Description of electron transport dynamics in molecular devices: A time-dependent density functional theoretical approach in momentum space makes it simple

Zhongyuan Zhou and Shih-I Chu

Department of Chemistry, University of Kansas, Lawrence, KS 66045

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Abstract

We propose a first-principles time-dependent density functional theoretical (TDDFT) approach in momentum (P) space for quantitative study of electron transport in molecular devices under arbitrary biases. In this approach, the basic equation of motion is a time-dependent integrodifferential equation obtained by Fourier transform of the time-dependent Kohn-Sham (TDKS) equation in spatial coordinate (R) space. It is formally exact and includes all the effects and information of the electron transport in molecular devices. The electron wavefunction is calculated by solving this equation in a closed finite P-space volume. This approach is free of self-energy function and memory term and beyond the wide-band limit (WBL). The feasibility and power of the approach are demonstrated by the calculation of current through one-dimensional (1D) systems.

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Building molecular electronic devices using individual molecules is one of the ultimate goals in nanotechnology [1, 2, 3, 4, 5, 6]. A typical molecular device consists of a molecule coupled to two (or more) electrodes [7]. Electrons in the molecular device can go anywhere along the electrodes during the electron transport and electron wavefunctions may extend to infinity in spatial coordinate (R) space. Thus, accurate calculation of the electron wavefunctions in the R space is an intractable task for the study of electron transport.

To resolve this problem one of the widely used methods is to separate the molecule from the electrodes and treat it as an open system. More specifically, the molecular device is partitioned into left (L), central (C), and right (R) zones [8, 9, 10, 11, 12, 13, 14]. The C zone is chosen to include the molecule and some atomic layers of the electrodes so that the Hamiltonian and electron density of the L and R zones are accurately described by the equilibrium bulk ones before the bias applied [8]. To calculate the electron wavefunctions, one separates the C zone from the L and R zones and treat the C zone as an open system. The effect of the L and R zones (environment) on the C zone (open system) is characterized by a self-energy function [8, 9, 10, 11, 12, 13, 14, 15, 16]. After taking this effect into account, an equation of motion for the C zone is derived. Solving this equation one achieves the electron wavefunctions for further calculation. This scheme has been extensively applied to the calculation of steady-state current in molecular devices [8, 9, 10, 11, 17, 18, 19].

However, this scheme is not completely applicable when a time-dependent bias is applied. In this case, the equation of motion of the C zone is derived from the time-dependent Kohn-Sham (TDKS) equation [12, 13, 14]. It not only contains a two-time self-energy function but also includes a memory term [12, 14, 15, 16]. The self-energy function is related to a two-time Green function that can only be calculated under the wide-band limit (WBL) [20], an approximation that neglects the energy dependence of the coupling between the molecule and electrodes [15]. Beyond the WBL, the two-time Green function is governed by a double integral equation which is generally unsolvable [15]. The memory term depends on the two-time self-energy function. To calculate the memory term at time t, one has to recalculate and store the self-energy function at all the past time steps before this time. As a result, computer resources such as CPU time and random-access memory (RAM) required in the calculation become increasingly and thus extremely large with increase of number of time steps.

To overcome these difficulties, a computationally feasible scheme was proposed based on directly solving TDKS equation [12, 13, 14]. In this scheme, the TDKS equation is discretized in the whole R space and converted to a matrix equation first, then an equation of motion is derived from the matrix equation for the C zone, and finally the equation of motion is solved to calculate the
electron wavefunctions. This scheme has been successfully applied to the study of 1D model systems \cite{12,13,14}. The time-dependent currents achieved tend to the steady-state currents obtained from the Landauer formula \cite{12,13} and Floquet method \cite{14} after a long time, providing a benchmark for the currents through the 1D model systems. The most striking characteristic of this pioneering scheme is that the effect of the L and R zones on the C-zone electrons and the reflection of the time-dependent wavefunction on the boundaries are completely taken good care of by a transparent boundary condition. This scheme can indeed eliminate the explicit dependence of the equation of motion on the two-time self-energy function. However, the equation of motion still contains a memory term used to represent the effect of the L and R zones and remove the reflection of the electron wavefunction on the boundaries. As a consequence, the computer resources required in the calculation also increase with the number of time steps.

In fact, the difficulties encountered in the \( \mathcal{R} \)-space calculations at least come from one of the memory term and self-energy function used to characterize the effect of the L and R zones on the electrons in the C zone. Since the electron wavefunction can extend to the infinity in the molecular device during the transport, the memory term or/and self-energy function can not be disregarded no matter how large the C zone is chosen. Because of this reason, quantitative study of electron transient transport in the \( \mathcal{R} \) space is currently a computational challenge for realistic molecular devices.

