

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 14358–14364

www.rsc.org/pccp

PAPER

# Existence of time-dependent density-functional theory for open electronic systems: Time-dependent holographic electron density theorem

Xiao Zheng,<sup>\*a</sup> ChiYung Yam,<sup>b</sup> Fan Wang<sup>c</sup> and GuanHua Chen<sup>\*b</sup>

Received 15th March 2011, Accepted 12th May 2011

DOI: 10.1039/c1cp20777f

We present the time-dependent holographic electron density theorem (TD-HEDT), which lays the foundation of time-dependent density-functional theory (TDDFT) for open electronic systems. For any finite electronic system, the TD-HEDT formally establishes a one-to-one correspondence between the electron density inside any finite subsystem and the time-dependent external potential. As a result, any electronic property of an open system in principle can be determined uniquely by the electron density function inside the open region. Implications of the TD-HEDT on the practicality of TDDFT are also discussed.

## I. Introduction

The Hohenberg–Kohn theorem<sup>1</sup> states that the ground state electron density function of an isolated time-independent system determines all electronic properties of the system, and thus lays the foundation of density-functional theory (DFT). The Kohn–Sham formalism<sup>2</sup> provides a practical scheme to calculate the ground-state properties of electronic systems. The Runge–Gross theorem extends the Hohenberg–Kohn theorem to the time-dependent electronic systems and asserts that the time-dependent electron density function determines uniquely all electronic properties of the corresponding time-dependent system.<sup>3</sup> Based on the Runge–Gross theorem, time-dependent density-functional theory (TDDFT) was developed to calculate the excited-state properties of electronic systems. The accuracy of DFT or TDDFT is determined by the quality of exchange–correlation (XC) functional. If the exact XC functional were known, the Kohn–Sham formalism would have provided the exact ground-state properties, and a time-dependent Kohn–Sham extension would have yielded exact time-dependent and excited-state properties. Despite their wide range of applications, DFT and TDDFT have been mostly limited to isolated systems.

In fact, all systems are in principle open systems which exchanges energy, matter, or phase information with the surrounding environments. The environment usually contains a much larger number of degrees of freedom than the system does, and significantly affects the system physical properties.

In quantum dissipation theory (QDT) which focuses on the reduced dynamics of open systems, the environment is commonly taken as a bath, and its effects are treated in a statistical manner.<sup>4</sup> A molecular electronic device is one example of open systems. Bulk electrodes in contact with the device play the roles of electron reservoir and energy sink, and hence can be treated as fermionic baths. The presence of realistic open system can also be found in dye-sensitized solar cells, where a dye molecule adsorbed on the surface of solid titanium dioxide (TiO<sub>2</sub>) can be deemed as an open system. The strong covalent bonding between the dye and the TiO<sub>2</sub> surface facilitates ultrafast photo-induced interfacial electron transfer.<sup>5,6</sup> Bulk TiO<sub>2</sub> can be regarded as the fermionic bath, which influences the excited-state electron dynamics at the dye–TiO<sub>2</sub> interface. There are also open systems whose number of electrons is considered to be conserved. For instance, for condensed-phase chemical reactions, the solvent vibration modes or solid phonon modes can be regarded as thermal (bosonic) baths,<sup>7</sup> which affect the electronic properties of substrate molecules.

Ground-state DFT methods were used to calculate the static electronic response of open systems under external fields. For instance, to calculate steady-state transmission coefficients of molecular devices for quantum transport, the ground-state Kohn–Sham Fock operator is taken as the effective single-electron model Hamiltonian, and electronic properties of interest are evaluated within the noninteracting electron model.<sup>8–12</sup> However, the investigated systems are not in their ground states, and applying ground-state DFT methods for such systems is only an approximation.<sup>13,14</sup> To resolve this issue, DFT formalisms adapted for current-carrying systems have been proposed, such as Kosov's Kohn–Sham equations with direct current.<sup>15</sup> Despite the progress, static DFT approaches cannot address the dynamic electronic properties or transient phenomena. To this end, one needs to resort to TDDFT for open systems.

<sup>a</sup> Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, China.  
E-mail: xz58@ustc.edu.cn

<sup>b</sup> Department of Chemistry, Centre of Theoretical and Computational Physics, The University of Hong Kong, Hong Kong.  
E-mail: ghc@everest.hku.hk

<sup>c</sup> College of Chemistry, Sichuan University, Chengdu, China

TDDFT for open quantum systems with conserved number of electrons have been proposed. Burke *et al.* have proved the existence of TDDFT for such open systems by establishing a Runge–Gross-type theorem. They have also constructed a Markovian Kohn–Sham master equation including dissipation to phonons.<sup>16</sup> Yuen-Zhou *et al.* have extended the Runge–Gross theorem to open quantum systems described by a master equation involving non-Markovian dissipation to environment.<sup>17</sup> Tempel *et al.* have proved the existence of TDDFT Kohn–Sham scheme for general open systems, and proposed a linear-response master equation approach to address the broadening and shifting of electronic excitation spectra of open systems by coupling to environment.<sup>18</sup> These approaches have been applied and tested on model systems.

