Current Nonconservation of Molecular Devices in the Presence of a Nonlocal Potential

L. Q. Lai, J. Chen, Q. H. Liu, Y. B. Yi

School of Physics and Electronics, Hunan University, Changsha 410082, China
(Dated: February 26, 2019)

The electronic transport characteristics are general topics in the studies of mesoscopic systems and molecular devices that have received considerable attentions in view of their future technological importance. The current densities are, however, often found to dissatisfy the continuity condition when nonlocal potentials are included in the Hamiltonian of interest, which is quite relevant in the context of first-principles calculations. In this paper, we discuss the problems of current conservation, and show that they stem from the improper approximations brought in for electron-electron interactions and the inappropriate definition in pseudopotential implementations, respectively. We propose a statistic average formalism as well as a reasonable definition to deal with related issues, and perform numerical simulations of a quasi-one-dimensional electron gas to further demonstrate the results.

I. INTRODUCTION

Over the past few decades, investigations on transport properties of mesoscopic systems and nanostructures have been extensively reported both on experimental advances and theoretical explorations. It has been acknowledged that these functional devices can be constituted by ultrasmall conjugated molecules, single- or multi-layer nanotubes and bulk organic molecules, etc., and plenty of interesting phenomena such as molecular field effects, Coulomb blockade, negative differential resistance and conductance switching effects have been revealed, which exhibit fundamental significance and potential microelectronic applications. In most of the works, attentions are focused on current-voltage (I-V) characteristics, because the I-V profiles provide opportunities for a deeper understanding of, e.g., the basic mechanism and structure properties, as well as promising guidance for future molecular nanoelectronics design and manipulation.

In recent years, theoretical calculations for the I-V characteristics of molecular device systems are mostly performed by employing the self-consistent field (SCF) method or the method of nonequilibrium Green’s functions combined with density functional theory (NEGF-DFT), and the widely used DFT calculations at present can be vested in the SCF method. In comparison with conventional SCF, in addition to self-consistent Hartree potential, DFT introduces the exchange-correlation potential, which is nonlocal if one wants to go beyond the local density approximation. It has been shown that in the presence of a nonlocal potential $V(\mathbf{r}, \mathbf{r}')$, generally the current calculated with the conventionally defined current density does not fulfill the charge conservation. Thus the current may give very incorrect results, even nonphysical results in the DFT calculations.

Li et al. proposed a scheme to reconsider the contribution of nonlocal potential to the current density and therefore gave a new definition. The approach therein appeared to yield the charge conservation in a computationally efficient way. However, either local or nonlocal exchange-correlation potential stems from the approximation to electron-electron interactions, and according to the conventional definition of current density the conservation can be exactly satisfied in the presence of the interactions. Hence we have reasons to believe that the problems of charge conservation, which comes from the nonlocal exchange-correlation potential, should not be settled by redefining the current density. Instead, it has to be resolved by finding a reasonable nonlocal potential that does not result in additional current. On the other hand, in first-principles calculations the norm-conserving pseudopotentials are generally utilized to reduce the size of plane-wave basis sets, which is another origin of the nonlocal potential. But we know that the pseudopotentials give the pseudo wave functions, while the wave functions used in the continuity equation $\partial_t \rho + \nabla \cdot J = 0$ should be real functions rather than the pseudo ones. The equation is the only criteria regardless of any approximations brought in as long as the particles are conserved, which can be easily proved according to the original Hamiltonian. It is the purpose of this work to investigate the above problems.

The paper is organized as follows. In Sec.II, the origins of nonlocal potentials and the consequent problems of charge conservation are discussed. We lay special emphasis on the nonlocal exchange-correlation potential from the starting point of second quantization, and subsequently demonstrate that in DFT calculations the nonconservation is caused by inappropriate definition of the current density but not the introduction of pseudopotentials. As an example, particle current densities and electric current densities of a quasi-one-dimensional electron gas are numerically calculated in Sec.III. Section IV gives the conclusions and discussions.
II. THEORETICAL FORMALISM

