Existence of A Density-Functional Theory for Open Electronic Systems

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Abstract: We prove that the electron density function of a time-dependent real physical system can be uniquely determined by its values on any finite subsystem. By introducing a new density functional for dissipative interactions between the reduced system and its environment, we subsequently develop a time-dependent density-functional theory which depends in principle only on the electron density of the reduced system.

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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 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 Kohn-Sham 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. DFT-based simulations have been carried out on such devices [4, 5]. In these simulations the Kohn-Sham 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. DFT formalisms adapted for current-carrying systems have also been proposed recently [6, 7]. However, practical implementation of these formalisms requires the electron density function of the entire system. In this paper, we present a DFT formalism for open electronic systems, which depends in principle only on the electron density function of the reduced system.

As early as in 1981, Riess and Münch [8] 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

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the holographic electron density theorem [9]. And in 2004 Fournais *et al.* proved again the real analyticity of the electron density functions of any atomic or molecular eigenstates [10]. 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 is less clear. Although it seems intuitive that the electron density function of any time-dependent real physical system is real analytic (except for isolated points in space-time), it turns out quite difficult to prove the analyticity rigorously. Fortunately we are able to establish a one-to-one correspondence between the electron density function of any finite subsystem and the external potential field which is real analytic in both t-space and $\mathbf{r}$-space, and thus circumvent the difficulty concerning the analyticity of time-dependent electron density function. For time-dependent real physical systems, we have the following theorem:

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

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

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

Following exactly the Eqs. (3)-(6) of Ref. [3], we have

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

where

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

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

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

for $\mathbf{r} \in D$. This confirms the existence of a one-to-one correspondence between $v(\mathbf{r}, t)$ and $\rho_D(\mathbf{r}, t)$. $\rho_D(\mathbf{r}, t)$ thus determines uniquely all electronic properties of the entire system. This completes the proof of the *Theorem*.

Note that if $\Phi(t_0)$ is the ground state, any excited eigenstate, or any state as a linear combination of finite number of eigenstates of a time-independent Hamiltonian, the prerequisite condition in *Theorem* that the electron density function $\rho(\mathbf{r}, t_0)$ be real analytic is automatically satisfied, as
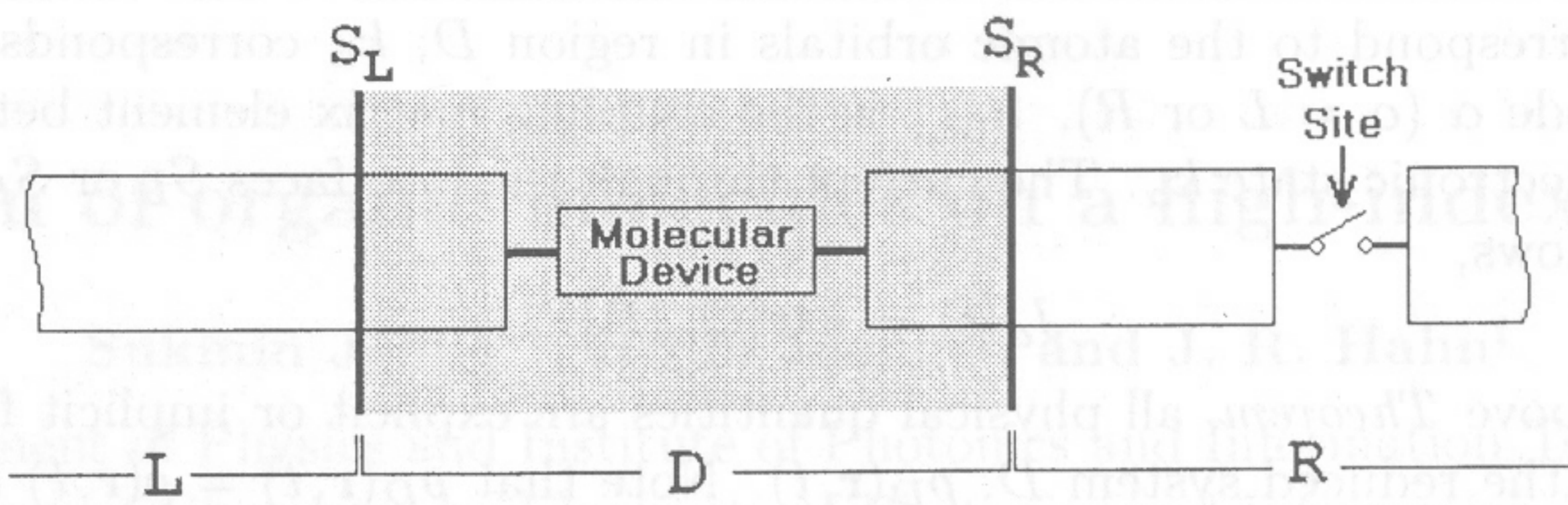
Figure 1: The experimental setup for quantum transport through a molecular device.

