Nanoscale capacitance: a quantum tight-binding model

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ABSTRACT

Landauer-Buttiker formalism with the assumption of semi-infinite electrodes as reservoirs has been the standard approach in modeling steady electron transport through nanoscale devices. However, modeling dynamic electron transport properties, especially nanoscale capacitance, is a challenging problem because of dynamic contributions from electrodes, which is neglectable in modeling macroscopic capacitance and mesoscopic conductance. We implement a self-consistent quantum tight-binding model to calculate capacitance of a nano-gap system consisting of an electrode capacitance C' and an effective capacitance C_d of the middle device. From the calculations on a nano-gap made of carbon nanotube with a buckyball therein, we show that when the electrode length increases, the electrode capacitance C' moves up while the effective capacitance C_d converges to a value which is much smaller than the electrode capacitance C' . Our results reveal *the importance of electrodes in modelling nanoscale ac circuits*, and indicate that *the concepts of semi-infinite electrodes and*

reservoirs well-accepted in the steady electron transport theory may be not applicable in modeling dynamic transport properties.

1. Introduction

The success of quantum mechanics can be reflected from the development of quantum chemistry and solid state physics. Quantum chemistry uses quantum mechanics to study finite structures like atoms and molecules, while solid state physics applies quantum mechanics to (infinite) bulk materials under periodic boundary conditions. For electronic structure calculations based on the density functional theory [1,2], commercial and academic software packages have been developed and widely used in both quantum chemistry and solid state physics. The development of nanoelectronics, however, introduces a new structure [3,4] consisting of two separated electrodes and a finite device in between [See Fig. 1(a)]. The two electrodes are usually bulk materials and assumed as semi-infinite. Obviously, this transport system is infinite but lacks periodicity. Both the methods from the quantum chemistry (for finite structures) and solid state physics (for bulk materials with a lattice periodicity) cannot be used in this new structure. It was Landauer and Buttiker, who established a standard model for nanoscale direct-current (dc) transport [5]. In their model each electrode is viewed as a reservoir with a given chemical potential, which is unaffected by the central device and the transport current. The difference between the chemical potentials in two electrodes is viewed as the bias voltage. The two-terminal conductance is then determined by the transmission of electrons from one electrode to the other.

Recently, this two-terminal transport system was proposed to detect the DNA sequence [6], where the middle device is taken as different DNA nucleotides [adenine (A),

cytosine (C), guanine (G), and thymine (T)]. This proposal relies on the nucleotide-resolved conductance, which, however, depends exponentially on the effective distances between the nucleotide and electrodes [7]. To wash out this distance dependence of the conductance [8], thousands of measurements and a good statistics might be needed. As an alternative proposal on transport-based DNA sequencing, alternative-current (ac) capacitance measurement [9] may provide a better signal/noise ratio than the dc conductance measurement. The reason is that the capacitance results mainly from direct Coulomb interaction between the nucleotide and electrodes and is thus rather less sensitive to the nucleotide-electrode distance than the dc conductance.

It is believed that ac transport would provide faster and more energy-efficient nanoelectronic devices. Many concepts and algorithms on dc conductance of nanoscale structures have been generalized to calculate dynamic conductance [10,11,12,13] and capacitances [14,15,16]. In these models the transport properties due to the middle device are focused and the electrodes are usually simplified by taking the *wide-band limit*. However, ac transport is distinct from dc transport even for a simple two-terminal system [see Figs. 1(a) and 1(b)]. In Fig. 1(a), the steady dc currents through any cross-area of the two electrodes are the same. This two-terminal current could be strongly affected by the middle device since it has to go through the middle device due to the current conservation. Thus the I-V curves measured in electrodes may reveal some properties of the middle device. In contrast, an ac current flowing back and forth in electrodes could bypass the middle device [Fig. 1(b)]. This indicates that the ac current amplitude in electrodes can be much bigger than that in the middle small device, for example, when the capacitance of the electrodes is much larger than that of the middle

device. The dynamic I-V character measured in electrodes may be irrelevant to the middle device. When ac transport properties of nanoscale circuits are concerned, we should notice that *the electrodes can contribute dominantly to the current and should be treated carefully*. To extract the dynamic properties of the middle device from the transport measurements, it is necessary to remove properly the contribution from the electrodes.