In the context of first-principles calculations, if we use real wave functions \( \psi(\mathbf{r}) \) of the system from the very beginning throughout the processes, then the continuity condition \( \partial_t \rho_e + \nabla \cdot J_e = 0 \) can be easily realized according to Schrödinger equation, where \( \rho_e = |\psi(\mathbf{r})|^2 \) is the conventional electron density and \( J_e \) is the conventional current density in the absence of magnetic field with the definition as

\[
J_e = -\frac{i\hbar}{2m} \left[ \psi^* \nabla \psi - \psi \nabla \psi^* \right].
\]

One of the origins of the nonconservation comes from approximations to electron-electron interactions, i.e. introducing some improper exchange-correlation potentials. We will demonstrate that according to the standard definition of current density, the charge conservation is still satisfied in the presence of interactions, but generally can be violated by introducing the nonlocal exchange-correlation potential. To see this, the simplest case of Hamiltonian of a finite many-electron system is considered, in which the electron-electron interactions are not taken into account firstly so that the second quantized nonrelativistic Hamiltonian (a quantity with a caret symbol denotes an operator) is

\[
\hat{H}_0 = \hat{T}_s + \hat{U}_{ex},
\]

where in terms of the field operators \( \hat{\psi}^\dagger(\mathbf{r}, t) \) and \( \hat{\psi}(\mathbf{r}, t) \), the single-particle kinetic energy operator and the external potential operator can be written respectively as

\[
\hat{T}_s = -\frac{\hbar^2}{2m} \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}, t) \nabla^2 \hat{\psi}(\mathbf{r}, t),
\]

\[
\hat{U}_{ex} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}, t) v(\mathbf{r}, t) \hat{\psi}(\mathbf{r}, t).
\]

The density operator can be defined as \( \hat{n}(\mathbf{r}, t) = \hat{\psi}^\dagger(\mathbf{r}, t) \hat{\psi}(\mathbf{r}, t) \) and the current density operator is

\[
\hat{J}_c(\mathbf{r}, t) = \frac{-i\hbar}{2m} \left[ \hat{\psi}^\dagger(\mathbf{r}, t) \nabla \hat{\psi}(\mathbf{r}, t) - \nabla \hat{\psi}^\dagger(\mathbf{r}, t) \hat{\psi}(\mathbf{r}, t) \right],
\]

by means of Heisenberg’s equation and the anticommutation relation that we obtain

\[
\frac{\partial \hat{n}(\mathbf{r}, t)}{\partial t} = \frac{1}{i\hbar} \left[ \hat{n}(\mathbf{r}, t), \hat{H}_0 \right]
= \int d\mathbf{r}' \left[ \hat{\psi}^\dagger(\mathbf{r}, t) \hat{\psi}(\mathbf{r}, t), \hat{\psi}^\dagger(\mathbf{r}', t) \hat{H}' \hat{\psi}(\mathbf{r}', t) \right]
= \int d\mathbf{r}' \left[ \hat{\psi}(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \hat{H}' \hat{\psi}(\mathbf{r}', t) - \hat{\psi}^\dagger(\mathbf{r}, t) \hat{H}' \delta(\mathbf{r} - \mathbf{r}') \hat{\psi}(\mathbf{r}, t) \right]
= \frac{i\hbar}{2m} \left[ \hat{\psi}^\dagger(\mathbf{r}, t) \nabla^2 \hat{\psi}(\mathbf{r}, t) - \hat{\psi}(\mathbf{r}, t) \nabla^2 \hat{\psi}^\dagger(\mathbf{r}, t) \right]
= -\nabla \cdot \hat{J}_c(\mathbf{r}, t),
\]

which is quite obvious that the current conservation is realized while only kinetic energy and external potential are included. Next, we introduce the interaction into the system, thus the corresponding Hamiltonian can be written as

\[
\hat{H}_w = \hat{T}_s + \hat{U}_{ex} + \hat{W}
\]