proven in Ref. [10]. As long as the electron density function at $t = t_0$, $\rho(\mathbf{r}, t_0)$, is real analytic, it is guaranteed that $\rho_D(\mathbf{r}, t)$ of the subsystem D determines all physical properties of the entire system at any time t if the external potential $v(\mathbf{r}, t)$ is real analytic.

According to the above *Theorem*, the electron density function of any subsystem determines all the electronic properties of the entire time-dependent physical system. This proves in principle the existence of a DFT-type formalism for open electronic systems. In principle all one needs to know is the electron density of the reduced system. The challenge that remains is to develop a practical first-principles formalism.

Fig. 1 depicts an open electronic system. Region D containing a molecular device is the reduced system of our interests, and the electrodes L and R are the environment. Altogether D, L and R form the entire system. Taking Fig. 1 as an example, we develop a practical DFT formalism for the open systems. Within the TDDFT formalism, a closed equation of motion (EOM) has been derived for the reduced single-electron density matrix $\sigma(t)$ of the entire system [11]:

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

where $h(t)$ is the Kohn-Sham Fock matrix of the entire system, and the square bracket on the right-hand side (RHS) denotes a commutator. The matrix element of σ is defined as $\sigma_{ij}(t) = \langle a_j^\dagger(t) a_i(t) \rangle$, where $a_i(t)$ and $a_j^\dagger(t)$ are the annihilation and creation operators for atomic orbitals i and j at time t, respectively. Expanded in the atomic orbital basis set, the matrix σ can be partitioned as:

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

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

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

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

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

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

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

$$J_\alpha(t) = -\text{tr}\left[Q_\alpha(t)\right]. \tag{10}$$

Based on the above *Theorem*, all physical quantities are explicit or implicit functionals of the electron density of the reduced system D, $\rho_D(\mathbf{r}, t)$. Note that $\rho_D(\mathbf{r}, t) = \rho(\mathbf{r}, t)$ for $\mathbf{r} \in D$. Q_α is thus also a functional of $\rho_D(\mathbf{r}, t)$. Therefore, Eq. (8) can be recast into a formally closed form,

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

Neglecting the second term on the RHS of Eq. (11) leads to the conventional TDDFT formulation in terms of reduced single-electron density matrix [11] for the isolated reduced system. The second term describes the dissipative processes between D and L or R. Besides the XC functional, an additional universal density functional, the dissipation functional $Q_\alpha[\mathbf{r}, t; \rho_D(\mathbf{r}, t)]$, is introduced to account for the dissipative interaction between the reduced system and its environment. Eq. (11) is the TDDFT EOM for open electronic systems. An explicit form of the dissipation functional Q_α is required for practical implementation of Eq. (11). Admittedly $Q_\alpha[\mathbf{r}, t; \rho_D(\mathbf{r}, t)]$ is an extremely complex functional and difficult to evaluate. As various approximated expressions have been adopted for the DFT XC functional in practice, the same strategy can be applied to the dissipation functional Q_α. Work along this direction is underway.

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References

[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. Taylor, H. Guo and J. Wang, *Phys. Rev. B* **63** 245407(2001).

[6] D. S. Kosov, *J. Chem. Phys.* **119** 1(2003).

[7] K. Burke, R. Car and R. Gebauer, *Phys. Rev. Lett.* **94** 146803(2005).

[8] J. Riess and W. Münch, *Theoret. Chim. Acta* **58** 295(1981).

[9] P. G. Mezey, *Mol. Phys.* **96** 169(1999).

[10] S. Fournais, M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, *Commun. Math. Phys.* **228** 401(2002).

[11] C. Y. Yam, S. Yokojima and G.H. Chen, *J. Chem. Phys.* **119** 8794(2003); *Phys. Rev. B* **68** 153105(2003).