First-Principles Study of Atomic-Scale Contact Effects on the Anomalous Electric Transport Through Molecules

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Abstract. We develop a first-principles calculation method for the quantum transport through nanostructures between electrodes by using the recursion-transfer-matrix (RTM) method combined with the nonequilibrium Green function (NEGF) method. This RTM/NEGF method is applied to the electronic states and current-voltage (I-V) characteristics of atomic-scale nanocontact system with and without nanosystems (single molecules) between electrodes. We observe similar non-linear behaviors in the I-V characteristics in various contact conditions. Such non-linear behaviors of I-V characteristics are determined not only by the electronic states of nanosystems between electrodes but also by the atomic-scale contact conditions. We find that the transitions from tunneling to ballistic regimes affect the I-V characteristics significantly.

1. Introduction

With the advancement of the fabrication process to construct atomic-scale nanodevices, understanding of electron transport in such systems becomes an important problem[1]. For the atomic-scale nanodevices, the transfer of an electron is achieved by tunneling between the nanostructure and electrodes through atomic-scale contacts. Since it is experimentally difficult at present to construct well-characterized nanostructures between electrodes and furthermore we cannot directly observe the atomic structures of nanodevices, theoretical approaches based on the first-principles calculations become more and more important to characterize the electronic states of nanodevices.

For such purposes, we developed a calculation method for the study of transport properties of nanostructures through atomic-scale contacts between electrodes. It combines the recursion-transfer-matrix method (RTM)[2], which is a powerful and reliable tool for obtaining accurate scattering waves, with the nonequilibrium Green function (NEGF) method[3]. The present RTM/NEGF method enables us to perform stable self-consistent procedures for the charge and effective potential based on the density-functional formalism and to treat the quantum transport properties of nanostructures bridged between electrodes. We apply this calculation method to investigate the quantum transport through single molecules with various atomic-scale contacts.
2. The RTM/NEGF Calculation

The procedure of the present calculation is as follows. First, we use the RTM method\cite{2} to obtain scattering waves between electrodes. This method is based on the plane-wave basis sets and thus not dependent on the atomic positions. So we can treat accurate tails of wavefunctions in the tunneling regime, which is essential for the analysis of scanning tunneling microscopy (STM)\cite{4}, as well as the wavefunctions in the ballistic regime on the same footing.

Expanding the wavefunction in a Laue representation

$$\Phi_{E,i}^{L/R}(r) = \sum_j u_{E,i}^{L/R}(g_j^{\parallel}, z)e^{i(k_j^{\parallel} + g_j^{\parallel})r^{\parallel}}$$

where we take z axis in the direction the current is flowing, we obtain a coupled-channel differential matrix equation for the Kohn-Sham equation

$$-\frac{d^2}{dz^2}U_{E}^{L/R}(z,E) = V(z,E)U_{E}^{L/R}(z,E)$$

where scattering states for all the incident channel numbers form the matrix $U_{E}^{L/R}(z,E)$. Dividing the z axis into fine meshes $z_p$ and defining the transfer matrix on the neighboring mesh points such as

$$S_{L/R}^{L/R}(z_p, E) = U_{E}^{L/R}(z_p+1, E)U_{E}^{L/R}(z_p, E)^{-1}$$

we obtain the recursive relation for $S_{L/R}^{L/R}(z_p, E)$ \cite{2}

$$S_{L/R}^{L/R}(z_{p-1}, E) = [b(z_{p}) - a(z_{p})S_{L/R}^{L/R}(z_{p}, E)]^{-1}c(z_{p}),$$

where we use the Numerov expansion for the second order matrix differential equation to construct the coefficients of $a(z_{p}), b(z_{p})$ and $c(z_{p}).$ We obtain the transfer matrix $S_{L/R}^{L/R}(z_p, E)$ for all the mesh points by using the recursive relation (4) and $\Phi_{E,i}^{L/R}(r)$ are calculated by giving the appropriate boundary conditions deep in each electrode\cite{5}.

Then we construct the usual retarded and advanced Green’s function by using these scattering waves\cite{6} and nonequilibrium Green’s function is constructed from

$$G^\leq = iG^r(f_L\Gamma_L + f_R\Gamma_R)G^a.$$ \hspace{1cm} (5)

Here $f_{L,R} = 1/\exp\{(E - \mu_{L,R})/k_BT\} + 1$ is the Fermi distribution function in each electrode with an applied bias voltage $V$ of $eV = \mu_L - \mu_R$. Coupling constant $\Gamma_{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^*)$ is obtained from the surface Green’s function.