\[
= \int d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}') \left[ -\frac{\hbar^2}{2m} \nabla'^2 + v(\mathbf{r}', t) \right] \hat{\psi}(\mathbf{r}')
+ \int d\mathbf{r}'' d\mathbf{r}' \psi(\mathbf{r}'') |\mathbf{r}' - \mathbf{r}''| \hat{\psi}^\dagger(\mathbf{r}') \hat{\psi}^\dagger(\mathbf{r}'') \hat{\psi}(\mathbf{r}'').
\]
Similarly, the field operator is
\[ \hat{n}(r, t), \hat{W} = \left[ \hat{\psi}^\dagger(r, t) \hat{\psi}(r, t), \int d\mathbf{r}' d\mathbf{r}'' w(|\mathbf{r}' - \mathbf{r}'|) \hat{\psi}^\dagger(r', t) \hat{\psi}(r'', t) \hat{\psi}(r', t) \right] \]

\[ = \int d\mathbf{r}' d\mathbf{r}'' w(|\mathbf{r}' - \mathbf{r}'|) \left( \hat{\psi}^\dagger(r, t) \delta(r - r') \hat{\psi}^\dagger(r'', t) \hat{\psi}(r', t) \hat{\psi}(r', t) \right) \]

\[ - \hat{\psi}^\dagger(r, t) \hat{\psi}^\dagger(r', t) \delta(r - r'') \hat{\psi}(r'', t) \hat{\psi}(r', t) \hat{\psi}(r', t) \]

\[ + \hat{\psi}^\dagger(r', t) \hat{\psi}^\dagger(r'', t) \delta(r - r''') \hat{\psi}(r', t) \hat{\psi}(r, t) \hat{\psi}(r, t) \]

\[ - \hat{\psi}^\dagger(r', t) \hat{\psi}^\dagger(r'', t) \hat{\psi}(r''', t) \delta(r - r') \hat{\psi}(r, t) \hat{\psi}(r, t) \]

\[ = 0, \quad (7) \]
indicating the satisfaction when the interaction is involved.

According to common methods, we now proceed to expand the wave function \( \Psi \) in terms of a complete basis set \( \varphi_m \) as

\[ \Psi = \sum_m c_m \varphi_m, \quad (8) \]

where \( c_m \) is a coefficient independent of \( r \). The Hamiltonian of the system and the Schrödinger-like equation can then be rewritten as

\[ \hat{H} = \sum_{mn} (H_{0mn} + V_{mn}) a_m^\dagger(t) a_n(t), \]

\[ H_0 \Psi(r, t) + \int d\mathbf{r}' V_{nl}(\mathbf{r}, \mathbf{r}') \Psi(\mathbf{r}', t) = \sum_m c_m H_0 \varphi_m(r, t) + \sum_m c_m \int d\mathbf{r}' V_{nl}(\mathbf{r}, \mathbf{r}') \varphi_m(\mathbf{r}', t), \quad (9) \]

where \( a_m^\dagger \) and \( a_n \) are creation and annihilation operators, respectively, and

\[ V_{mn}(t) = \int d\mathbf{r} d\mathbf{r}' \varphi_m^*(\mathbf{r}, t) V_{nl}(\mathbf{r}, \mathbf{r}') \varphi_n(\mathbf{r}', t). \quad (10) \]

Similarly, the field operator is

\[ \hat{\psi}(r, t) = \sum_n \varphi_n(\mathbf{r}) a_n(t), \quad a_n(t) = \int d\mathbf{r} \varphi_n^*(\mathbf{r}, t) \hat{\psi}(\mathbf{r}, t), \quad (11) \]

so we obtain the current operator

\[ \hat{n}(r, t) = \sum_{mn} \varphi_m^*(\mathbf{r}, t) \varphi_n(\mathbf{r}, t) a_m^\dagger(t) a_n(t). \quad (12) \]

Since

\[ \sum_{mn} V_{mn}(t) \varphi_m^*(\mathbf{r}, t) \varphi_m(\mathbf{r}', t) = \int d\xi d\xi' V(\xi, \xi') \sum_{mn} \varphi_m^*(\xi, t) \varphi_n(\xi', t) \varphi_m(\xi', t) \varphi_m(\mathbf{r}', t), \quad (13) \]

the potential operator can be written as

\[ \hat{V}(t) = \sum_{mn} V_{mn}(t) a_m^\dagger(t) a_n(t) \]

