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MULTI-SCALE SIMULATIONS OF TRANSPORT PROPERTIES THROUGH MOLECULES AND CARBON NANOTUBES

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ABSTRACT
We present multi-scale calculations for the transport properties of single molecules and carbon nanotubes (CNT) bridged between electrodes. Here we use two calculation methods. One is the recursion-transfer-matrix (RTM) method, which is a tool to calculate accurate scattering waves in plane-wave expansions. Combined with the NEGF method and density-functional formalism, we perform calculations of transport properties through single molecules and molecular wires. The other method is the time-dependent wave-packet approach. Based on the linear-response Kubo formula, we perform the O(N) calculation for the transport of large systems. We apply the method for the CNT-FET device and find that the controls of the contact to electrodes are crucial for the device performance.

KEY WORDS
Modelling, Device Simulation, Quantum Transport, Carbon Nanotube, Molecular Electronics

1. Introduction

Recently much effort has been focused to measure the transport properties of single molecules and carbon nanotubes (CNT) bridged between electrodes for the molecular electronics and CNT devices. Since it is still difficult to construct well-characterized nanometer-scale device system between electrodes, theoretical approaches based on the first-principles calculations become important to characterize the transport properties of such nanometer-scale devices.

For such purposes, we developed two calculation methods. One is to use the recursion-transfer-matrix (RTM) method, which is a reliable tool to calculate accurate scattering waves in plane-wave expansions, combined with non-equilibrium Green's functional (NEGF) method. Based on the density-functional theory (DFT), we can perform ab initio calculations for the transport through nanometer-scale structures. We show calculated results for the single molecule conduction and its electron-phonon coupling between electrodes.

The other is the time-dependent wave-packet approach. We calculate the time-dependent wave-packet for the electron diffusion and use the linear-response Kubo formula to calculate the conductance. This O(N) method enables us to treat transport properties for very large systems. We apply this method for the transport through CNT. We show the results on the electron-phonon coupling and contact effects to electrodes on the device performance of CNT-field effect transistor (CNT-FET).

These multi-scale simulation methods for the transport properties enable us to study the nanometer-scale devices.

2. Methods of Calculations

2.1 Ab initio RTM/NEGF method

First we show briefly an *ab initio* calculation method based on the scattering-wave approach for the quantum transport. This method is suitable for the accurate calculations of the atomic and molecular-scale transport

problems corresponding to various atomic configurations. We expand the wavefunctions in a Laue representation

$$\Psi_E^{L/R}(\mathbf{r}) = \sum_m u_E^{L/R}(\mathbf{g}_\parallel^m, z) e^{i(\mathbf{k}_\parallel + \mathbf{g}_\parallel^m)\mathbf{r}_\parallel} \quad (1)$$

where the z axis is in the direction the current flows. We obtain the coupled-channel differential matrix equation of the Kohn-Sham equation and the transfer matrix defined on the neighboring mesh points z_p, z_{p+1} such as

$$\hat{S}^{L/R}(z_p) = \hat{U}^{L/R}(z_{p+1})\hat{U}^{L/R}(z_p)^{-1} \quad (2)$$

follows the recursive relation. Giving the boundary conditions deep in the electrodes, we obtain the scattering-states flowing between electrodes [1]. On the basis of these states, the non-equilibrium Green's function is constructed from the retarded and advanced Green's functions with coupling constant to the electrodes $\Gamma_{L/R}$ by

$$\hat{G}^< = i\hat{G}^r(f_L\hat{\Gamma}^L + f_R\hat{\Gamma}^R)\hat{G}^a \quad (3)$$

where $f_{L/R}$ is the Fermi distribution function of each electrode and the applied bias voltage eV is the difference of chemical potentials $\mu_{L/R}$ at each electrode. Then charge density is obtained through density matrix as a sum over the occupied states

$$\hat{\rho} = -\frac{1}{\pi}\mathrm{Im}\int_C \hat{G}^r dZ + \frac{1}{2\pi i}\int_{\mu_R}^{\mu_L} \hat{G}^< dE \quad (4)$$

where integration of G^r is done in the complex upper plane C, which avoids singularity due to localized nature of the states, van Hove singularities, and others [2].

This charge density is utilized to construct the effective potential V_{eff} based on the DFT and these procedures are iterated until self-consistent solutions are obtained. Finally, the current flowing between electrodes is calculated from the Fisher-Lee relation

$$I = \frac{2e}{h}\int_{-\infty}^{\infty}(f_L - f_R)Tr\{\Gamma^L G^r \Gamma^R G^a\}dE \quad (5)$$

2.2 Time-dependent wave-packet approach

Second we show the O(N) transport calculation method based on the tight-binding approach [3]. Here O(N) is defined so that the calculation time is proportional to the system size. We calculate the time evolution operator using the expansion of the Bessel function and Chebychev polynomials such as

$$U(t+\Delta t) = \prod_{N-0}^{(t/\Delta t)-1}\left[\sum_{n=0}^{\infty} h_n i^n J_n(\Delta t)\times T_n(H(t))\right] \quad (6)$$

Here due to a tiny amount of time evolution, we need only small terms n for the expansion of Bessel function. We calculate the conductance using the Kubo formula in the real time domain

$$G(E) = \frac{2e^2}{L}\rho(E)D(E,\tau(L))$$
$$= lim_{t->\tau(L)}\frac{2e^2}{L}Tr\left[\frac{\delta(E-H)}{L}\frac{(X(t)-X(0))^2}{2t}\right] \quad (7)$$

where D is the diffusion coefficient and the time evolution is $X(t) = U^+(t)X(0)U(t)$.