For open systems with variable number of electrons, we have proved the existence of a rigorous TDDFT through the establishment of the time-dependent holographic electron density theorem (TD-HEDT).<sup>19–23</sup> Based on the TD-HEDT, we have further developed a Kohn–Sham equation-of-motion formalism for the transient reduced dynamics of the open system.<sup>22</sup> Practical TDDFT schemes have also been proposed by other authors, mostly in the context of quantum transport, such as Kurth *et al.*'s formulation for propagation of Kohn–Sham wavefunctions with open boundary condition,<sup>14</sup> and Cui *et al.*'s quantum master equation employing complete second-order QDT.<sup>24,25</sup>

This paper aims at providing a comprehensive account for TD-HEDT, which lays the foundation of TDDFT for open systems that allow both particle exchange and energy dissipation. In addition to reviewing some of the existing work, this paper also provides substantial new result, such as a neat proof for the holographic property of real analytic functions, and new understanding and insight, such as the extensive discussions on the conceptual and practical implications of the HEDT, particularly for time-dependent open systems.

The remainder of this paper is organized as follows. In section 2 we revisit the mathematical background and physical aspects of ground-state HEDT (GS-HEDT). In section 3 we give a detailed proof of TD-HEDT, and clarify some important issues. We then highlight the fundamental significance of TD-HEDT by elaborating its implication on the existence and practicality of TDDFT for open systems. Concluding remarks are finally given in section 4.

## II. Ground-state holographic electron density theorem

As early as in 1981, Riess and Münch proposed<sup>26</sup> a conjecture which states that any nonzero volume piece of the ground-state electron density determines the electron density distribution of a molecular system. This was based on their hypothesis that the electron density functions of atomic and molecular eigenfunctions are real analytic away from nuclei. In their proof, they argued that the real analyticity of ground-state many-body wavefunction leads directly to the real analyticity of corresponding electron density function. However, this is neither obvious nor trivial, and was not proved rigorously yet. In 1999 Mezey has extended Riess and Münch's work, and termed their conjecture as the GS-HEDT.<sup>27</sup> In 2004

Fournais *et al.* have proved the real analyticity of electron density function of any atomic or molecular eigenstate.<sup>28,29</sup> This lays a solid mathematical basis for the GS-HEDT. A new proof for the real analyticity of electron density has been given by Jecko in 2010.<sup>30</sup> The GS-HEDT has been constantly related to quantum similarity measures in the scope of conceptual DFT.<sup>31,32</sup>

Mathematically, a real function is real analytic if it possesses derivatives of all orders and agrees with its Taylor series in a neighborhood of every point. For real physical systems, such as systems made of atoms and molecules, the external potential acting on each electron,  $v(\mathbf{r})$ , is real analytic except at nuclei. Nuclei are treated as point charges. This only leads to non-analytic electron density at isolated points. Apart from the isolated nuclear positions, the  $\mathbf{r}$ -space is all connected, on which  $\rho(\mathbf{r})$  is real analytic. In practical quantum mechanical calculations, real analytic functions such as Gaussian functions and plane waves are commonly used as basis sets, which naturally results in real analytic electron density function.

As a consequence of real analyticity,  $\rho(\mathbf{r})$  inside a subspace determines uniquely its values on the entire physical space. In principle, this can be realized by the analytic continuation of a real analytic function. The proof for the univariable real analytic functions can be found in textbooks such as ref. 33. Although the extension to multivariable real analytic functions is not difficult, such a proof has not been found by us. Here, we provide a simple proof for the holographic property of real analytic  $\rho(\mathbf{r})$  in three-dimensional physical space.

*Lemma:* Let  $\rho$  be a continuous function on  $\mathbb{R}^3$ , and  $\rho$  is real analytic on an open connected subset  $U$ , with its complementary subset  $\bar{U}$  consisting of isolated points only. If  $\rho$  is known on an open subset  $W \subseteq U$  and  $W \neq \emptyset$ , then  $\rho$  is uniquely determined on  $\mathbb{R}^3$ .

*Proof:* For brevity, we introduce the notation  $\mathbb{Z}^+ = \{0, 1, 2, \dots\}$ , and the multiindex  $\gamma = (\gamma_1, \gamma_2, \gamma_3) \in (\mathbb{Z}^+)^3$ . We use three-dimensional variable  $x = (x_1, x_2, x_3) \in \mathbb{R}^3$  to represent the displacement vector  $\mathbf{r}$ , and we have

$$\begin{aligned} \gamma! &= \gamma_1! \gamma_2! \gamma_3!, \\ x^\gamma &= x_1^{\gamma_1} x_2^{\gamma_2} x_3^{\gamma_3}, \\ \frac{\partial^\gamma}{\partial x^\gamma} &= \frac{\partial^{\gamma_1}}{\partial x_1^{\gamma_1}} \frac{\partial^{\gamma_2}}{\partial x_2^{\gamma_2}} \frac{\partial^{\gamma_3}}{\partial x_3^{\gamma_3}}. \end{aligned} \quad (1)$$

First we show that  $\rho$  is uniquely determined on  $U$ . The proof is trivial if  $W = U$ , so we only need to consider the case of  $\emptyset \neq W \subset U$  ( $W$  is a proper subset of  $U$ ). Suppose there is another function  $\rho'(x)$  also continuous on  $\mathbb{R}^3$ , real analytic on  $U$ , and equal to  $\rho(x)$  for all  $x \in W$ . Based on the real analytic properties of both  $\rho$  and  $\rho'$ , we immediately have  $\frac{\partial^\gamma \rho(x)}{\partial x^\gamma} = \frac{\partial^\gamma \rho'(x)}{\partial x^\gamma}$ ,  $\forall x \in W$  and  $\gamma \in (\mathbb{Z}^+)^3$ . We set

$$V \equiv U \cap \left\{ x : \frac{\partial^\gamma \rho(x)}{\partial x^\gamma} = \frac{\partial^\gamma \rho'(x)}{\partial x^\gamma}, \forall \gamma \in (\mathbb{Z}^+)^3 \right\}. \quad (2)$$