\[ = \int d\mathbf{r} d\mathbf{r}' \sum_{mn} V_{mn}(t) \varphi_m^*(\mathbf{r}, t) \varphi_m(\mathbf{r}', t) \hat{\psi}^\dagger(\mathbf{r}', t) \hat{\psi}(\mathbf{r}, t) \]

\[ = \int d\mathbf{r} d\mathbf{r}' V_{nl}(\mathbf{r}', \mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}', t) \hat{\psi}(\mathbf{r}, t), \quad (14) \]
and after some calculations we get
\[
\left[ \hat{n}(\mathbf{r}, t), \hat{V}(t) \right] = \left[ \hat{\psi}^{\dagger}(\mathbf{r}) \hat{\psi}(\mathbf{r}), \int d\mathbf{r}'' d\mathbf{r}' V(\mathbf{r}'', \mathbf{r}') \hat{\psi}^{\dagger}(\mathbf{r}'', t) \hat{\psi}(\mathbf{r}', t) \right] \\
= \int d\mathbf{r}'' d\mathbf{r}' \hat{\psi}^{\dagger}(\mathbf{r}, t) V(\mathbf{r}'', \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'') \hat{\psi}(\mathbf{r}', t) \\
- \int d\mathbf{r}'' d\mathbf{r}' V(\mathbf{r}'', \mathbf{r}) \hat{\psi}^{\dagger}(\mathbf{r}'', t) \delta(\mathbf{r} - \mathbf{r}') \hat{\psi}(\mathbf{r}, t) \\
= \int d\mathbf{r}' \hat{\psi}^{\dagger}(\mathbf{r}, t) V(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{r}', t) - \int d\mathbf{r}'' \hat{\psi}^{\dagger}(\mathbf{r}'', t) V(\mathbf{r}'', \mathbf{r}) \hat{\psi}(\mathbf{r}, t) \\
\neq 0, \\
\]  \hspace{1cm} (15)

where the continuity condition is no longer satisfied.

Thus far an inference can be drawn that an unreasonable approximation for the interaction has been brought in, and it exits in most of the modern implementations with nonlocal exchange-correlation potentials. Currents, of course, including both the contributions of local and nonlocal potential are required to be included, so we rewrite the potential energy
\[
\int d\mathbf{r} d\mathbf{r}' \frac{\langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|} \\
\rightarrow \int d\mathbf{r} \hat{\Psi}(\mathbf{r}) \left[ \int d\mathbf{r}' \frac{\langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|} \right] \hat{\Psi}(\mathbf{r}) - \int d\mathbf{r} d\mathbf{r}' \hat{\Psi}(\mathbf{r}) \frac{\langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}(\mathbf{r}) \\
= \int d\mathbf{r} \hat{\Psi}(\mathbf{r}) U(\mathbf{r}) \hat{\Psi}(\mathbf{r}) + \int d\mathbf{r} d\mathbf{r}' \hat{\Psi}(\mathbf{r}) V_{xc}(\mathbf{r}', \mathbf{r}) \hat{\Psi}(\mathbf{r}'), \\
\]  \hspace{1cm} (16)

where
\[
U(\mathbf{r}) = \int d\mathbf{r}' \frac{\langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|}, \quad V_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|}. \\
\]  \hspace{1cm} (17)

Introduce an auxiliary variable \( \hat{F} \) as
\[
\hat{F}(\mathbf{r}) = \int d\mathbf{r}' \left[ V_{xc}(\mathbf{r}, \mathbf{r}') \hat{\Psi}(\mathbf{r}) \hat{\Psi}(\mathbf{r}') - V_{xc}(\mathbf{r}', \mathbf{r}) \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \right], \\
\]  \hspace{1cm} (18)

and we obtain the expectation of this variable
\[
\langle \hat{F}(\mathbf{r}) \rangle = \int d\mathbf{r}' \left[ V_{xc}(\mathbf{r}, \mathbf{r}') \langle \hat{\Psi}(\mathbf{r}) \hat{\Psi}(\mathbf{r}') \rangle - V_{xc}(\mathbf{r}', \mathbf{r}) \langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle \right] \\
= \int d\mathbf{r}' \left[ \frac{\langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle}{|\mathbf{r} - \mathbf{r}'|} \langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle - \frac{\langle \hat{\Psi}(\mathbf{r}) \hat{\Psi}(\mathbf{r}') \rangle}{|\mathbf{r} - \mathbf{r}'|} \langle \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}) \rangle \right] \\
= 0, \\
\]  \hspace{1cm} (19)

which means that with this method the conservation can be fulfilled in the meaning of statistic average.

