrium Green's functions (NEGF) in the framework of TDDFT. By introducing a new functional for the interaction between the reduced system and the environment, we develop further a reduced-single-electron-density-matrix-based TDDFT formulation. Finally, we derive an exact expression for the current which leads to the existing DFT-NEGF formula in the steady-state limit. This shows that the conventional DFT-NEGF formalism can be exact so long as the correct exchange-correlation functional is adopted. Both Hohenberg-Kohn theorem and Runge-Gross extension apply to isolated systems. Applying Hohenberg-Kohn-Sham's DFT and Runge-Gross's TDDFT to open systems requires in principle the knowledge of the electron density distribution of the total system which consists of the reduced system and the environment. This presents a major obstacle in simulating the dynamic processes of open systems. Our objective is to develop an exact DFT formulation for open systems. In fact, we are interested only in the physical properties and processes of the reduced system. The environment provides the boundary conditions and serves as the current source and energy sink. We thus concentrate on the reduced system.

Any electron density distribution function $\rho(\mathrm{r})$ of a real physical system is a real analytic function. We may treat nuclei as point charges, and this would only lead to non-analytic electron density at isolated points. In practical quantum mechanical simulations, analytic functions such as Gaussian functions and plane wave functions are adopted as basis sets, which results in analytic electron density distribution. Therefore, we conclude that any electron density functions of real systems are real analytic on connected physical space. Note that the isolated points at nuclei can be excluded for the moment from the physical space that we consider, so long the space is connected. Later we will come back to these isolated points, and show that their inclusion does not alter our conclusion. Based on this, we show below that for a real physical system the electron density distribution function on a subspace determines uniquely its values on the entire physical space. This is nothing but the analytic continuation of a real analytic function. The proof for the univariable real analytical functions can be found in textbooks, for instance, reference (Krantz and Parks, 2002). The extension to the multivariable real analytical functions is straightforward.

Lemma 1. The electron density distribution function $\rho(\mathrm{r})$ is real analytic on a connected physical space U. $W \subseteq U$ is a sub-space. If $\rho(\mathrm{r})$ is known for all $\rho(\mathrm{r}) \in W$, $\rho(\mathrm{r})$ can be uniquely determined on entire U.

Proof. To facilitate our discussion, the following notations are introduced. Set $\mathbb{Z}^+ = \{0, 1, 2, \ldots\}$, and $\boldsymbol{\gamma}$ is an element of $(\mathbb{Z}^+)^3$, *i.e.*, $\boldsymbol{\gamma} = (\gamma_1, \gamma_2, \gamma_3) \in (\mathbb{Z}^+)^3$. The displacement vector $\mathbf{r}$ is denoted by the three-dimensional variable $x = (x_1, x_2, x_3) \in U$. Denote that $\boldsymbol{\gamma}! = \gamma_1!\gamma_2!\gamma_3!$, $x^{\boldsymbol{\gamma}} = x_1^{\gamma_1} x_2^{\gamma_2} x_3^{\gamma_3}$, and $\frac{\partial^{\boldsymbol{\gamma}}}{\partial x^{\boldsymbol{\gamma}}} = \frac{\partial^{\gamma_1}}{\partial x_1^{\gamma_1}} \frac{\partial^{\gamma_2}}{\partial x_2^{\gamma_2}} \frac{\partial^{\gamma_3}}{\partial x_3^{\gamma_3}}$.