Because of the continuity of  $\frac{\partial^\gamma \rho(x)}{\partial x^\gamma}$  and  $\frac{\partial^\gamma \rho'(x)}{\partial x^\gamma}$ ,  $V$  is obviously a closed subset in the relative topology of  $U$ . On the other hand, due to the fact that both  $\rho$  and  $\rho'$  are real analytic on  $V$ , for every  $x_0 \in V$ , there exists  $b > 0$  such that the power series

$\sum_{\gamma \in (\mathbb{Z}^+)^3} \frac{1}{\gamma!} \frac{\partial^\gamma \rho(x_0)}{\partial x^\gamma} (y - x_0)^\gamma$  and  $\sum_{\gamma \in (\mathbb{Z}^+)^3} \frac{1}{\gamma!} \frac{\partial^\gamma \rho'(x_0)}{\partial x^\gamma} (y - x_0)^\gamma$  converge to  $\rho(y)$  and  $\rho'(y)$  on the neighborhood  $D_b(x_0) = U \cap \{y: |y - x_0| < b\}$ , respectively. This infers that  $\frac{\partial^\gamma \rho}{\partial x^\gamma} = \frac{\partial^\gamma \rho'}{\partial x^\gamma}$  holds for all  $y \in D_b(x_0)$ . Based on eqn (2) any  $y$  in  $D_b(x_0)$  also belongs to  $V$ . Therefore,  $V$  is also an open subset based on the definition of openness. In a word,  $V$  is found to be a clopen subset of  $U$ . However, because the set  $U$  is connected, it should not contain any proper clopen subset. Since  $W \neq \emptyset$ , we have  $V \neq \emptyset$ , and thus  $V$  has to be exactly the same as  $U$ . By taking specifically  $\gamma = (0,0,0)$  in eqn (2), we have  $\rho(x) = \rho'(x)$  for all  $x \in U$ .

To complete the proof we need to verify that  $\rho$  is also uniquely determined on  $\bar{U}$ . These nonanalytic points are collected by the continuity of  $\rho$ . Suppose there is another function  $\rho'$  equal to  $\rho$  on  $U$ , but different at  $y \in \bar{U}$ . For that particular  $y$ , there always exists a sequence  $\{q_n\} \in U$  ( $n \in \mathbb{Z}^+$ ) which converges to  $y$ , since  $\bar{U}$  consists of isolated points. Define  $\delta = |\rho(y) - \rho'(y)|$ . Since  $\{q_n\} \in U$ ,  $\rho(q_n) = \rho'(q_n)$  holds for all  $n$ . Due to the continuity of both  $\rho$  and  $\rho'$  on  $\mathbb{R}^3$ ,  $\forall \epsilon$  with  $0 < \epsilon < \frac{\delta}{2}$ ,  $\exists q_m$  ( $m \in \mathbb{Z}^+$ ) so that  $|\rho(y) - \rho(q_m)| < \epsilon$  and  $|\rho'(y) - \rho'(q_m)| < \epsilon$ . This leads to

$$\begin{aligned} \delta &= |\rho(y) - \rho'(y)| = |\rho(y) - \rho(q_m) + \rho(q_m) - \rho'(y)| \\ &= |\rho(y) - \rho(q_m) + \rho'(q_m) - \rho'(y)| \leq |\rho(y) - \rho(q_m)| \\ &\quad + |\rho'(q_m) - \rho'(y)| < 2\epsilon < \delta. \end{aligned} \quad (3)$$

This cannot be true anyway, therefore  $\rho(y) = \rho'(y)$  holds for all  $y \in \bar{U}$ .

In conclusion, we have proved that  $\rho$  is uniquely determined on  $\mathbb{R}^3$  as the theorem states. In this sense, if  $\rho$  is taken as the electron density function and  $W$  as the region  $D$  which spans the open system of primary interest, any functional of  $\rho$  can thus be viewed as a functional of  $\rho_D$  without any ambiguity.

Based on the lemma, we proceed to prove the GS-HEDT.

**GS-HEDT:** The electron density  $\rho(\mathbf{r})$  inside a subsystem of a connected real physical system in its ground state determines uniquely all electronic properties of the entire system.

*Proof:* Suppose the physical space spanned by the subsystem and the real physical system are  $D$  and  $U$ , respectively. By definition  $D$  is a subspace of  $U$ , i.e.  $D \subseteq U$ . According to the above lemma,  $\rho(\mathbf{r})$  inside subsystem  $D$ ,  $\rho_D(\mathbf{r})$ , determines uniquely its values on the entire system  $U$ .

For a system in its ground state, the Hohenberg–Kohn theorem establishes the one-to-one correspondence between external potential  $v(\mathbf{r})$  and electron density  $\rho(\mathbf{r})$ . It states that  $\rho(\mathbf{r})$  determines uniquely  $v(\mathbf{r})$ , and hence determines uniquely all electronic properties of the system. Combining the above facts, we come to the conclusion that  $\rho(\mathbf{r})$  inside a subsystem determines  $\rho(\mathbf{r})$  of the entire system, and hence determines uniquely all electronic properties of the real physical system. Q.E.D.