Another origin of the nonconservation is the inappropriate definition of the current density. In DFT calculations, one often needs to bring in pseudopotential approximations for simplification of the intractable computations, where nonlocal potential emerges. We first discuss that in introducing the nonlocal pseudopotential, the current calculated with pseudo wave function does not satisfy the charge conservation. Pseudopotentials were originally introduced to simplify electronic structure calculations by adding some core functions to the wave function \( \psi(\mathbf{r}) \) to obtain a smooth pseudo wave function\(^{38, 39, 40}\)
\[
\psi(\mathbf{r}) = \phi(\mathbf{r}) - \sum_n \langle \psi_n | \phi \rangle \psi_n(\mathbf{r}), \\
\]  \hspace{1cm} (20)

where \( \phi(\mathbf{r}) \) is the pseudo wave function and \( \psi_n(\mathbf{r}) \) is the core function, and the general form of the pseudopotential (only its nonlocal part) is
\[
V_{nl} = \sum_n (E - E_n) |\psi_n(\mathbf{r})|, \\
\]  \hspace{1cm} (21)
from which we obtain
\[
\sum_n |\psi_n\rangle \langle \psi_n| = (E - H)^{-1} V_{nl} = GV_{nl},
\]
where \( G = (E - H)^{-1} \) is the Green’s function, and \( H \) is the original Hamiltonian. The real wave function can then be denoted by
\[
\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle = \langle \mathbf{r} | \phi \rangle - \langle \mathbf{r} | G V_{nl} | \phi \rangle \\
= \phi(\mathbf{r}) - \int d\mathbf{r}'' \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \langle \mathbf{r}' | V_{nl} | \mathbf{r}'' \rangle \langle \mathbf{r}'' | \phi \rangle \\
= \phi(\mathbf{r}) - \int d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}') V_{nl}(\mathbf{r}', \mathbf{r}'') \phi(\mathbf{r}'').
\]
Therefore, the corresponding Schrödinger equation for the pseudo wave function is
\[
H \phi(\mathbf{r}) + \int d\mathbf{r}' V_{nl}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') = E \phi(\mathbf{r}),
\]
where
\[
V_{nl}(\mathbf{r}, \mathbf{r}') = \sum_n (E - E_n) \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') = (E - H) \sum_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}').
\]
It is easy to verify that the conventionally defined current density \( \mathbf{J} = \frac{-i\hbar}{2m} [\phi^*(\mathbf{r}) \nabla \phi(\mathbf{r}) - \phi(\mathbf{r}) \nabla \phi^*(\mathbf{r})] \) along with the obtained pseudo electron density \( \rho_{ps} = |\phi(\mathbf{r})|^2 \) do not satisfy the charge conservation. Nevertheless, this nonconservation is not caused by introducing the pseudopotential, but is that the above definition of current density cannot be used to the pseudo wave function \( \phi(\mathbf{r}) \). The current density must be defined by using the real wave function \( \psi(\mathbf{r}) \). According to the definition \( \mathbf{J}_r = \frac{-i\hbar}{2m} [\psi^*(\mathbf{r}) \nabla \psi(\mathbf{r}) - \psi(\mathbf{r}) \nabla \psi^*(\mathbf{r})] \) we get
\[
\mathbf{J}_r = \mathbf{J}_{ps} + \mathbf{J}_{nl},
\]
where
\[
\mathbf{J}_{ps} = \frac{-i\hbar}{2m} [\phi^*(\mathbf{r}) \nabla \phi(\mathbf{r}) - \phi(\mathbf{r}) \nabla \phi^*(\mathbf{r})],
\]
and
\[
\mathbf{J}_{nl} = \frac{i\hbar}{2m} [\phi^*(\mathbf{r}) \nabla \Pi(\mathbf{r}) + \Pi(\mathbf{r}) \nabla \phi^*(\mathbf{r}) - \Pi^*(\mathbf{r}) \nabla \Pi(\mathbf{r}) - \text{c.c.}].
\]
Here, \( \Pi(\mathbf{r}) = \int d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}') V_{nl}(\mathbf{r}', \mathbf{r}'') \phi(\mathbf{r}''). \) On the basis of Eq. (24), in steady states we can easily give \( \nabla \cdot \mathbf{J}_{ps} = -\nabla \cdot \mathbf{J}_{nl} \), which verifies the definition of current in Eq. (26) satisfying the charge conservation.