Suppose that another density distribution function $\rho'(x)$ is real analytic on U and equal to $\rho(x)$ for all $x \in W$. We have $\frac{\partial^{\boldsymbol{\gamma}}\rho(x)}{\partial x^{\boldsymbol{\gamma}}} = \frac{\partial^{\boldsymbol{\gamma}}\rho'(x)}{\partial x^{\boldsymbol{\gamma}}}$ for all $x \in W$ and $\boldsymbol{\gamma} \in (\mathbb{Z}^+)^3$. Taking a point x_0 at or infinitely close to the boundary of W, we may expand $\rho(x)$ and $\rho(x')$ around x_0, *i.e.*, $\rho(x) = \sum_{\boldsymbol{\gamma}\in(\mathbb{Z}^+)^3} \frac{1}{\boldsymbol{\gamma}!} \frac{\partial^{\boldsymbol{\gamma}}\rho(x)}{\partial x^{\boldsymbol{\gamma}}}\Big|_{x_0} (x - x_0)^{\boldsymbol{\gamma}}$ and $\rho'(x) = \sum_{\boldsymbol{\gamma}\in(\mathbb{Z}^+)^3} \frac{1}{\boldsymbol{\gamma}!} \frac{\partial^{\boldsymbol{\gamma}}\rho'(x)}{\partial x^{\boldsymbol{\gamma}}}\Big|_{x_0} (x-x_0)^{\boldsymbol{\gamma}}$. Assuming that the convergence radii for the Taylor expansions of $\rho(x)$ and $\rho'(x)$ at x_0 are both larger than a positive finite real number b, we have thus $\rho(x) = \rho'(x)$ for all $x \in D_b(x_0) = \{x : |x - x_0| < b\}$ since $\frac{\partial^{\boldsymbol{\gamma}}\rho(x)}{\partial x^{\boldsymbol{\gamma}}}\Big|_{x_0} = \frac{\partial^{\boldsymbol{\gamma}}\rho'(x)}{\partial x^{\boldsymbol{\gamma}}}\Big|_{x_0}$. Therefore, the equality $\rho'(x) = \rho(x)$ has been expanded beyond W to include $D_b(x_0)$. Since U is connected the above procedure can be repeated until $\rho'(x) = \rho(x)$ for all $x \in U$.

We have thus proven that ρ can be uniquely determined on U once it is known on W, and are ready to prove the following theorem.

Theorem 1. Electron density function $\rho(\mathrm{r})$ for a subsystem of a connected real physical system determines uniquely all electronic properties of the entire system.

Proof. Assuming the physical space spanned by the subsystem and the connected real physical system are W and U, respectively. W is thus a sub-space of U, i.e., $W \subseteq U$. According to the above lemma, $\rho(\mathrm{r})$ on W determines uniquely their value on U, i.e., $\rho(\mathrm{r})$ of the subsystem determines $\rho(\mathrm{r})$ of the entire system.

Inclusion of isolated points, lines or planes where $\rho(\mathrm{r})$ is non-analytic into the connected physical space does not violate the theorem; so long $\rho(\mathrm{r})$ is continuous on these points, lines or planes. This can be shown clearly by performing analytical continuation of $\rho(\mathrm{r})$ infinitesimally close to them. Therefore, we conclude that $\rho(\mathrm{r})$ of any finite subsystem determines uniquely $\rho(\mathrm{r})$ of the entire physical system including the nuclear sites. Hohenberg-Kohn theorem and Runge-Gross extension state that the electron density distribution of a system determines uniquely all its electronic properties. Therefore, we conclude that $\rho(\mathrm{r})$ for a subsystem determines all the electronic properties of the real physical system.

The above theorem guarantees the existence of an exact DFT-type method for open systems. In principle, all we need to know is the electron density of the reduced system. The electron density distribution in the environment can be obtained by the analytic continuation of the electron density function at or near the boundary. In practice the reduced system must be chosen appropriately so that this analytic continuation procedure can be conveniently performed. For instance, Fig. 20.1 depicts one type of open systems, a molecular device. It consists of the reduced system or

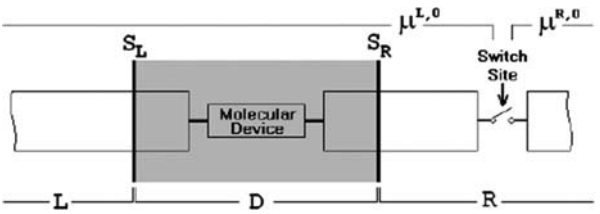

Fig. 20.1 Schematic representation of the experimental setup for quantum transport through a molecular device

device region D and the environment, the left and right leads L and R. Note that the reduced system D contains not only the molecular device itself, but also portions of the left and right electrodes, in this way the extension of the density function can be facilitated by the knowledge on the electron density distribution of the bulk electrodes.