The GS-HEDT establishes a one-to-one correspondence between the external potential  $v(\mathbf{r})$  and ground-state electron density function inside any subsystem  $D$ ,  $\rho_D(\mathbf{r})$ . It thus affirms the existence of a rigorous DFT for open systems. In principle, all information we need is the electron density inside the subsystem of our primary interest. It is important to point out that the analytical continuation is only for the formal

proof of the GS-HEDT. In practice, such a continuation would be numerically unstable and intractable. Similar scenario applies also for the TD-HEDT to be discussed in below.

### III. Time-dependent holographic electron density theorem

#### A. The TD-HEDT and its proof

Extending GS-HEDT to time-dependent open systems is not trivial. Although it seems intuitive that the time-dependent electron density function  $\rho(\mathbf{r}, t)$  is real analytic except for isolated points in space-time, to the best of our knowledge, there is no rigorous proof which can justify the real analyticity of  $\rho(\mathbf{r}, t)$ . Fortunately, we are able to circumvent this uncertainty, and establish a one-to-one correspondence between the time-dependent electron density function of any finite subsystem  $D$ ,  $\rho_D(\mathbf{r}, t)$ , and the external potential field  $v(\mathbf{r}, t)$ , provided that external potential is real analytic in both  $t$ -space and  $\mathbf{r}$ -space. This gives the TD-HEDT as follows.

**TD-HEDT:** 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 a real analytic (in both  $t$ -space and  $\mathbf{r}$ -space) external potential field  $v(\mathbf{r}, t)$  is applied to the system after  $t_0$ , the time-dependent electron density function on any finite subspace  $D$ ,  $\rho_D(\mathbf{r}, t)$ , has a one-to-one correspondence with  $v(\mathbf{r}, t)$  (up to an additive merely time-dependent function), 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  $t \geq t_0^+$ . Their corresponding electron density functions are  $\rho(\mathbf{r}, t)$  and  $\rho'(\mathbf{r}, t)$ , respectively. There must exist a minimal nonnegative integer  $k$ , so that the  $k$ -th order derivative differentiates these two potentials at  $t_0$  by a non-constant function  $w(\mathbf{r})$ :

$$w(\mathbf{r}) \equiv \frac{\partial^k}{\partial t^k} [v(\mathbf{r}, t) - v'(\mathbf{r}, t)] \Big|_{t=t_0^+} \neq \text{const}. \quad (4)$$

Following exactly eqn (3)–(6) of ref. 3, we have

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [\rho(\mathbf{r}, t) - \rho'(\mathbf{r}, t)] \Big|_{t=t_0^+} = -\nabla \cdot \mathbf{u}(\mathbf{r}), \quad (5)$$

where  $\mathbf{u}(\mathbf{r})$  is a vector function of  $\mathbf{r}$  expressed by

$$\mathbf{u}(\mathbf{r}) = \rho(\mathbf{r}, t_0) \nabla w(\mathbf{r}) \quad (6)$$

Due to the real 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. In ref. 3 it has been argued that  $\nabla \cdot \mathbf{u}(\mathbf{r})$  can *not* be everywhere zero in  $\mathbf{r}$ -space, provided that (i)  $\rho(\mathbf{r}, t_0)$  falls off rapidly enough away from the system, and (ii) there is no finite subregion in  $\mathbf{r}$ -space in which  $\rho(\mathbf{r}, t_0) = 0$  and  $w(\mathbf{r}) = \text{const}$ . Here, condition (i) is satisfied for any finite physical system, and the pathological situation raised in (ii) can also be excluded, since  $\rho(\mathbf{r}, t_0)$  is presumed to be real analytic (otherwise  $\rho(\mathbf{r}, t_0)$  is everywhere zero based on the lemma proved in section II). Therefore, it is impossible to have  $\nabla \cdot \mathbf{u}(\mathbf{r}) = 0$  everywhere in any finite subsystem  $D$ , because of its real analyticity in  $\mathbf{r}$ -space. Denoting  $\rho_D(\mathbf{r}, t)$  for  $\rho(\mathbf{r}, t)$  on  $D$ ,

we have

$$\left. \frac{\partial^{k+2}}{\partial t^{k+2}} [\rho_D(\mathbf{r}, t) - \rho'_D(\mathbf{r}, t)] \right|_{t=t_0^+} \neq 0 \quad (7)$$

on subsystem  $D$ , *i.e.*, the  $(k+2)$ -th order derivative differentiates the two electron density functions in any finite subsystem  $D$ . This confirms the existence of a one-to-one correspondence between  $v(\mathbf{r}, t)$  and  $\rho_D(\mathbf{r}, t)$ . As a consequence,  $\rho_D(\mathbf{r}, t)$  determines uniquely  $v(\mathbf{r}, t)$ , and hence determines all electronic properties of the entire system. Q.E.D.

The TD-HEDT for time-dependent open systems plays an analogous role as Runge–Gross theorem for isolated systems. It affirms the existence of a rigorous TDDFT for general time-dependent open systems with variable number of electrons. In principle, all one needs to know is the electron density function in a local subsystem.

