Ab initio calculation of contact effects on electron transport through single molecules by the RTM/NEGF method

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Abstract. Using the recursion-transfer-matrix (RTM) method combined with the nonequilibrium Green’s function (NEGF) method, we study the electronic states and current-voltage (I-V) characteristics of atomic-scale nanocontact systems. We find that non-linear behaviors appear in the I-V characteristics even without molecules between electrodes. Such non-linear behaviors emerge when the nanocontacts are not well constructed and the transport properties change from tunneling to ballistic regimes.

1. Introduction
Recently much attention has been focused on understanding of electron transport in atomic-scale systems[1]. For the atomic-scale devices, the transfer of an electron is achieved mainly by tunneling between nanostructure and electrodes through atomic-scale contacts. Since it is experimentally difficult at present to construct well-characterized nanostructures between electrodes and 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 develop 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’s 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. We apply this calculation method to study quantum transport through atomic-scale contacts. We find non-linear behaviors appear in the I-V characteristics even without molecules between electrodes. Such non-linear behaviors emerge when transport properties change from tunneling to ballistic regimes.

2. The RTM/NEGF calculation method
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 is not dependent on the atomic positions. So we can treat accurate tails of wavefunctions in the tunneling regime as well as those of wavefunctions in the ballistic regime on the same footing.

Next, by using these states as basis functions which constitute a complete set of solutions for the Kohn-Sham differential equation with appropriate boundary conditions, we can construct the usual Green’s function $G^{r,a}$. The nonequilibrium Green’s function (NEGF) $G^{<}$ is obtained from $G^{r,a}$ and the self-energy $\Sigma^{<}$, which includes the Fermi functions for each electrode with chemical potentials $\mu_L$ and $\mu_R$\cite{4}. The charge density is constructed by the integration of $G^{r,<}$

\[ \rho = -\frac{1}{\pi} \text{Im} \int_C G^r dZ + \frac{1}{2\pi i} \int_{\mu_L}^{\mu_R} G^{<} dE, \]

where the contour $C$ is taken in the complex upper plane, which avoids the singular energy points due to quasi-localized states, resonances, and so on\cite{5}. The charge is utilized to construct the effective potential based on the density-functional formalism and these procedures are iterated until self-consistency is obtained. The steady current is obtained from\cite{3}

\[ I = \frac{2e}{h} \int \{ f_L - f_R \} \text{Tr} \left\{ \Gamma^L G^r \Gamma^R G^a \right\} dE. \]

3. Calculated Results

3.1. Single atom and molecule between jellium electrodes

In order to study the atomic-scale contact effects on transport properties, we consider electronic states of two nanosystems (Figure 1)\cite{6}. The first is the case with a single Al atom fixed in the middle of semi-infinite jellium electrodes with $r_s = 2$, which corresponds to Al metal (left). We see that the density of states (DOS) shows extremely spiky structures. This reflects the situation where the Al atom has little connection to both electrodes. Near the Fermi energy, the states split into two, one from $p_x, p_y$ orbitals and the other from $p_z$ orbital, which implies small coupling to electrodes to occur for higher energies. The transfer of an electron occurs by resonant tunneling or a Coulomb gap appears in conductance due to strong interaction.

Next we consider the case in which a single molecule (benzene-dithiolate molecule) is attached strongly to both semi-infinite jellium electrodes with $r_s = 2$ (right). In this case, DOS has overall broad structures, implying that molecule has strong connection to electrodes. We see that DOS has two peaks corresponding to HOMO-LUMO ($\pi-\pi^*$) states of molecules and that the Fermi energy lies between these peak energies.

3.2. Transport through atomic-scale point contacts

Recently, a number of experiments have been performed for the measurements of transport properties through single molecules connected to electrodes\cite{1, 7}. In these measurements, similar I-V characteristics have been observed frequently. Namely they exhibit almost no current flow up to several bias voltages. When the applied bias exceeds threshold voltages, the electric current starts to flow. It is argued that these threshold bias voltages correspond to the HOMO-LUMO energy gap of the attached single molecules. The possibility of the Coulomb gap is also pointed out. Since we cannot directly observe how the single molecules connect to electrodes, the analysis of the observed I-V characteristics needs careful treatment.

To understand the transport properties of atomic-scale contacts, we consider the junction system without single molecules between electrodes and treat the atomic-scale contacts as a function of the distance between electrodes. Since HOMO-LUMO energy gap and the Coulomb gap due to single molecules are absent, we can focus on the I-V characteristics in various atomic-scale contact conditions.
Figure 1. (Left) DOS for the system with a single Al atom fixed in the middle of jellium electrodes with $r_s = 2$. DOS for 3s orbital has extremely spiky nature, while those for 3p orbitals have some width and split into two due to small coupling to electrodes. (Inset) Charge density profile and integrated total charge as a function of the angle $\theta$ shown in the right. The total number of electrons converges close to the number of Al atom. (Right) Charge density profile of the benzene-dithiolate molecule suspended between jellium electrodes with $r_s = 2$. Contour for energy integral and DOS for the molecular-bridged system are shown in the right.

Figure 2 (left) shows the conductance as a function of the distance between electrodes, which defines the tunneling and ballistic regimes corresponding to the formation of the atomic-scale contacts. We see that the conductance decreases exponentially as the distance becomes large. On the other hand, the conductance becomes almost constant around $1 \times (2e^2/h)$ when the distance becomes smaller than $d = 5$ bohr. This shows that an effective one channel is formed between apex atoms [8] and the current flows ballistically in this regime. We find that the I-V characteristics show linear, Ohmic behaviors in this regime[9].

Figure 2 (right) shows the I-V characteristic when the distance is 10 bohr (top) and 14 bohr (bottom). We see that strong non-linear behavior appears in the I-V characteristic as a distance becomes large and the apex atoms at each electrode are well separated. We note that these I-V characteristics are similar to those frequently observed in the conductance measurements for molecular-bridged systems between electrodes[7].

To consider the mechanism of non-linear I-V behaviors, we show the effective potentials along the $z$ direction for the bias voltages of 0V, 3V, and 5V in the inset of 14 bohr case. We see that the effective barrier disappears when the applied bias exceeds 5V, at which the I-V characteristic changes its behavior from exponential to linear one. This shows that the non-linear behavior appears when the transport properties change from tunneling to ballistic regimes[10].

4. Discussion and Conclusion
Here we study the I-V characteristics of the Na systems, for which the electron density is low and the tails of wavefunctions reach deep in the potential barrier. Therefore we see non-linear behaviors of currents at relatively large distances. In the Al system where the electron density is high, non-linear behaviors should appear at much smaller distance.

In conclusion, we study the electronic states and I-V characteristics of atomic-scale nanocontact systems using the RTM/NEGF method. We find that non-linear behaviors appear in the I-V characteristics even without molecules between electrodes. Such non-linear behaviors emerge when the nanocontacts are not well constructed. This effect should be taken into account for the analysis of conductance observed in the experiments for the molecular-bridged systems.
**Figure 2.** (Left) Conductance as a function of the distance between electrodes. The distance $d$ is measured from the equilibrium positions of the apex atoms. The conductance is obtained with an applied bias of 10 mV. (inset) Charge density profiles of the nanocontact systems with $d=2$, $d=10$, and $d=14$ bohrs. (Right) I-V characteristics of the nanometer-scale contact with $d=10$ (upper) and $d=14$ bohr (lower). (inset) Effective potentials with $d=14$ bohr along the $z$ direction for the bias voltages of 0V, 3V, and 5V, respectively.

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