The challenge is to develop a practical first-principles method. Taking the open system displayed in Fig. 20.1 as an example, we develop an exact DFT formalism for the open systems. To calculate the properties of a molecular device, we need only the electron density distribution in the device region. The influence of the electrodes can be determined by the electron density distribution in the device region. Within the TDDFT formalism, a closed nonlinear self-consistent EOM has been derived for the reduced single-electron density matrix σ(t) of the entire system (Yam et al., 2003):

$$i\dot{\sigma}(t) = [h(t), \sigma(t)], \tag{20.1}$$

where $h(t)$ is the Kohn-Sham Fock matrix, and the square bracket on the right-hand side (RHS) denotes the commutator. The matrix element of σ is defined as

$$\sigma_{ij}(t) = \langle a_j^{\dagger}(t) a_i(t) \rangle, \tag{20.2}$$

where $a_i(t)$ and $a_j^{+}(t)$ are the Heisenberg annihilation and creation operators for atomic orbitals i and j at time t, respectively. Expanded in a real space basis set, the matrix representation of σ can be partitioned as

$$\sigma = \begin{bmatrix} \sigma_L & \sigma_{LD} & \sigma_{LR} \\ \sigma_{DL} & \sigma_D & \sigma_{DR} \\ \sigma_{RL} & \sigma_{RD} & \sigma_R \end{bmatrix}, \tag{20.3}$$

where σ_L, σ_R, and σ_D represent the diagonal blocks correspond to the left lead, the right lead and the device region, respectively, and σ_{LD}, σ_{RD}, σ_{LR}, σ_{DL}, σ_{DR} and σ_{RL} are the electron coherence between two different subsystems. The only block of finite dimensions is σ_{D}, The Kohn-Sham Fock matrix h can be partitioned in the same way with σ replaced by h in Eq. (20.3). Thus the EOM for σ_{D} which is of our central interest can be written down readily as

$$i\dot{\sigma}_D = [h_D, \sigma_D] + \sum_{\alpha=L.R} (h_{D\alpha}\sigma_{\alpha D} - \sigma_{D\alpha}h_{\alpha D}) . \tag{20.4}$$

The reduced system D and the leads L/R are spanned by the atomic orbitals $\{l\}$ and the single-electron states $\{k_\alpha\}$, respectively. And hence Eq. (20.4) is equivalent to

$$i\sigma_{\dot{n}m} = \sum_{l\in D} (h_{nl}\sigma_{lm} - \sigma_{nl}h_{lm}) - i \sum_{\alpha=L,R} Q_{\alpha,nm}. \tag{20.5}$$

Here the $Q_{\alpha,\mathrm{nm}}$ on the RHS is the dissipative term due to the lead α (L or R) whose expanded form is

$$Q_{\alpha,nm} = i \sum_{k\epsilon\alpha} \left(h_{n,k_\alpha}\sigma k_\alpha, m - \sigma_{m,k_\alpha}h_{k_\alpha,m}\right), \tag{20.6}$$

where $h_{\mathrm{n,k}\alpha}$ is the coupling matrix element between the atomic orbital n and the single-electron state k_α. $\sigma_{\mathrm{k}\alpha,\mathrm{m}}$ is precisely the lesser Green's function of identical time variables, i.e.,

$$\sigma_{k_{\alpha,m}}(t) = -iG^<_{k_{\alpha,m}}\left(t.t'\right)|_{t'=t}.$$

Based on the Keldysh formalism (1965), the analytic continuation rules of Langreth and Nordlander (1991) and the NEGF formulation developed by Jauho et al. (1994), $Q_{\alpha,\mathrm{nm}}(t)$ can be calculated by