### B. Important insight into the TD-HEDT

For the TD-HEDT to be valid, the total physical system (including the environment) has to be finite, which means one can define a finite region in  $\mathbf{r}$ -space, beyond which electrons cannot be bound locally by  $v(\mathbf{r}, t)$ . The finiteness condition is required to ensure  $\rho(\mathbf{r}, t_0)$  vanish at the “surface” of the system, which is needed for the above proof of the TD-HEDT. Moreover, one may understand the finiteness requirement by considering a system consisting of two remotely separated atoms. For any finite time-dependent system, the real analyticity of  $v(\mathbf{r}, t)$  ensures any change in  $v(\mathbf{r}, t)$  at any finite distance away from subsystem  $D$  immediately modify the local potential  $v_D(\mathbf{r}, t)$ , and  $v_D(\mathbf{r}, t)$  will invoke instantaneous response in local electron density  $\rho_D(\mathbf{r}, t)$ . For the two-atom system, if the interatomic distance is finite, and one of the nuclei is displaced after time  $t_0$ . The local electrostatic potential at the other atom is perturbed through the long-range Coulomb interaction, which results in instantaneous response in local electron density. However, if the two atoms are infinitely far away, the response in local electron density is infinitesimally small. Therefore, in the practical sense the electron density can neither feel nor determine the external potential infinitely far away. On the other hand, a finite system can be very large. In an overall finite system, the environment surrounding an open subsystem can be properly treated in a statistical manner, as long as the recurrence time of the environment is much longer than the characteristic dynamic time of the subsystem. For instance, for quantum transport through a nanoelectronic device, the macroscopic but finite leads have orders of magnitude more degrees of freedom than the device, and can thus be treated as the electron reservoir (fermionic bath) for the open system, the nanodevice. Furthermore, for a finite total system, its number of electrons,  $N$ , is known *via* the initial state  $\Phi(t_0)$ .  $N$  together with external field  $v(\mathbf{r}, t)$  determine uniquely the Hamiltonian of entire system.

The proof of GS-HEDT is based on the analytical continuation of real analytic ground-state electron density function from within a finite subregion to the entire  $\mathbf{r}$ -space. In contrast, the validity of TD-HEDT does not require the time-dependent electron density function  $\rho(\mathbf{r}, t)$  be real analytic in  $\mathbf{r}$ -space except at  $t = t_0$ . Instead, it requires the external potential

$v(\mathbf{r}, t)$  to be real analytic in space-time (after initial time  $t_0$ ), which is indeed the case for physical systems, such as systems made of atoms and molecules. It is often the case that the initial state  $\Phi(t_0)$  is a ground state, so that  $\rho(\mathbf{r}, t_0)$  automatically possesses the analyticity property based on the lemma in section II. It is important to emphasize that the real analyticity of  $\rho(\mathbf{r}, t_0)$  and  $v(\mathbf{r}, t)$  is utilized only to establish the formal one-to-one mapping between  $\rho_D(\mathbf{r}, t)$  and  $v(\mathbf{r}, t)$ . Although in principle  $\rho_D$  determines completely and uniquely  $\rho$  of total system, one should not take analytical continuation as a practical scheme to extend electron density from inside of a subsystem to the outer region, as it is numerically extremely unstable, and also unjustified for time-dependent systems where the validity of real analyticity is unknown. Therefore, in practice more convenient and reliable approaches are needed to exploit the explicit or implicit dependence of electronic properties on  $\rho_D(\mathbf{r}, t)$ .

The TD-HEDT for time-dependent open systems given in section 3.1 parallels the Runge–Gross theorem for isolated systems. The real analyticity of external potential in  $t$ -space is adopted implicitly in the proof of the Runge–Gross theorem. van Leeuwen has extended the Runge–Gross theorem by explicitly using the real analyticity of time-dependent potential in  $t$ -space.<sup>34,35</sup> The extended theorem illustrates a formal scheme of constructing the single-electron potential of a reference system,  $v'(\mathbf{r}, t)$ , in which the electron density,  $\rho'(\mathbf{r}, t)$ , reproduces exactly that of the original physical system,  $\rho(\mathbf{r}, t)$ . At the initial time  $t_0$ , a set of Sturm-Liouville-type equations are derived for  $v'(\mathbf{r}, t_0)$  and all the time derivatives  $\frac{\partial^k v'}{\partial t^k} |_{t=t_0}$  ( $k = 1, 2, \dots$ ), which are solved from the information of  $\rho(\mathbf{r}, t)$  and initial state, subject to the boundary condition  $v'(\mathbf{r}, t_0) = \frac{\partial^k v'}{\partial t^k} |_{t=t_0} = 0$  at  $\mathbf{r} \rightarrow \infty$ . At a later time  $t_1 > t_0$ ,  $v'(\mathbf{r}, t_1)$  can be constructed by an analytical continuation from  $t_0$  to  $t_1$ , provided that  $t_1$  is within the convergence radius of the Taylor expansion of  $v'(\mathbf{r}, t)$  at  $t_0$ . This procedure can be repeated by propagating the reference system to  $t_1$  and taking  $t_1$  as a new initial time. In this way  $v'(\mathbf{r}, t)$  in all  $t > t_0$  is established completely and uniquely.<sup>34,35</sup>

Extension of the van Leeuwen scheme to open systems is nontrivial. If a such extension exists for the TD-HEDT, it would provide a formal scheme to construct  $v'(\mathbf{r}, t)$  of a reference system, so that the reference electron density reproduces that of the original physical system inside the open region  $D$ , *i.e.*,  $\rho'_D(\mathbf{r}, t) = \rho_D(\mathbf{r}, t)$ . Note that  $v'(\mathbf{r}, t)$  in the entire  $\mathbf{r}$ -space is needed to define the Hamiltonian of the reference system without ambiguity. The same set of Sturm–Liouville-type equations can be derived for  $v'$  and  $\frac{\partial^k v'}{\partial t^k}$  ( $k = 1, 2, \dots$ ) inside  $D$ . A boundary condition is needed to obtain a unique solution to these equations. At the initial time  $t_0$ ,  $v'(\mathbf{r}, t_0)$  can be extracted from the initial state of reference system. However, it remains unclear how to determine the values of  $\frac{\partial^k v'}{\partial t^k}$  at the boundary of  $D$ . Moreover, even with the Sturm–Liouville-type equations uniquely solved inside  $D$ , the values of  $v'$  and  $\frac{\partial^k v'}{\partial t^k}$  outside  $D$  remain unspecified. In principle any value that is physically sound can be assigned to these unspecified quantities, which lead to possible multiple solutions for  $v'(\mathbf{r}, t)$ . For the uniqueness of  $v'(\mathbf{r}, t)$ , one would presume that  $v'$  and