However, the momentum of electron is always finite and less than certain maximum value \( k_{\text{max}} \) in the molecular device. The probability of electron with momentum greater than \( k_{\text{max}} \) is negligible or zero. Thus, in momentum (\( \mathcal{P} \)) space the electron wavefunction is localized (e.g., the wavefunction of a free electron spreads out to the whole space in the \( \mathcal{R} \) space but localizes in a very small volume depicted by a \( \delta \) function in the \( \mathcal{P} \) space) \cite{21} and can be calculated in a finite volume as long as the boundary of the volume is set at the place with properly large momentum \( k_{\text{max}} \). In this case, all the troublesome terms related to the open system in the \( \mathcal{R} \) space, such as the self-energy function and memory term, will be wiped out completely and the difficulties encountered in the \( \mathcal{R} \)-space calculations can be resolved in the \( \mathcal{P} \) space. Based on this idea, we propose in this work a first-principles time-dependent density functional theoretical (TDDFT) approach in the \( \mathcal{P} \) space for the quantitative study of electron transient transport in realistic molecular devices under arbitrary biases.

The molecular device is in an equilibrium state described by a unique temperature and chemical potential when time \( t < 0 \). The charge of the two electrodes is perfectly balanced and no current flows through the device. At time \( t = 0 \) a bias of voltage \( v_b(t) \) is applied to the electrodes. This
bias drives the molecular device out of equilibrium and induces the current through the device.

In the $R$ space, the time-dependent electron wavefunction $\psi(\mathbf{r}, t)$ is governed by the TDKS equation within TDDFT (atomic units are used throughout the paper)

$$i \frac{d}{dt} \psi(\mathbf{r}, t) = [h_0(\mathbf{r}) + v_D(\mathbf{r}, t)] \psi(\mathbf{r}, t),$$

(1)

where, $h_0(\mathbf{r})$ is the unperturbed KS Hamiltonian of the electron and $v_D(\mathbf{r}, t)$ is the driving potential characterizing the effect of bias on the electron. Within the partition above, the unperturbed KS Hamiltonian can be written as $h_0(\mathbf{r}) = -\nabla^2/2 + v_0(\mathbf{r})$, where, $v_0(\mathbf{r}) = v_{BK\alpha}(\mathbf{r})$ with $\alpha = L$ and $R$ for the L and R zones and $v_0(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}, 0)$ for the C zone. Here, $v_{BK\alpha}(\mathbf{r})$ is the bulk potential of the electrodes, $v_{\text{ext}}(\mathbf{r})$ is the external potential related to the interaction between the electron and nuclei of the system [22], and $v_{\text{eff}}(\mathbf{r}, 0)$ is the effective potential of the electron comprising the Hartree potential $v_H(\mathbf{r}, 0)$ and exchange-correlation potential $v_{xc}(\mathbf{r}, 0)$. For the metallic electrodes considered here, the driving potential $v_D(\mathbf{r}, t)$ is represented by $v_L(t)$ and $v_R(t)$ in the L and R zones, respectively, and $v_L(t) - v_R(t) = v_b(t)$. These potentials undergo uniform time-dependent shifts due to the screening effect and thus do not change with spatial coordinates if $v_b(t)$ is slowly varying during a typical time scale (less than a fs) [13]. In the C zone, the driving potential $v_D(\mathbf{r}, t)$ is represented by $v_C(\mathbf{r}, t)$ and $v_C(\mathbf{r}, t) = v_{\text{eff}}(\mathbf{r}, t) - v_{\text{eff}}(\mathbf{r}, 0)$ is the perturbing potential induced by the field of bias, where $v_{\text{eff}}(\mathbf{r}, t)$ is the bias-induced effective potential including the Hartree potential $v_H(\mathbf{r}, t)$ and exchange-correlation potential $v_{xc}(\mathbf{r}, t)$ [23]. The bias-induced effective potential is associated with the response of the C-zone electrons to the field of bias. It may change dramatically and nonlinearly with spatial coordinates and can only be calculated self-consistently with the C-zone electron wavefunctions. The procedure proposed here is nonperturbative and goes beyond the linear response approximation [23].