Figure 1 shows the calculation time as a function of system size of carbon nanotube devices. We can see that the calculation procedure cannot be performed if we use the direct matrix diagonalization of the Hamiltonian up to 40nm length (it takes more than 1000 hours using the super computer). However, we see that if we use the present time-dependent wave-packet method with the Chebyshev polynomial the calculation time is proportional to the system length and that we can treat the 10 μm length with **more than 1 million atoms** in CNT. Therefore we can study the transport properties of CNT-FET device comparable to size in experiments.

This O(N) calculation method is suitable to treat the conductance of large systems.

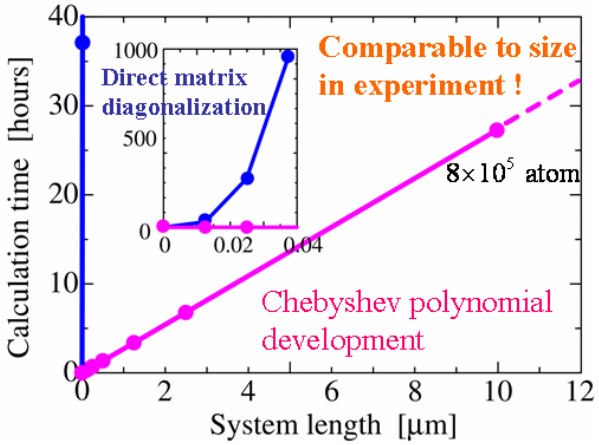

Figure 1. Calculation time as a function of the system length of CNT-FET device with tight-binding calculation. Scales in the inset is the same as those in the main figure

3. Results of Calculations

3.1 Transport and Local Heating of Molecular Device

Using ab initio RTM/NEGF method in Sec.2.1, we show the I-V characteristics and local heating for the transport properties through molecules sandwiched between jellium electrodes in Figure 2. It is at present difficult in experiments to fabricate the nanometer-scale gap structure with high precision. So we expect that the molecules have imperfect contact to the electrodes.

The top panel shows the I-V data when the benzene-dithiolate (BDT) molecule is attached to the left electrode, but there is a separation with d=5 (atomic units(a.u.) =0.529 Å) to the right electrode. We see non-linear behaviour of the current and several peaks (negative differential resistance (NDR)), which appears due to resonances with the molecular states and gap states.

The bottom panel shows the electron-phonon coupling

$$\left|\left\langle i\left|V_{e-ph}(z)\right|f\right\rangle\right|^2=\left|\sum_{m,n}\int d\mathbf{k}_{\parallel}u^{L}_{E_F}(\mathbf{g}^{m}_{\parallel},z)^{*}\nabla V_{eff}(\mathbf{r})u^{R}_{E_F-\hbar\omega}(\mathbf{g}^{n}_{\parallel},z)\right|^2 \quad (8)$$

of the molecular wire composed of 4 benzene molecules. The applied bias is 2V and the separation is d=3 (a.u.) to the left electrode. We see that very strong electron-phonon interaction appears at contact part. This shows that local heating due to phonon emission occurs at contact when the contact part is not well constructed.