$\frac{\partial^k v'}{\partial t^k}$  are real analytic functions in  $\mathbf{r}$ -space, so that their values can be analytically continued from inside  $D$  to the entire  $\mathbf{r}$ -space. However, real analyticity of  $v'$  and its time derivatives would necessarily require the real analyticity of time-dependent electron density in  $\mathbf{r}$ -space, as  $v'$  and  $\rho$  ( $\rho'$ ) are related by the Sturm-Liouville-type equation.

Alternatively, one could extend the domain for the set of Sturm-Liouville-type equations from inside  $D$  to the entire  $\mathbf{r}$ -space, so that  $v' = \frac{\partial^k v'}{\partial t^k} = 0$  at  $\mathbf{r} \rightarrow \infty$  can be used as the boundary condition, same as in the van Leeuwen scheme for isolated systems. Extra pieces of information, the reference electron density and its time derivatives outside  $D$ , are required to complete the equations. One obvious choice is to set  $\rho' = \rho$  and  $\frac{\partial^k \rho'}{\partial t^k} = \frac{\partial^k \rho}{\partial t^k}$  ( $k = 1, 2, \dots$ ) outside  $D$  at any time  $t$ . This amounts to treating the whole system as an isolated system, and the construction of  $v'$  follows exactly the original van Leeuwen scheme. However, one cannot exclude other possibilities of assigning values to  $\rho'$  and  $\frac{\partial^k \rho'}{\partial t^k}$  outside  $D$ , as long as the resulting  $\rho'(\mathbf{r}, t)$  is physically sound, correctly normalized, and continuously connected to  $\rho$  at the boundary of  $D$ . Consequently, for open systems there may exist multiple solutions for  $v'(\mathbf{r}, t)$ , which yield  $\rho'_D(\mathbf{r}, t) = \rho_D(\mathbf{r}, t)$ . To have a unique  $v'(\mathbf{r}, t)$ , extra constraints need to be imposed. In the TD-HEDT described in section 3.1, only those potentials that are real analytic in both  $\mathbf{r}$ - and  $t$ -space are considered. In contrast, here one cannot directly impose real analyticity on  $v'(\mathbf{r}, t)$  since it is determined by the Sturm-Liouville-type equation. Instead, to have a unique  $v'(\mathbf{r}, t)$  that is real analytic in  $\mathbf{r}$ -space, it is necessary for  $\rho'$  to be real analytic in the entire  $\mathbf{r}$ -space, so that  $\rho'$  outside  $D$  is uniquely determined by  $\rho$  inside  $D$ . This also requires the electron density of original physical system,  $\rho(\mathbf{r}, t)$ , always be real analytic inside  $D$ .

Based on the above discussions, we conclude that a van Leeuwen like scheme can be established for open electronic systems. For any physical open system, a reference system can be constructed, so that the reference electron density reproduces exactly the physical electron density within the open system. Unlike the original van Leeuwen scheme for isolated systems in which the single-electron reference potential is uniquely constructed, for open systems there exist multiple solutions for the reference potential. To make such a construction scheme an extension for the TD-HEDT theorem, an extra constraint, real analyticity in  $\mathbf{r}$ -space, needs to be imposed on the reference potential. However, this would necessarily require the time-dependent electron density be real analytic in  $\mathbf{r}$ -space, for which a rigorous mathematical proof is still in pursue.

It is worth pointing out that piecewise time-analytic physical potentials are admitted in van Leeuwen schemes for both isolated and open systems. This is because the isolated non-analytic time (say  $t_1$ ) can be taken as a new initial time, and the corresponding new initial state is obtained by system evolution under the external potential which is time-analytic until  $t_1$ . From the new initial state, the construction of reference potential can be continued to a later time.

### C. Implication for practical calculations

Noting the formal analogy between the TD-HEDT and Runge-Gross theorem, we can define an action integral

functional,  $A[\rho_D(\mathbf{r}, t)]$ , by following the original Runge-Gross paper<sup>3</sup>

$$A[\rho_D] = \int_{t_0}^{t_1} dt \langle \Phi[\rho_D] | i\partial_t - \hat{H}(t) | \Phi[\rho_D] \rangle. \quad (8)$$

Here,  $\Phi[\rho_D]$  is the time-dependent many-body wavefunction, and  $\hat{H}(t)$  is the many-body Hamiltonian.  $A[\rho_D]$  is uniquely determined by  $\rho_D$ , since the phase associated with the merely additive time-dependent constant potential cancels out automatically. Applying the stationary action principle, the exact electron density function on subsystem  $D$  can be obtained by solving  $\delta A / \delta \rho_D(\mathbf{r}, t) = 0$ . Note that the electron density on total system is also completely determined by  $\rho_D$ , i.e.  $\rho(\mathbf{r}, t) = \rho[\mathbf{r}, t; \rho_D]$ , based on the TD-HEDT. In practice, one can also construct universal functionals such as  $A_{xc}[\rho_D]$  in the same fashion as in ref. 3, and develop a Kohn-Sham scheme for calculations of realistic open systems. The dependence of Kohn-Sham effective potential on  $\rho_D(\mathbf{r}, t)$  is also universal under any external field. It is worth mentioning that the definition of action functional  $A[\rho_D]$ , eqn (8), leads to the well-known causality paradox. A number of approaches have been proposed to resolve this paradox, such as van Leeuwen's action functional established within Keldysh formalism,<sup>36</sup> Mukamel's unified description of density response and spontaneous fluctuation in Liouville space,<sup>37</sup> and Vignale's correction term to the action functional derivative.<sup>38</sup>