Fig. 1 (Color online) (a) and (b) A typical two-terminal transport system consisting of two separated electrodes and a device on the nanoscale. The red arrows illustrate space distributions of (a) the steady direct currents and (b) the dynamic alternating currents. (c) and (d) A nano-gap made of carbon nanotubes, with and without a buckyball in between.

To illustrate the role of electrodes in determining physical quantities related to ac transport, in this work we calculate capacitances of a nano-gap system as shown in Fig. 1(b) and define effective capacitances for the nanoscale device therein. The capacitances of the electrodes and device will play an important role in determining dynamic current in ac transport, but will not affect steady current in dc transport. The nano-gap system consists of two metallic electrodes at a distance of several nanometers. We adopt both a classical atomic charge model [17, 18] and a quantum tight-binding model to calculate the static capacitance. For a nano-gap [shown in Figs. 1(c) and 1(d)] made of carbon nanotubes (CNTs), our calculations based on both models show that the inclusion of a nanoscale device like a buckyball (C_{60}) brings only a tiny change on the capacitance of the system. This indicates that when connecting in a nanoscale circuit, it is the electrodes rather than the middle device will contribute mainly to dynamic currents.

2. Models on capacitances of nano-gap systems

To calculate the capacitance of a nano-gap system schematically shown in Fig. 1(c), for each electrode we take a finite length N_c which starts from the electrode's terminal [19]. The length N_c is in unit of the size of a unit cell of electrodes and will be gradually increased in calculations so that each electrode can approach the corresponding semi-infinite electrode. The whole system $\mathbf{H}_{2E+D}$ in calculations is finite and consisting of two finite electrodes and a middle device. We assign a positive charge $+Q$ on the left electrode and a negative charge $-Q$ on the right one. The potential difference ΔV between the two electrodes can be calculated and the capacitance of this finite system is defined as $C = Q/\Delta V$. For the finite system $\mathbf{H}_{2E}$ including only the two electrodes, as shown in Fig. 1(d), we can similarly calculate its capacitance from $C' = Q/\Delta V'$. Then the

contribution from the middle device can be calculated by $C_d = C - C'$ and defined as the effective capacitance of the device [20]. As shown below, the value of C_d at large length N_C is a constant and thus can be viewed as an intrinsic capacitance contribution of the middle device.

To calculate the potential difference ΔV , here we adopt a self-consistent tight-binding model. The finite system $\mathbf{H}_{2E+D}$ can be described by the Hamiltonian

$$H = \sum_{i=1}^N (E_i + V_i) C_i^\dagger C_i - \sum_{\langle i,j \rangle} t_{i,j} C_i^\dagger C_j \quad (1)$$

Here N is the total number of atoms, C_i is the annihilation operator of electrons on atom i , E_i and V_i are the zero-field onsite energy and electric potential energy at atom i , and $t_{i,j}$ is the hopping energy from atom j to atom i . Note that there is no hopping between atoms belonging to different parts (left electrode, right electrode, and device). We assume that the tight-binding parameters $t_{i,j}$ and E_i depend only on the materials. The electric potential energies V_i are solved in a self-consistent manner. For the initial guess values of electric potential energies, we use the results from classical calculations as described in the classical model below. We then diagonalize the Hamiltonian (1) to yield a set of energy levels and corresponding wave functions. For each electrode, the energy levels are occupied by electrons until reaching the assigned charge. From the wave functions of occupied energy levels, we can calculate the charge q_j of each atom j for the whole system. The charge distribution of each atom is then approximated by a Gaussian distribution. The charge density $\rho_j(\mathbf{r})$ of atom j is $\rho(\mathbf{r}; q_j) = \frac{q_j}{\pi^{3/2} R^3} \exp \left[-\left(\frac{|\mathbf{r} - \mathbf{r}_j|}{R} \right)^2 \right]$, where $\mathbf{r}_j$ is the position of the atom j and R is the width of the distributions. Then a new set of