$$\begin{aligned} Q_{\alpha,nm}(t) = -\sum_{l\in D}\int_{-\infty}^{\infty} d\tau \Big[& G^<_{nl}(t,\tau)\sum\nolimits^{\alpha}_{\alpha,lm}(\tau,t) + \\ & G^r_{nl}(t,\tau)\sum\nolimits^{<}_{\alpha,lm}(\tau,t) - \sum\nolimits^{<}_{\alpha,nl}(t,\tau)G^{\alpha}_{lm}(\tau,t) \\ & - \sum\nolimits^{n}_{\alpha,nl}(t,\tau)G^<_{lm}(\tau,t)\Big]. \end{aligned} \tag{20.7}$$

where G^r, G^a and $G^<$ are the retarded, advanced and lesser Green's function for the reduced system D, and Σ^{r}, Σ^{a}, and $\Sigma^<$ are the retarded, advanced and lesser self-energies, respectively. The current through the interfaces S_{L} or S_{R} (see Fig. 20.1) can be expressed as

$$\begin{aligned} J_\alpha(t) &= -\int_\alpha d\mathrm{r}\frac{\partial}{\partial t}\rho(\mathrm{r},t) = -\sum_{k\in\alpha}\frac{d}{dt}\sigma_{k_\alpha,k_\alpha}(t) \\ &= i\sum_{l\in D}\sum_{k\in\alpha}\left(h_{k_{\alpha,l}}\sigma_{l,k_\alpha} - \sigma_{k_\alpha,l}h_{l,k_\alpha}\right) \\ &= -\sum_{l\in D} Q_{\alpha,ll} = -\mathrm{tr}\left[Q_\alpha(t)\right]. \end{aligned} \tag{20.8}$$

i.e., the current through S_α (α=L or R) is the negative of the trace of Q_α. Combining Eqs. (20.7) and (20.8), we recover the current expression (Eq. 20.8) of (Stefanucci and Almbladh, 2004).

At first glance Eq. (20.5) is not self-closed since the dissipative terms $Q_{\alpha.}$ remain unsolved. According to the theorem we proved earlier, all physical quantities are explicit or implicit functionals of the electron density in D, $\rho_D(t)$. Q_α are thus also universal functionals of ρ_D(t). Therefore, Eq. (20.5) can be recast into a formally closed form,

$$i\dot{\sigma}_D = \left[h_D\left[\rho_D\left(t\right)\right], \sigma_D\right] - i\sum_{\alpha=L,R} Q_\alpha\left[\rho_D\left(t\right)\right]. \tag{20.9}$$

Neglecting the second term on the RHS of Eq. (20.9) leads to the conventional TDDFT formulation in terms of reduced single-electron density matrix (Yam et al., 2003). The second term describes the dissipative processes where electrons enter and leave the region D. Besides the exchange-correlation functional, the additional universal density functional $Q_\alpha[\rho_D(t)]$ is introduced to account for the dissipative interaction between the reduced system and its environment. Equation (20.9) is thus the TDDFT formulation in terms of the reduced single-electron matrix for the open system. In the frozen DFT approach (Wesolowski and Warshel, 1993) an additional exchange-correlation functional term was introduced to account for the exchange-correlation interaction between the system and the environment. This additional term is included in $h_D(t)$ of Eq. (20.5). Yokojima et al. (2003) developed a dynamic mean-field theory for dissipative interacting many-electron systems. 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. The major difference is that the number of electrons in the reduced system is conserved in reference (Yokojima et al., 2003) while in our case it is not. Admittedly, $Q_\alpha[\rho_D(t)]$ can be an extremely complex functional. Progressive approximations are needed for the practical solution of Eq. (20.9).