The TD-HEDT applies to the same phenomena and/or properties as those intended by Runge-Gross theorem, i.e., where the electron density, in principle, provides the minimal amount of information necessary for establishing a one-to-one mapping with the scalar external field. This is true when the interaction between electrons and magnetic field is negligible. However, in the presence of an appreciable magnetic field, electron density alone becomes insufficient to determine the system properties. In such cases, extra system information, the current density, is needed. The above theorem for TDDFT should be generalized into the framework of time-dependent current-density-functional theory (TDCDFT).<sup>39,40</sup> Progress has been made along this direction. Di Ventura *et al.* have developed a TDCDFT method for open systems *via* the real-time propagation of a stochastic Schrödinger equation.<sup>41</sup> Yuen-Zhou *et al.* have proposed a TDCDFT Kohn-Sham scheme for generalized open systems.<sup>42</sup>

Without the HEDT, to investigate an open system in the DFT framework, one has to treat the total system (open system along with its environment) as a whole isolated entity, and apply Hohenberg-Kohn-Sham's ground-state DFT and/or Runge-Gross's TDDFT. In practice, this presents a major obstacle in simulating realistic open systems, due to the enormous number of degrees of freedom in the environment. It is thus ideal to establish DFT and TDDFT for open systems based on the HEDT, since in principle it only requires the electron density function inside the open system of primary interest, which means that the amount of necessary information required is greatly reduced.

We have developed a practical TDDFT equation-of-motion (EOM) formalism, in which the basic variable is the

Kohn–Sham reduced single-electron density matrix of the open system  $D$ ,  $\sigma_D(t)$ .<sup>22</sup> The form of the EOM is as follows:

$$i\dot{\sigma}_D = [\mathbf{h}_D[t; \rho_D(\mathbf{r}, t)], \sigma_D] - i\mathbf{Q}[t; \rho_D(\mathbf{r}, t)]. \quad (9)$$

Here,  $\mathbf{h}_D[t; \rho_D(\mathbf{r}, t)]$  is the Kohn–Sham Fock matrix of the open system, including the XC potential as a functional of  $\rho_D(\mathbf{r}, t)$ ; and  $\mathbf{Q}[t; \rho_D(\mathbf{r}, t)]$  is also a functional of  $\rho_D(\mathbf{r}, t)$ , which describes the dissipative interaction between the open system  $D$  and its environment. Eqn (9) is formally closed, since  $\rho_D(\mathbf{r}, t) = \sigma_D(\mathbf{r}, \mathbf{r}; t)$ . If the dissipation functional,  $\mathbf{Q}[t; \rho_D(\mathbf{r}, t)]$ , is omitted, eqn (9) reduces to the TDDFT-EOM for the isolated system  $D$ . Fourier-transforming the EOM for an isolated system into frequency domain while considering only the linear response, the conventional Casida's equation<sup>43</sup> is recovered.<sup>44</sup>

In the context of time-dependent quantum transport, practical schemes for  $\mathbf{Q}[t; \rho_D(\mathbf{r}, t)]$  have been developed by using non-equilibrium Green's function formalism<sup>22</sup> or hierarchical quantum dissipation theory.<sup>23</sup> The TDDFT-EOM approach based on eqn (9) has been applied to simulate the transient electron transport through carbon-nanotube-based nanoelectronic devices.<sup>45,46</sup>

#### IV. Concluding remarks

To conclude, in this paper we have proved the HEDT for ground-state and time-dependent open electronic systems, respectively. The HEDT establishes a one-to-one mapping between electron density inside the open system and the external potential, and hence affirms the existence of rigorous DFT (TDDFT) for ground-state (time-dependent) open systems. While the GS-HEDT is based on real analyticity (or “holographic” property) of ground-state electron density function, the TD-HEDT does not require the time-dependent electron density to be real analytic in space-time. Instead, the TD-HEDT only requires the electron density at initial time is real analytic in  $\mathbf{r}$ -space, which is obviously true when the initial state is a ground state. The HEDT lays the foundation of DFT/TDDFT methods for open systems, and provides a rigorous theoretical framework, in which accurate and efficient practical methods can be developed for the simulations of realistic open systems.

#### Acknowledgements

We thank the Hong Kong University Grant Council (AoE/P-04/08), Hong Kong Research Grant Council (HKU700909P, HKUST9/CRF/08, HKU700808P and HKU701307P) and The University of Hong Kong (UDF on Fast Algorithm, Seed Funding Programme for Basic Research 2010-11159085 and 201010159001) for the support. X. Z. thanks University of Science and Technology of China (USTC) for startup funding.

#### References

- 1 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
- 2 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133.
- 3 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997.