Note that the form of pseudopotential above depends explicitly on the eigenvalue \( E \), which is unpractical. It would be especially difficult to be used in time-dependent cases.

**III. NUMERICAL IMPLEMENTATION**

To illustrate the theoretical formalism proposed above, we consider a double-barrier model of a quasi-one-dimensional electron gas confined transversely to simulate the device system, as shown in Fig.1. The nonlocal potential is placed only in the region between \(-a\) and \(a\), and the barriers can be regarded as part of two ideal leads without nonlocal potential. We imagine a central region \( C \) (the dashed-line box) that encloses both the core device and the barriers, and the total Hamiltonian for this model can be written as
\[
\hat{H}_{tot} = \hat{H}_0 + \hat{V}_H + \hat{V}_{xc},
\]
where \( \hat{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 + U_0 \) with \( U_0 \) the local potential within the barriers, \( \hat{V}_H \) is the Hartree potential and \( \hat{V}_{xc} \) is the exchange-correlation potential operator: \( \langle \mathbf{r} | \hat{V}_{xc} | \psi \rangle = \int V_{xc}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}' \). We use a reduced interaction in one dimension as
\[
V_H(x) = \int \sum_k v(x, x') |\psi_k(x')|^2 dx',
\]
FIG. 1: Schematic view of the transversely confined double-barrier model. The dashed-line box C is a hypothetical region including the core device and part of two ideal leads, and L/R symbolize the leads.

\[ V_{xc}(x, x') = -\sum_k v(x, x') \psi_k^*(x) \psi_k(x'), \tag{31} \]

where

\[ v(x, x') = \int \rho_1 d\rho_1 \int \rho_2 d\rho_2 \int \frac{d\phi}{2\pi} \frac{\phi^2(\rho_1) \phi^2(\rho_2)}{\sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1 \rho_2 \cos \phi + (x - x')^2}} \tag{32} \]

which is averaged over the transverse wave functions. A single wave function \( \phi(\rho) = 1/\sqrt{2\pi l^2} \exp(-\rho^2/4l^2) \) was chosen universally, and a transverse radius \( 2l \) characterizes the size of the confinement. To proceed, we first solve the energy eigenvalues of the double-barrier model with only local potential, and numerically calculate the wave functions with eigenenergies that are within the Fermi energy \( E_F \) are known, we can obtain the current density at each point. Energy unit \( \hbar^2/2ma^2 \) is used throughout the calculations as a reduced coefficient, where \( a \) is the lattice constant, and the current unit is \( (2e^2/h) V \). The Fermi energy here is set as \( E_F = 1.0 \), and the potential magnitude of the barriers is fixed to be \( U_0 = 6.0 \). In addition, all the calculations are performed in low-temperature limit, i.e., the temperature \( T = 0 \).

We first study the influences of an optional nonlocal potential and the formalism in Eq. (29) on the particle current, respectively. The nonlocal potential is nonzero when \( x \) is from \(-1 \) to \( 1 \), and the barriers are located in \([-2, -1]\) and \([1, 2]\). The optional nonlocal potential here is chosen as \( V_{nl}(x, x') = \lambda \exp(\eta (x - x')^2) \), where \( \lambda \) and \( \eta \) are two independent coefficients. From Fig.2a and Fig.2b, we can see that when single particle with a certain energy \( E \) is considered, the lead currents \( I_L \) and \( I_R \) hold to be a constant in both cases, while the current \( I_C \) obtained from the central region turns out to be varying with \( x \), revealing a dissatisfaction of the conservation. If we consider the collective properties of all the particles within \( E_F \), as shown in Fig.2c, the case for optional nonlocal potential still violates the continuity condition, while the currents calculated with the formalism of Eq. (29) are seen to be conservative in the whole simulation region. Moreover, particle currents in all three regions serve as a minor correction to the ones with Hartree potential only (see Fig.3).