values of the electric potential energies can be calculated by $V_i = -e(\sum_{j=1}^N T_{ij} q_j + \chi_i)$, and be used as the new guess V_i in the Hamiltonian (1). Here e is the proton's charge, $T_{ij} = \text{erf}(r_{ij}/\sqrt{2}R)/(4\pi\epsilon_0 r_{ij})$, and χ_i is the electron affinity of atom i . This procedure is repeated until a self-consistent solution of electric potential energies V_i is reached. Finally, one obtain the potential difference between the two electrodes $\Delta V = |\varepsilon_{\max L} - \varepsilon_{\max R}|/e$, where $\varepsilon_{\max L}$ ($\varepsilon_{\max R}$) is the energy of highest occupied energy levels in the left (right) electrode.

We have also present results from a classical model for comparison. The classical charge q_j of the atom j satisfies the following equations:

$$\left\{ \begin{array}{l} \sum_{j=1}^N T_{ij} q_j + \chi_i - V_L = 0; i \in L \\ \sum_{j=1}^N T_{ij} q_j + \chi_i - V_R = 0; i \in R \\ \sum_{j \in L} q_j = +Q; \\ \sum_{j \in R} q_j = -Q, \end{array} \right.$$

where $i \in L(R)$ means atom i belongs to left (right) electrode, V_L and V_R are classical electric potential of the left and right electrodes. By solving these $N+2$ equations, we obtain all q_j , V_L and V_R . The classical potential difference is $\Delta V = V_L - V_R$.

3. Capacitances of a carbon nano-gap

We demonstrate the idea and model outlined above by calculating the capacitances of a CNT nano-gap [depicted in Figs. 1(c) and 1(d)] and effective capacitance of a C_{60} therein.

To illustrate the idea and simplify the calculations, both the CNTs and the C_{60} are described by a nearest-neighbor π -orbital tight-binding parameters [10, 21] where $E_i = 0$, $t_{ij} = 2.79$ eV for two carbon atoms in the nearest neighbor and zero otherwise. In the calculations, the two electrodes are made of (5, 5) CNTs. The gap between them is 1.23 nm. For the electric potential calculations, we use electron affinity of carbon atom $\chi_i = 1.26$ eV, and width of Gaussian distributions $R = 0.06862$ nm [17]. We then assume the charge on the left electrode is $+2e$ and that on the right electrode is $-2e$, and calculate the charge distributions and determine potential difference between the two electrodes. Figure 2 shows the charge distributions calculated by the tight-binding model at two different lengths of electrodes [$N_C = 4$ in Fig. 2(a) and $N_C = 16$ in Fig. 2(b)]. In both length cases, the C_{60} in the gap is polarized with positive charge on the right and negative charge on the left due to the assigned charges in the electrodes. The polarization of the C_{60} will then affect the charge distributions and potential profiles in the electrodes through Coulomb interaction and hence contribute to the capacitance of the nano-gap. This contribution is the effective capacitance of the middle device defined earlier. An interesting observation is that the assigned charges distribute through the whole length of electrodes in both Figs. 2(a) and 2(b). Because of these unique charge distribution, the potential difference between the two electrodes decreases when the length of electrodes increases, which leads to the increase of the capacitance of the nano-gap (as shown in Fig. 3). The polarization of the middle C_{60} decreases correspondently, resulting in a converged effective capacitance eventually.

Fig. 2 (Color online) Contour plot of charge density distribution of a carbon nanotube nano-gap with a C_{60} in between calculated by the tight-binding model. In (a) and (b), each electrode consists of 4 and 16 unit cells of the carbon nanotube, respectively. The unit of the charge density is e/nm^3 .