The charge density is obtained through the density matrix as a sum over the occupied states

$$\rho = \frac{1}{2\pi i} \int_{-\infty}^{\infty} G^\leq dE = -\frac{1}{\pi} \text{Im} \int_C G^r dZ + \frac{1}{2\pi i} \int_{\mu_R}^{\mu_L} G^\leq dE$$ \hspace{1cm} (6)

where the numerical energy integration is performed in the complex plane $C$, which avoids the singular energy points for the integral on the real axis\cite{7}. The obtained $\rho$ is utilized to construct the effective potential based on the density-functional formalism and these procedures are iterated until self-consistency is obtained. Finally the current is calculated using the formula\cite{3}

$$I = \frac{ie}{h} \int \left\{ \text{Tr} \left\{ (f_L\Gamma_L - f_R\Gamma_R) (G^r - G^a) \right\} + \text{Tr} \left\{ (\Gamma_L - \Gamma_R)G^\leq \right\} \right\} dE$$

which, in the mean field approach, reduces to

$$I = \frac{2e}{h} \int \left\{ f_L - f_R \right\} \text{Tr} \left\{ \Gamma_L^r \Gamma_R^a G^a \right\} dE.$$ \hspace{1cm} (8)
3. Transport Properties through Nanostructures with various Nanocontacts

3.1. Atomic-Scale Point Contact

First, we apply the present RTM/NEGF method for the transport properties of the atomic-scale point contact systems. Left and right electrodes have an apex facing to each other for the construction of atomic-scale nanocontacts composed of Na atoms.

Figure 1 shows the I-V characteristics at the distances of \( d = 10 \) bohr (left) and \( d = 14 \) bohr (right), respectively\[8\]. The distance is measured from the equilibrium position of the apex atoms in the absence of applied bias. The charge density profile of the present system is shown in the inset of the left panel for the reference. We note that the current is dominated in the narrow region between the apex atoms, which creates the effective channel for electron transport\[9\]. From the conductance calculation as a function of the distance \( d \), we find that the ballistic regime is realized when the distance is less than \( d = 5 \) bohr, where the I-V characteristics show linear behaviors since the effective channel is completely open and the current contribution is proportional to the difference of chemical potentials in each electrode. As a distance becomes large and the apex atoms at each electrode are well separated, we find that a nonlinear behavior emerges for the I-V characteristics. We can see that the I-V curve changes its behavior at the bias voltages of \( \pm 3V \) for \( d = 10 \) bohr case. Correspondingly, its differential conductance \( dI/dV \) in the inset shows a gap structure around the zero bias regime. The non-linear behavior of the I-V characteristics become much pronounced as the distance becomes large as shown in the right panel for \( d = 14 \) bohr case. Again we can see a large gap structure in the differential conductance, together with small oscillation behaviors due to the interference of conducting electrons between electrodes.

![Figure 1.](image)

To consider the mechanism for this non-linear I-V characteristic, we show in the inset of right panel the effective potentials along the \( z \) direction for the bias voltages of 0V, 3V, and 5V and (lower right) Differential conductance \( dI/dV \) as a function of applied bias voltages for \( d = 14 \) bohr, respectively.

To consider the mechanism for this non-linear I-V characteristic, we show in the inset of right panel the effective potentials along the \( z \) direction for the bias voltages of 0V, 3V, and 5V, respectively. We see that the effective energy barrier disappears when the applied bias is close to \( \pm 5V \). Correspondingly, the current changes its behavior from exponential to linear one. This
shows that the present non-linear behavior of the I-V characteristic appears when the transport properties change from tunneling to ballistic regimes.

### 3.2. Single Molecules

Next, we study the transport properties through single molecules sandwiched between electrodes. Recently, a number of experiments have been performed for the measurements of transport properties through single molecules connected to electrodes with finite bias voltages[1]. We note that, very frequently, similar I-V characteristics have been observed in experiments. Namely, they exhibit almost no electric currents up to several bias voltages. When the applied bias exceeds threshold bias voltages, the electric current starts to flow. Correspondingly, the differential conductance shows a gap structure within these threshold voltages around the zero bias regimes. It is frequently argued that such a gap structure corresponds to the HOMO-LUMO energy gap of the attached single molecules. Since we cannot directly observe the single molecules sandwiched between electrodes, it is not completely sure that the single molecules have strong connection to both electrodes. Here we adopt the benzene dithiol molecule as a prototype of single molecules and calculate its transport properties. Especially, we focus on the I-V characteristics when one of the contacts to the electrodes is not well constructed. For simplicity, we use the metallic jellium with $r_s = 2$ as electrodes[10], and apply the present RTM/NEGF method for the transport properties of these junction systems.