To obtain the steady-state solution of Eqs. (20.5) or (20.9), we adopt a similar strategy as that of reference (Stefanucci and Almbladh, 2004). As $\tau \to \infty$, $\Gamma^{k_\alpha}_{nm}(t,\tau) \equiv h_{nk_\alpha}(t)h_{k_\alpha m}(\tau)$ becomes asymptotically time-independent, and Gs and Σs rely simply on the difference of the two time-variables (Stefanucci and Almbladh, 2004). The steady-state current can thus be expressed as

$$\begin{aligned} J_L\left(\infty\right) &= -J_R\left(\infty\right) = -\sum_{n\in D} Q_{L,nn}\left(\infty\right) \\ &= \int\left[f^L\left(\epsilon\right) - f^R\left(\epsilon\right)\right] T\left(\epsilon\right) d\epsilon, \end{aligned} \tag{20.10}$$

$$\begin{aligned} T\left(\epsilon\right) = {} & 2\pi\,\eta_L\left(\epsilon\right)\eta_R\left(\epsilon\right) \times \\ & \mathrm{tr}\left[G^r_D\left(\epsilon\right)\Gamma^R\left(\epsilon\right)G^\alpha_D\left(\epsilon\right)\Gamma^L\left(\epsilon\right)\right] \end{aligned} \tag{20.11}$$

Here $T(\varepsilon)$ is the transmission coefficient, $f^{\alpha}(\varepsilon)$ is the Fermi distribution function, and $\eta_{\alpha}(\varepsilon) = \sum_{k\in\alpha} \delta(\varepsilon - \varepsilon_k^{\alpha})$ is the density of states for the lead α (L or R). Equation (20.10) is exactly the Landauer formula (Datta, 1995; Landauer, 1970) in the DFT-NEGF formalism (Taylor et al., 2001; Ke et al., 2004). The only difference is that Eq. (20.10) is derived within the TDDFT formalism in our case while it is evaluated within the DFT framework in the case of the DFT-NEGF formulation (Taylor et al., 2001; Ke et al., 2004). In other words, *the DFT-NEGF formalism can be exact so long as the correct exchange-correlation functional is used!* This is not surprising, and is simply a consequence of that (*i*) DFT and TDDFT can yield the exact electron density and (*ii*) the current is the time derivative of the total charge.

Just as the exchange-correlation functional, the exact functional form of Q_{α} on density is rather difficult to derive. Various approximated expressions have been adopted for the DFT exchange-correlation functional in practical implementations. Similar strategy can be employed for Q_{α} One such scheme is the adiabatic approximation, which implies that the dissipation functional Q_{α} depends instantaneously on the electron density of the reduced system D, i.e.,

$$Q_{\alpha}\left[\rho_D\left(t\right)\right] \approx Q_{\alpha}^{AD}\left[\rho_D^t\right], \tag{20.12}$$

where Q_{α} is a functional of the density function $\rho_{\mathrm{D}}(t)$ over both time and space and Q_{α}^{AD} is a functional of $\rho_{\mathrm{D}}(t)$ over space only. For those $\rho_{\mathrm{D}}(t)$ corresponding to the steady-state solutions of Eq. (20.9), the exact functional values of $Q_{\alpha}^{AD}[\rho_D(t)]$ can be acquired by the TDDFT-NEGF formalism with the correct exchange-correlation functional being adopted, i.e.,

$$Q_{\alpha}^{AD}\left[\rho_D^t\right]|_{\rho_D^t\in\{\rho_D^{SS}\}} = Q_{\alpha}^{TDDFT-NEGF}[\rho_D^t], \tag{20.13}$$

where $\{\rho_D^{SS}\}$ denotes the set of all accessible steady-state density functions on the reduced system D. The explicit functional form of Q_{α}^{AD} can thus be obtained by fitting to the data available from Eq. (20.13) and then smoothly extrapolating to ρ_{D}(t) not in $\{\rho_D^{SS}\}$. In this way Q_{α} becomes an explicit functional of ρ_{D} and the Eq. (20.9) spontaneously leads to the same correct steady-state solution as that offered by the TDDFT-NEGF formalism.