Figure 4 plots the dependence of the electric current density on the selection of each region. The width of the barriers are fixed while the whole central region is changeable, and the nonlocal potential is absent therein. As we shall see, when the core region is chosen as small as \( x = [-0.2, 0.2] \), it exhibits a sublinear relation between the current \( I \) and the voltage \( V \), which is similar to that of a general single-barrier model, and the scattering effect in the central box vanishes. With the increase of the width as \( x = [-0.5, 0.5] \) and \( x = [-1, 1] \), the curves shift downwards gradually and finally become nonlinear ones, indicating that careful considerations on relevant area selection must be taken into actual systems to ensure the computational accuracy.

In Fig.5, we present the \( I-V \) characteristics of different sites along the \( x \) axis when the above optional nonlocal potential \( V_{nl}(x, x') \) is included. Current densities of \( x = 0 \), \( x = 0.5 \) and \( x = 2 \) differ mutually, as expected, which means that currents calculated with \( V_{nl} \) in the central region and the leads do not meet the conservation. We further explore the comparative characteristics obtained with our approximation. Figure 6 shows that when only Hartree potential \( V_H \) is taken into account, currents of all sites are equal to each other with the increase of the voltage. When the exchange-correlation potential \( V_{xc} \) is also considered, the whole of the curve bears an upward shift, whose corresponding current is a bit larger than that calculated with Hartree potential only, and the currents obtained can be still conservative.
FIG. 2: Particle current densities for: (a) the optional nonlocal potential \( V_{nl} \) with single-particle energy of \( E = 0.8 \), (b) the proposed formalism with energy of \( E = 0.8 \), and (c) the collective properties of all the particles with energy \( E = [0, 1] \). Here, \( \lambda = 0.009 \), \( \eta = 0.01 \), and the width of the barriers is 1.

FIG. 3: Comparison of the particle current densities for each region. The case that involves the reasonable nonlocal exchange-correlation potential \( V_{xc} \) (dash-dot line) is a correction to the one that only considers the Hartree potential \( V_{H} \) (solid line).

IV. CONCLUSIONS AND DISCUSSIONS

In summary, it is of great importance to give correct dynamic charge and potential distributions of transport systems, which is the key point to obtain valid current and to the prospective applications of molecular devices. Once we are able to calculate strictly according to the original Hamiltonian, the problems of charge conservation induced by nonlocal potential would not exist, and the results are no doubt reasonable. However, it is impossible to obtain rigorous solutions under intricate interactions. We demonstrate these issues and attest the origins of the dissatisfaction, and further propose a statistic average approximation for the electron-electron interactions as well as an efficacious definition of current density for steady states in the presence of pseudopotentials to ensure the conservation. With this method, we have also studied a double-barrier model of a quasi-one-dimensional electron gas.
FIG. 4: Dependence of the electric currents on the selection of the central region. Nonlocal potential is not included, and the width and magnitude of the barriers are both fixed.

FIG. 5: Current properties of different sites of the system with the optional nonlocal potential $V_{nl}$. The central region is fixed to be $x = [-1,1]$, and the barriers are located in $x = [-2,-1]$ and $x = [1,2]$. Discrepancies of the currents for all three positions enlarge with the increasing voltage.

to simulate the molecular device system, confirming that currents in the central region can be conserved to be equal to that of the leads.

* Electronic address: apybyu@hnu.edu.cn.