- 4 Y. J. Yan and R. X. Xu, *Annu. Rev. Phys. Chem.*, 2005, **56**, 187.
- 5 N. A. Anderson and T. Q. Lian, *Annu. Rev. Phys. Chem.*, 2005, **56**, 491.
- 6 W. R. Duncan and O. V. Prezhdo, *Annu. Rev. Phys. Chem.*, 2007, **58**, 143.
- 7 S. Yokojima, G. Chen, R. Xu and Y. Yan, *J. Comput. Chem.*, 2003, **24**, 2083.
- 8 N. D. Lang, *Phys. Rev. B: Condens. Matter*, 1995, **52**, 5335.
- 9 J. Taylor, H. Guo and J. Wang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 245407.
- 10 S. H. Ke, H. U. Baranger and W. Yang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **70**, 085410.
- 11 W.-Q. Deng, R. P. Muller and W. A. G. III, *J. Am. Chem. Soc.*, 2004, **126**, 13562.
- 12 M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor and K. Stokbro, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 165401.
- 13 Y. Q. Xue, S. Datta and M. A. Ratner, *Chem. Phys.*, 2002, **281**, 151.
- 14 S. Kurth, G. Stefanucci, C. O. Almbladh, A. Rubio and E. K. U. Gross, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 035308.
- 15 D. S. Kosov, *J. Chem. Phys.*, 2003, **119**, 1.
- 16 K. Burke, R. Car and R. Gebauer, *Phys. Rev. Lett.*, 2005, **94**, 146803.
- 17 J. Yuen-Zhou, D. G. Tempel, C. A. Rodriguez-Rosario and A. Aspuru-Guzik, *Phys. Rev. Lett.*, 2010, **104**, 043001.
- 18 D. G. Tempel, M. A. Watson, R. Olivares-Amaya and A. Aspuru-Guzik, *J. Chem. Phys.*, 2011, **134**, 074116.
- 19 X. Zheng, F. Wang and G. H. Chen, arXiv:quant-ph/0606169 (2006).
- 20 C. Y. Yam, X. Zheng and G. H. Chen, *J. Comput. Theor. Nanosci.*, 2006, **3**, 857.
- 21 G. H. Chen, in *Lecture Series on Computer and Computational Nanosciences, Recent Progress in Computational Sciences and Engineering*, ed. T. Simos and G. Maroulis, Brill, Leiden, 2006, vol. 7, p. 803.
- 22 X. Zheng, F. Wang, C. Y. Yam, Y. Mo and G. H. Chen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 195127.
- 23 X. Zheng, G. H. Chen, Y. Mo, S. K. Koo, H. Tian, C. Y. Yam and Y. J. Yan, *J. Chem. Phys.*, 2010, **133**, 114101.
- 24 P. Cui, X. Q. Li, J. S. Shao and Y. J. Yan, *Phys. Lett. A*, 2006, **357**, 449.
- 25 X. Q. Li and Y. J. Yan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 075114.
- 26 J. Riess and W. Münch, *Theor. Chim. Acta*, 1981, **58**, 295.
- 27 P. G. Mezey, *Mol. Phys.*, 1999, **96**, 169.
- 28 S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof and T. O. Sorensen, *Commun. Math. Phys.*, 2002, **228**, 401.
- 29 S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof and T. O. Sorensen, *Ark. Mat.*, 2004, **42**, 87.
- 30 T. Jecko, *Letters in Mathematical Physics*, 2010, **93**, 73.
- 31 P. Geerlings, G. Boon, C. van Alsenoy and F. D. Proft, *Int. J. Quantum Chem.*, 2005, **101**, 722.
- 32 R. Carbó-Dorca and E. Besalú, *J. Comput. Chem.*, 2010, **31**, 2452.
- 33 S. G. Krantz and H. R. Parks, *A Primer of Real Analytic Functions*, Birkhäuser Boston, Cambridge, 2nd edn, 2002.
- 34 R. van Leeuwen, *Phys. Rev. Lett.*, 1999, **82**, 3863.
- 35 R. van Leeuwen, in *Lecture Notes in Physics, Time-Dependent Density Functional Theory*, ed. M. A. L. Marques et al., Springer-Verlag, New York, vol. 706, 2006.
- 36 R. van Leeuwen, *Phys. Rev. Lett.*, 1998, **80**, 1280.
- 37 S. Mukamel, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2005, **71**, 024503.
- 38 G. Vignale, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2008, **77**, 062511.
- 39 G. Vignale and M. Rasolt, *Phys. Rev. Lett.*, 1987, **59**, 2360.
- 40 C. J. Grayce and R. A. Harris, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1994, **50**, 3089.
- 41 M. Di Ventra and R. D'Agosta, *Phys. Rev. Lett.*, 2007, **98**, 226403.
- 42 J. Yuen-Zhou, C. Rodriguez-Rosario and A. Aspuru-Guzik, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4509.

- 
- 43 M. E. Casida, in *Recent Advances in Computational Chemistry, Recent Advances in Density Functional Methods*, ed. D. E. Chong, World Scientific, Singapore, 1995, vol. 1, pp. 155–192.
- 44 F. Wang, C. Yam, G. H. Chen and K. Fan, *J. Chem. Phys.*, 2007, **126**, 134104.
- 45 C. Y. Yam, Y. Mo, F. Wang, X. Li, G. H. Chen, X. Zheng, Y. Matsuda, J. Tahil-Kheil and W. A. Goddard III, *Nanotechnology*, 2008, **19**, 495203.
- 46 S. Wen, S. K. Koo, C. Y. Yam, X. Zheng, Y. J. Yan, Z. Su, K. Fan, L. Cao, W. Wang and G. H. Chen, *J. Phys. Chem. B*, 2011, **115**, 5519.