**Figure 2.** (Left) Differential conductance $dI/dV$ of the benzene dithiol single molecule between jellium electrodes as a function of applied bias voltages when contacts to both electrodes are very well formed. (inset) Charge density profile and I-V characteristic. (Right) Current-voltage (I-V) characteristic of the single molecule with one of the contacts are not well formed. The separation from the equilibrium atomic positions in the perfect contact case is 8 bohr. (inset) Charge density of the present system.

Figure 2 (left) shows the conductance and I-V characteristic (inset) of the benzene dithiol molecule sandwiched between metallic jellium electrodes when the contacts to both electrodes are perfectly well constructed. We show the charge density profile for reference in the inset. We see that the I-V characteristic shows again strong non-linear behavior and correspondingly the gap structure appears in the conductance. We can see that there are two peaks of conductance, which correspond to the resonant tunneling through $\pi^*$ states of the single molecule[11]. Next, we consider the situation in which one of the contacts to the electrodes is not well constructed. Since, in experiments, it is difficult to construct the nanometer-scale gap structure with just the appropriate length of the desired specific single molecule, these situations to have an imperfect contact to one electrode are considered to be frequently realized in experiments[12].
Figure 2 (right) shows the I-V characteristics when one of the contacts to the electrodes is not well constructed. The separation from the other jellium electrode is 8 bohr. We can see that very strong non-linear behavior of the I-V characteristic is observed, which has a similar behavior for the situation with perfect contact case. It is important to note that this non-linear behavior of the I-V characteristic has a different origin. When we look at the effective potential for the imperfect contact case, we find that there is a potential barrier between the single molecule and one of the electrode. Therefore the electronic process in this case is dominated by the tunneling between the single molecule and one of the electrodes. In such a case, even if we see the non-linear behavior in the I-V characteristics, it is apparent that such non-linearity of the current does not correspond to the molecular states, but is due to the change of the transport from tunneling to ballistic regimes at the bad contact by applying finite bias voltages.

In conclusion, we have developed a first-principles calculation method for quantum transport by using the RTM method combined with the NEGF method. This RTM/NEGF method has been used to perform calculations of transport properties through single molecules with various atomic-scale contacts. We find non-linear behaviors in the I-V characteristics, close to the frequently observed features in experiments, appear according to the various contact conditions even when the single molecules are absent between electrodes. Non-linear behaviors of I-V characteristics are determined not only by the electronic states of single molecules between electrodes but also by the atomic-scale contact conditions. We find that the transitions of effective potentials from tunneling to ballistic regimes affect the I-V characteristics significantly.

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References
[1] Reed M A, Zhou C, Muller C J, Buring T P, and Tour J M 1997 Science 278 252; Heath J R and Ratner M A 2003 Molecular Electronics, Phys. Today 56, 43
[2] Hirose K and Tsukada M 1994 Phys. Rev. Lett. 73 150; also 1995 Phys. Rev. B 51 5278
[3] Meir Y and Wingreen N S 1992 Phys. Rev. Lett. 68 2512; Haug H and Jauho A -P 1996 Quantum Kinetics in Transport and Optics of Semiconductors (Berlin: Springer)
[4] Kobayashi N, Hirose K, and Tsukada M 1997 Jpn. J. Appl. Phys. 36 3791
[5] The nonlocal parts of pseudopotentials are included following by the procedures described in Hirose K, Kobayashi N, and Tsukada M 2004 Phys. Rev. B 69 245412
[6] Datta S 1995 Electronic Transport in Mesoscopic Systems (Cambridge: Cambridge University Press)
[7] Taylor J, Guo H, and Wang J 2001 Phys. Rev. B 63 245407; Xue Y, Datta S, and Ratner M A 2002 Chem. Phys. 281 151; Brandbyge M, Mozos J -L, Ordejon P, Taylor J, and Stokbro K 2002 Phys. Rev. B 65 165401
[8] We don’t consider the onset of energy dissipation due to the excitation of electrons; see Agrait N, Untiedt C, Rubio-Bollinger G, and Vieira S 2002 Phys. Rev. Lett. 88 216803; Assai Y 2004 Phys. Rev. Lett. 93 246102
[9] Kobayashi N and Tsukada M 1999 Jpn. J. Appl. Phys. 38 9805; Kobayashi N, Aono M, and Tsukada M 2001 Phys. Rev. B 64 121402
[10] $r_s$ is the inter-particle distance in units of Bohr radius.
[11] Ventra M D, Pantelides S T, and Lang N D 2000 Phys. Rev. Lett. 84 979
[12] Reichert J, Ochs R, Beckmann D, Weber H B, Mayor M, and Lohneysen H V 2002 Phys. Rev. Lett. 88 176804; Kushmerick J G, Holt D B, Yang J C, Naciri J, Moore M H, and Shashidhar R 2002 Phys. Rev. Lett. 89 086802