The relation between the time-dependent $R$-space electron wavefunction $\psi(\mathbf{r}, t)$ and $\mathcal{P}$-space electron wavefunction $\phi(\mathbf{k}, t)$ is given by the Fourier transform $\psi(\mathbf{r}, t) = (2\pi)^{-3/2} \int d\mathbf{k} \phi(\mathbf{k}, t) \exp(i\mathbf{k} \cdot \mathbf{r})$. Applying this transform to Eq. (1), we obtain the $\mathcal{P}$-space TDKS integrodifferential equation

$$i \frac{\partial}{\partial t} \phi(\mathbf{k}, t) = \int d\mathbf{k}' \left[ H_0(\mathbf{k}, \mathbf{k}') + V_D(\mathbf{k}, \mathbf{k}', t) \right] \phi(\mathbf{k}', t),$$

(2)

where, $H_0(\mathbf{k}, \mathbf{k}') = k^2 \delta(\mathbf{k} - \mathbf{k}')/2 + V_0(\mathbf{k}, \mathbf{k}')$ is the $\mathcal{P}$-space unperturbed Hamiltonian, $V_0(\mathbf{k}, \mathbf{k}')$ and $V_D(\mathbf{k}, \mathbf{k}', t)$ are the $\mathcal{P}$-space potentials calculated from the $R$-space potentials $v_0(\mathbf{r})$ and $v_D(\mathbf{r}, t)$ by the transform $V_0(\mathbf{k}, \mathbf{k}') = (2\pi)^{-3} \int d\mathbf{r} v_0(\mathbf{r}) \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}]$ with $\alpha = 0$ and $D$, respectively.
To calculate the $\mathcal{P}$-space electron wavefunction, we solve Eq. (2) numerically in a finite 3D volume $[-k_{\alpha \text{max}} \leq k_{\alpha} \leq k_{\alpha \text{max}} | \alpha = x, y, z]$. The integrals in Eq. (2) are discretized using the generalized Legendre-Gauss-Lobatto pseudospectral method on 3D grid points $[0, 1, \cdots, N_{\alpha} | \alpha = x, y, z]$ in the finite 3D volume. Since the $\mathcal{P}$-space electron wavefunction is localized, the boundary condition for solving Eq. (2) is simply that the electron wavefunction is zero on the boundary. After discretization, Eq. (2) is converted to a time-dependent matrix equation

$$i \frac{\partial}{\partial t} \Phi(t) = [H_0 + V_D(t)] \Phi(t),$$

(3)

where, $\Phi(t)$ is an $N_G$-dimensional vector with the components being the $\mathcal{P}$-space electron wavefunction $\phi(k, t)$ on the 3D grid points, where $N_G = N_x \times N_y \times N_z$, $H_0$ and $V_D(t)$ are $N_G \times N_G$ matrices with the matrix elements constructed by the unperturbed Hamiltonian $H_0(k, k')$ and potential $V_D(k, k', t)$ on the 3D grid points together with the weights of quadrature, respectively.

The $\mathcal{P}$-space electron wavefunctions at any time can be calculated from Eq. (3) if initial electron wavefunctions are given. At finite temperature, the electrons populate on the single electron states of the unperturbed system according to the Fermi distribution function. While in the case of low temperature limit considered here, the electrons will occupy all the single electron states from the lowest energy up to the Fermi energy. Thus, the initial electron wavefunctions are the eigenfunctions of the unperturbed system below the Fermi energy. The eigenvalue equation for the eigenfunctions is obtained by setting $t = 0$ in Eq. (3) and replacing the term on the left hand side of Eq. (3) by $E \Phi(0)$. Note that $V_D(t) = 0$ when $t = 0$.

Applying the second-order split-operator method to Eq. (3), one obtains the propagation equation $\Phi(t + \Delta t) = P_D(\tau) P_0 P_D(\tau) \Phi(t)$, where, $\Delta t$ is the time step size, $\tau = t + \Delta t/2$, $P_0 = e^{-iH_0 \Delta t}$ and $P_D(\tau) = e^{-iV_D(\tau) \Delta t/2}$ are the propagators, and $V_D(\tau) = [V_D(t) + V_D(t + \Delta t)]/2$. The propagators can be calculated using the eigendecomposition scheme of matrix $[26]$. If the uniform time step size ($\Delta t = \text{const.}$) is employed, the propagator $P_0$ only needs to be calculated once. In contrast, the time-dependent propagator $P_D(\tau)$ has to be calculated at every time step.

Using the $\mathcal{P}$-space electron wavefunctions, the current through the molecular device is calculated by

$$I(t) = \frac{1}{(2\pi)^3} \sum_{j=\text{occ.}} \int d\sigma \hat{n} \cdot \text{Re} \left[ \int dk \phi_j^*(k, t)e^{-ik \cdot r} \int dk' \phi_j(k', t)kk' e^{ik' \cdot r} \right],$$

(4)
where, $S_C$ is the surface enclosing the C zone, $\hat{n}$ is the unit vector perpendicular to the surface element $d\sigma$, $\phi_j(k, t)$ is the $j$th electron wavefunction with the momentum $k$, and the sum $j$ is over all the occupied electron states of the C zone.