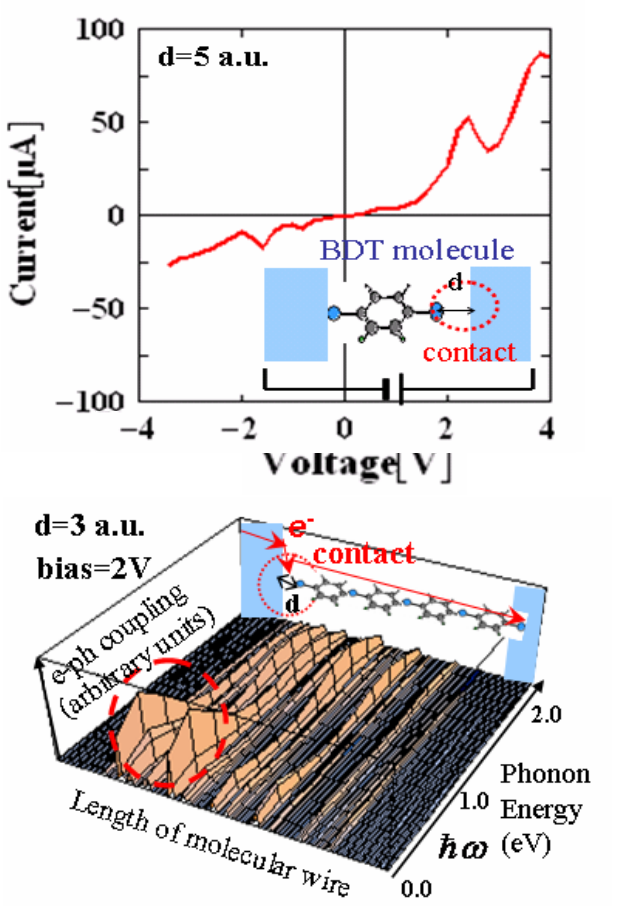

Figure 2: (top) I-V characteristics of the BDT molecule sandwiched between electrodes when one of contacts is not well constructed with the separation of *d=5.0* a.u. (bottom) Electron-phonon coupling of molecular wire as functions of its length and phonon energy. The applied bias voltage is *V=2.0 V* with the separation of *d=3.0* a.u.

3.2 Transport characteristics of CNT-FET devices

Next by using the time-dependent wave-packet approach in Sec.2.2, we show the transport properties of CNT-FET devices with back gate structure. Single-walled CNTs are remarkable quasi-one-dimensional materials and recently they have been utilized for the channel of the FET devices [4]. It is reported that the mobility can be as high as 79000 cm^2/Vs maximally. Here we study the CNT-FET device with 1 μm channel length by the time-dependent wave-packet approach. The effects of Schottky barrier and electron-phonon scattering are included in the calculations. The left panel of figure 3 shows the diffusion coefficient D as a function of time with various gate voltages. The right panel shows the mobility μ obtained from $\mu = e\tau/m^*$ ($\mu \propto dG/dV_G$). We see that the mobility becomes zero under the gate voltage of $V_G=0.7V$ with the semiconductor gap and it reaches up to 15000 cm^2/Vs. We find that the control of the contact to electrodes (Schottky barrier) becomes crucial for the device performance of CNT transistors.

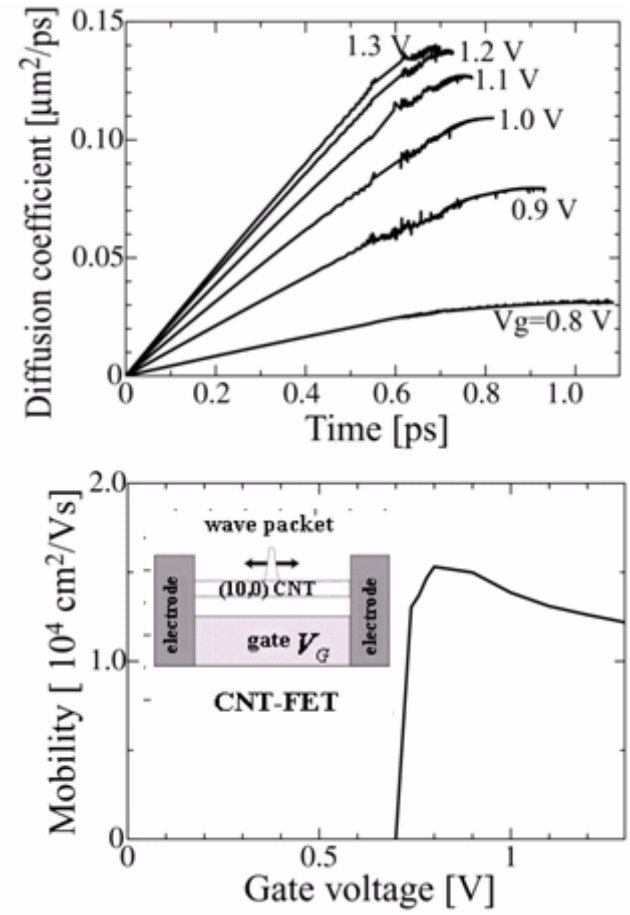

Figure 3: Calculation of the performance of CNT-FET device. Inset is the schematic view of the device structure. Semi-conducting CNT with (10,0) is sandwiched between the metallic electrode together with back gate structure.

Acknowledgements

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References

[1] K. Hirose, N. Kobayashi, and M. Tsukada, "Ab initio calculations of transport properties of atomic wires by the RTM method", Physical Review, B69, 245412-1-5, 2004.
[2] K. Hirose and N. Kobayashi, "Theory of electron hopping through nanometer-scale contacts –from tunneling to ballistic regimes", Physica, E29, 515-518, 2005.
[3] H. Ishii, N. Kobayashi, and K. Hirose, "Electron-phonon coupling effect on quantum transport in carbon nanotubes using time-dependent wave-packet approach", Physica E40, 249-252 2007.
[4] For a recent review, see J.-C Charlier, X. Blasé, and S. Roche, "Electronic and transport properties of nanotubes", Review of Modern Physics, vol. 79, 677-732, 2007.