Another scheme is the wide-band limit (WBL) approximation (Jauho et al., 1994), which consists of a series of approximations imposed on the leads: (*i*) their band-widths are assumed to be infinitely large, (*ii*) their linewidths $\Lambda_k^{\alpha}(t,\tau)$ defined by $\pi\eta_{\alpha}(\varepsilon_k^{\alpha})\Gamma^{k_{\alpha}}(t,\tau)$ are regarded as energy independent, i.e.,

$$\Lambda_k^{\alpha}\left(t,\tau\right) \approx \Lambda^{\alpha}\left(t,\tau\right) \approx \Lambda^{\alpha},$$

and (*iii*) the energy shifts are taken as level independent, i.e., $\delta\varepsilon_k^{\alpha}(t) \approx \delta\varepsilon^{\alpha}(t) \approx \delta\varepsilon^{\alpha}$ for L or R. The physical essence of the transport problem is captured under these reasonable hypotheses [18]. In the practical implementation, the effects of the specific electronic structures of the leads can be captured by enlarging the device region

to include enough portions of the electrodes. Following the procedures similar to those in reference (Jauho et al., 1994), we obtain that

$$Q_\alpha = P^\alpha(t) + \left[P^\alpha(t)\right]^\dagger + \left\{\Lambda^\alpha \cdot \sigma_D\right\}, \tag{20.14}$$

where the curly bracket on the RHS denotes the anticommutator. Taking $t = 0$ as the switch-on instant, $P^\alpha(t)$ can be written down as

$$P^\alpha(t) = \frac{2i}{\pi} U^{(-)}(t) \left\{ \int_0^t d\tau \frac{e^{i\delta\epsilon^\alpha(t-\tau)}}{t-\tau} U^{(+)}(\tau) + \int_{-\infty}^0 d\tau \frac{i e^{i\delta\epsilon^\alpha\tau}}{t-\tau} G_D^{\tau,0}(-\tau) \right\} \Lambda^\alpha - 2\Lambda^\alpha. \tag{20.15}$$

where G_D^r is the retarded Green's function of D before the switch-on instant. The propagators for the reduced system D are defined as

$$U^{(\pm)}(t) = \exp\left\{ \pm i \int_0^t h_D(\tau)\, d\tau \pm \sum_{\alpha=L,R} \Lambda^\alpha t \right\} \tag{20.16}$$

Equations (20.14) $\sim$ (20.16) constitute the WBL formulation of the TDDFT-NEGF formalism where Q_α exhibit an implicit dependence on $\rho_D(t)$.

To summarize, we have proven the existence of the exact TDDFT formalism for the open electronic systems, and have proposed a TDDFT-NEGF formulation to calculate the quantum transport properties of molecular devices. Since TDDFT results in formally exact density distribution, the TDDFT-NEGF formulation is in principle an exact theory to evaluate the transient and steady-state currents. In particular, the TDDFT-NEGF expression for the steady-state current has the exact same form as that of the conventional DFT-NEGF formalism (Taylor et al., 2001; Ke et al., 2004; Deng et al., 2004; Brandbyge et al., 2002; Xue et al., 2001), and this provides rigorous theoretical foundation for the existing DFT-based methodologies (Lang, 1995; Taylor et al., 2001; Ke et al., 2004; Deng et al., 2004; Brandbyge et al., 2002; Xue et al., 2001) calculating the steady currents through molecular devices. In addition to the conventional exchange-correlation functional, a new density functional is introduced to account for the dissipative interaction between the reduced system and the environment. In the WBL approximation, the new functional can be expressed in a relatively simple form which depends implicitly on the electron density of the reduced system. Since the basic variable in our formulation is the reduce single-electron density matrix, the linear-scaling techniques such as that of reference (Yam et al., 2003) can be adopted to further speed up the computation.

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