Fig. 3 (Color online) (a) and (c) Capacitances plotted as a function of electrode length for a pure carbon nanotube nano-gap (black line) and a carbon nanotube nano-gap with a buckyball in-between (red line). (b) and (d) Effective capacitances of the buckyball as a function of electrode length. In (a) and (b), the calculations are under the classical atomic-charge approximation, while in (c) and (d) the numerical results are obtained in the tight-binding model.

In Figs. 3(a) and 3(c) the calculated capacitances for the H_{2E+D} and H_{2E} systems is plotted as a function of the length N_C of either electrode. The left and right panels represent the results under the classical model and the tight-binding model. The capacitances obtained from the two models show up similar features. With the increase of N_C , both the capacitance C and C' moves up monotonously. Note that for dc transport the surface Green's function of the electrode converges quickly as N_C increases. This observation indicates that *the concepts of semi-infinite electrodes and reservoirs well-accepted in the dc transport theory may be not applicable in modelling ac transport*. The two curves in Fig. 3(c) almost coincide. Consequently, in the tight-binding model the insertion of a C_{60} in the nano-gap brings only a tiny change on the system's capacitance. This change is defined as the effective capacitance C_d of the C_{60} .

As shown in Fig. 3(d), the effective capacitance C_d under the tight-binding model increases firstly for small values of N_C and then decreases gradually to a convergent value $C_{d0}^{TB} \approx 0.0103$ e/V. The convergent value of C_d is much smaller than the capacitance C' of two electrodes. This can be understood as follows. Under the electric field created by the two electrodes, the neutral C_{60} will be positively charged on the right side and negatively charged on the left side. On the distance much larger than its size, the polarized C_{60} can be viewed as a dipole and thus creates only a weak electric field.

This weak dielectric effect is characterized by the effective capacitance. Obviously, the converged C_d for C_{60} still depends on the materials of electrodes and the relative positions of C_{60} to electrodes. The effective capacitance under the classical model [shown in Fig. 3(b)] increases monotonously and converges quickly to the value $C_{d0}^{classical} \approx 0.0213 \text{ e/V} > C_{d0}^{TB}$. (This convergent value of the effective capacitance is, however, smaller than that obtained in the full atomic charge-dipole model (0.0353 e/V) [20].)

Fig. 4 (Color online) (a) Capacitance of a carbon nanotube nano-gap as a function of the electrode length calculated in the tight-binding model (black line) and the classical atomic charge model (red line). (b) Quantum capacitance as a function of the electrode length.

In our calculations, we also find that the value of the capacitance of nanogap $C'_{classical}$ in the classical model is always larger than the value C'_{TB} in the tight-binding model, as shown in Fig. 4(a). Their difference is due to the presence of a quantum capacitance [22] C'_Q defined from $1/C'_Q = 1/C'_{TB} - 1/C'_{classical}$. The quantum capacitance arises from the non-classical Pauli repulsion between electrons. From Fig. 4(b) we see that C'_Q increases almost linearly with the length N_C . The quantum capacitance will be discussed in a future work, where the nanoscale capacitance will be calculated from the density functional theory.

4. Conclusions

In summary, we have presented a self-consistent tight-binding model to calculate capacitances of nano-gap systems. By assuming a finite net charge in the two electrodes, the capacitance of the nano-gap system is determined by the energy difference between the highest occupied energy levels in the two electrodes. The system's capacitance C can be divided into two parts: the electrode capacitance C' due only to two electrodes and the effective capacitance C_d of the nanoscale structure inside the gap. We have applied both the tight-binding model and a classical atomic-charge model to calculate the capacitance of a CNT nano-gap with a C_{60} inside. It is found that in either model the electrode capacitance C' increases with the length N_C of electrodes, while under sufficient large values of N_C the effective capacitance of the C_{60} converges to a value which is much smaller than C' . This indicates that for *ac transport quantities of nanoscale circuits the electrodes can contribute dominantly and should be treated*

carefully. Both the convergent C_d and the electrode capacitance C' in the tight-binding model are smaller than their counterpart in the classical model. The difference of C' values calculated in the two models arises from the quantum capacitance.

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