1 J. Paloheimo, P. Kuivalainen, H. Stubb, et al., Appl. Phys. Lett. 56, 1157(1990).
2 L. P. Kouwenhoven, A. T. Johnson, et al., Phys. Rev. Lett. 67, 1626(1991).
3 J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science 286, 1550(1999).
4 C. P. Collier, E. W. Wong, et al., Science 285, 391(1999).
5 C. Joachim, J. K. Gimzewski, and A. Aviram, Nature 408, 541(2000).
6 J. Park, A. Pasupathy, J. Goldsmith, C. Chang, et al., Nature 417, 722(2002).
7 N. J. Tao, Nat. Nanotechnol. 1, 173(2006).
8 S. Lindsay and M. Ratner, Adv. Mater. 19, 23(2007).
FIG. 6: I–V characteristics of different sites for: (1) with only Hartree potential $V_H$, and (2) with both the Hartree potential $V_H$ and the nonlocal exchange-correlation potential $V_{xc}$. The currents obtained from the proposed formalism satisfy the charge conservation.

9 Y. M. Lin, K. A. Jenkins, et al., Nano Lett. 9, 422 (2009).
10 N. Rauhut, M. Engel, M. Steiner, et al., ACS Nano 6, 6416(2012).
11 B. Q. Xu and Y. Dubi, J. Phys.: Condens. Matter 27, 263202 (2015).
12 K. Ono, G. Giavaras, T. Tanamoto, et al., Phys. Rev. Lett. 119, 156802(2017).
13 Y. Iishiki, S. Fujii, T. Nishino, and M. Kiguchi, J. Am. Chem. Soc. 140, 10(2018).
14 R. Landauer, IBM J. Res. Dev. 1, 233(1957).
15 M. Büttiker, Y. Imry, R. Landauer, and S. Pinhas, Phys. Rev. B 31, 6207(1985).
16 A. Pretre, H. Thomas, and M. Büttiker, Phys. Rev. B 54, 8130(1996).
17 A. P. Jauho, N. S. Wingreen, and Y. Meir, Phys. Rev. B 50, 5528(1994).
18 B. Wang, J. Wang, and H. Guo, Phys. Rev. Lett. 82, 398(1999).
19 J. Taylor, H. Guo, and J. Wang, Phys. Rev. B 63, 245407(2001).
20 M. Brandbyge, et al., Phys. Rev. B 65, 165401(2002).
21 S. Kurth, G. Stefanucci, C. O. Almladl., et al., Phys. Rev. B 72, 035308(2005).
22 C. Y. Yam, X. Zheng, G. H. Chen, et al., Phys. Rev. B 83, 245448(2011).
23 K. Varga, Phys. Rev. B 83, 195130(2011).
24 L. Zhang, B. Wang, and J. Wang, Phys. Rev. B 84, 115412(2011).
25 K. T. Cheung, B. Fu, Z. Z. Yu, and J. Wang, Phys. Rev. B 95, 125422(2017).
26 H. Wang and M. Thoss, J. Chem. Phys. 138, 134704(2013).
27 G. Cabra, A. Jensen, and M. Galperin, J. Chem. Phys. 148, 204103(2018).
28 S. Datta, Quantum Transport: Atom to Transistor, Cambridge University Press, Cambridge(2005).
29 V. A. Sablikov, S. V. Polyaakov, M. Büttiker, Phys. Rev. B 61, 13763(2000).
30 V. A. Sablikov and B. S. Shchamkhalova, Phys. Rev. B 58, 13847(1998).
31 J. P. Perdew, J. A. Chevary, S. H. Vosko, et al., Phys. Rev. B 46,6671(1992).
32 C. S. Li, L. H. Wan, Y. D. Wei, and J. Wang, Nanotechnology 19, 155401(2008).
33 L. Zhang, Y. X. Xing, and J. Wang, Phys. Rev. B 86, 155438(2012).
34 D. H. Hamalm, M. Schluter, and C. Chiang, Phys. Rev. Lett. 43, 1494(1979).
35 M. C. Payne, M. P. Teter, D. C. Allan, et al., Rev. Mod. Phys. 64, 1045(1992).
36 R. van Leeuwen, Phys. Rev. Lett. 82, 3863(1999).
37 M. Ruggenthaler and D. Bauer, Phys. Rev. A 80, 052502(2009).
38 J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287, 880(1959).
39 Morrel H. Cohen and V. Heine, Phys. Rev. 122,1821(1961).
40 Neil W. Ashcroft and N. David Mermin, Solid State Physics, Harcourt, Orlando(1976).
41 S. W. Gao and Z. Yuan, Phys. Rev. B 72, 121406(2005).