To demonstrate the feasibility of the proposed $\mathcal{P}$-space approach, we first apply it to a one-dimensional (1D) system driven by a DC bias. The potential of the unperturbed 1D system is zero everywhere in the whole $\mathcal{R}$ space. The C zone extends from $x = -6$ to $+6$ a.u. Initially, all the single electron states are occupied up to the Fermi energy $\epsilon_F = 0.3$ a.u. At $t = 0$, a DC bias $v_b$ is applied to the electrodes. We choose $v_L = -v_R = v_b/2$, $k_{\text{max}} = 2.0$ a.u., and $\Delta t = 0.1$ a.u. The identical 1D problem has been considered in Ref. [12, 13] by using the transparent-boundary approach in the $\mathcal{R}$ space. In FIG. 1, we plot the current densities at $x = 0$ as a function of time for three biases. It is shown that a steady-state current is achieved for each bias and approaches the steady-state current value obtained from the Landauer formula [12, 13]. Furthermore, the currents of the proposed $\mathcal{P}$-space approach are in very excellent agreement with those of the $\mathcal{R}$-space transparent-boundary approach [12, 13]. However, the computational effort in the calculation with the $\mathcal{P}$-space approach is considerably smaller than that with the $\mathcal{R}$-space approach.

The second 1D system we consider is a double square barrier potential driven by a time-dependent bias. The potential of the unperturbed system is $v(x) = 0.5$ a.u. for $5 \leq |x| \leq 6$ a.u. and zero otherwise [12, 13]. The C zone extends from $x = -6$ to $+6$ a.u. A time-dependent bias, $v_b(t) = v_{b0} \left[ \theta(t) - \theta(t - t_0) \right]$, which is turned on at $t = 0$ and turned off at $t = 75$ a.u., is applied to the electrodes, where $\theta$ is the step function and $t_0 = 75$ a.u. We choose $\epsilon_F = 0.3$ a.u., $v_L = v_b(t)$, $v_R = 0$, $k_{\text{max}} = 2.0$ a.u., and $\Delta t = 0.1$ a.u. In FIG. 2 we display the current densities at $x = 0$ as a function of time for four biases. It is shown that for each bias the current oscillates after the bias is turned off and the amplitude is proportional to the bias. It is also shown that the currents tend to zero steady-state current quickly after turning off the bias and the transient time for turning off a bias is much shorter than that for turning on the bias [12, 13]. Moreover, the results of the $\mathcal{P}$-space approach are in very good agreement with those of the $\mathcal{R}$-space transparent-boundary approach [12, 13]. Again the proposed $\mathcal{P}$-space approach reproduces the results of the $\mathcal{R}$-space transparent-boundary approach with considerably less computational effort.

In summary, we propose a first-principles TDDFT approach in the $\mathcal{P}$ space for the study of electron transport dynamics in molecular devices under the arbitrary biases. This approach is effective in theoretical treatment and efficient and feasible in computation. In this approach, the electron wavefunction is calculated by solving a time-dependent integrodifferential equation in a finite $\mathcal{P}$-space volume. This equation is obtained by the Fourier transform of the $\mathcal{R}$-space TDKS equation.
It is exact and contains all the effects and information of the electron transport of molecular devices. It is free of the tricky self-energy function and memory term and beyond the extensively used WBL. In addition, unlike the \( R \)-space approach, the procedure based on this approach does not need to impose any complicated boundary condition to the electron wavefunctions. The computer resources such as CPU time used at each time step and the RAM required in the calculation with this approach do not increase with the number of time steps. The proposed \( P \)-space approach has been successfully applied to the study of 1D systems with less computational effort, demonstrating it promising to extend the proposed approach to the study of electron transport dynamics in realistic molecular devices.

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Figure captions

FIG. 1 (Color online) Current densities at $x = 0$ for the biases $v_b = 0.1, 0.3, \text{ and } 0.5 \text{ a.u.}$ For each bias, the short dash curve is the result of the $\mathcal{R}$-space transparent-boundary approach [12, 13], the dash line is the steady-state current from the Landauer formula [12, 13], and the solid curve is the result of the $\mathcal{P}$-space approach.

FIG. 2 (Color online) Current densities at $x = 0$ for the biases with $v_{\delta 0} = 0.05, 0.15, 0.25 \text{ and } 0.35 \text{ a.u.}$ For each bias, the short dash curve is the result of the $\mathcal{R}$-space transparent-boundary approach [12, 13] and the solid curve is the result of the $\mathcal{P}$-space approach.
FIG. 2