Charge relaxation resistance at atomic scale: An *ab initio* calculation

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We report an investigation of ac quantum transport properties of a nanocapacitor from first principles. At low frequencies, the nanocapacitor is characterized by a static electrochemical capacitance C_μ and the charge relaxation resistance R_q. We carry out a first principle calculation within the nonequilibrium Green's function formalism. In particular, we investigate charge relaxation resistance of a single carbon atom as well as two carbon atoms in a nanocapacitor made of a capped carbon nanotube (CNT) and an alkane chain connected to a bulk Si. The nature of charge relaxation resistance is predicted for this nanocapacitor. Specifically, we find that the charge relaxation resistance shows resonant behavior and it becomes sharper as the distance between plates of nanocapacitor increases. If there is only one transmission channel dominating the charge transport through the nanocapacitor, the charge relaxation resistance R_q is half of resistance quantum $h/2e^2$. This result shows that the theory of charge relaxation resistance applies at atomic scale.

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I. INTRODUCTION

As one of the fundamental building blocks of nanodevices, the nanocapacitor has been the subject of more and more attention recently.[1–13] For a macroscopic capacitor, the electron-electron interaction is largely screened in the two metallic plates and we have the classical capacitance whose value depends only on the geometric properties of the capacitor. While for a nanocapacitor consisting of two nanoconductors with finite density of states (DOS), quantum effect becomes important. In this case, the quantum (electrochemical) capacitance C_μ consists of the classical capacitance C_0 in series with a contribution from the DOS of the two nanoconductors C_{DOS}: $1/C_\mu = 1/C_0 + 1/C_{\mathrm{DOS}}$.[1,14] Due to the presence of electron reservoirs, the dynamical response of a nanocapacitor has a dissipative component and is characterized by the charge relaxation resistance R_q at low frequencies.[1] Therefore, the dynamical conductance of a nanocapacitor can be expressed in terms of the electrochemical capacitance C_μ and the charge relaxation resistance R_q at low frequencies,

$$G(\omega) = -i\omega C_\mu + \omega^2 C_\mu^2 R_q + O(\omega^3) \tag{1}$$

Here, the first term describes the nondissipative response when the electrochemical potential of a reservoir is changed by a small amount, while the second term represents dissipative component. For a nanocapacitor that permits a single spin-resolved transmission channel, R_q is predicted to be half of resistance quantum[1]

$$R_q = \frac{h}{2e^2} \tag{2}$$

which is independent of the incoming electron energy. Note that the factor two here is not from the spin, but a hallmark of charge relaxation resistance.[1] It has been shown that the charge relaxation resistance remains unchanged in the Coulomb blockade regime at zero temperature.[12] Physically, the dynamical response of a nanocapacitor at low frequencies can be described by a RC circuit that consists of a resistor with charge relaxation resistance in series with a capacitor with electrochemical capacitance. At finite frequencies, quantum inductance sets in and the system can be described by a RLC circuit.[13]

The prediction of charge relaxation in the single transmission channel has been confirmed experimentally by Gabell *et al.*[11] In this experiment, a quantum cavity on submicrometer 2DEG was fabricated as one of the capacitor plates that is in contact with the electron reservoir via a quantum point contact (QPC). A gate voltage was used to control the number of transmission channels through the QPC. The other capacitor plate was simulated by a gold plate on top of the cavity. To resolve the spin degeneracy, a strong magnetic field was applied and the electron was spin polarized. Experimental results[11] showed that the charge relaxation resistance R_q in the single transmission channel is indeed given by half of the resistance quantum, in agreement with the prediction by Büttiker *et al.*[1] An interesting question arises: does this theory apply for molecular junctions and what is nature of the charge relaxation resistance of a single atom? It is the purpose of this paper to answer this question. Specifically, we have carried out a first principle calculation to calculate the charge relaxation resistance R_q for a nanocapacitor consisting of one or several atoms. From a self-consistent calculation of quantum scattering together with the Poisson equation for the potential distribution in the capacitor,[15] we obtained the charge distribution in real space as well as the eigenchannels of DOS. We found that the charge relaxation resistance shows resonant behaviors that depend on the system details. If there is only one transmission channel dominating the charge transport through the nanocapacitor, the charge relaxation resistance R_q is half of resistance quantum $h/2e^2$. Our result confirms Buttiker's conclusion at atomic scale.

II. THEORETICAL FORMALISM

The nanocapacitor (CNT-C-Alk-Si) discussed in this paper is shown in Fig. 1 where a semi-infinite (5,5) capped carbon nanotube (CNT) is capacitively in contact with an insulator through a carbon atom. The insulator consists of an

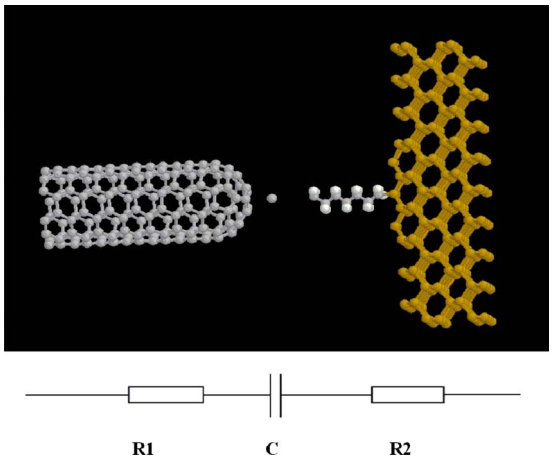

FIG. 1. (Color online) Upper panel: Optimized geometry of the CNT-C-Alk-Si nanocapacitor. The semi-infinite CNT (5, 5) serves as the left lead and the bulk Si along the (100) direction is the right lead. The gray, white, and yellow balls represent C, H, and Si atoms, respectively. Lower panel: schematics of the corresponding classical RC circuit consisting of two resistors and one capacitor.

alkane chain connected to a bulk silicon (100) surface that has a gap at Fermi level. Here the capped carbon nanotube and the bulk silicon serve as two leads where the capped CNT simulates the STM tip and can control the distance between two leads. By changing the distance between the single carbon atom and the cap of CNT, a large barrier is created so that the presence of the carbon atom gives rise to an impurity state that serves as the resonant state.[16] The life time of the resonant state is determined by the distance between the carbon atom and the CNT cap as well as the alkane chain. The reason to include the alkane chain in contact with the right lead is the following. First, it can be realized experimentally due to the thermodynamic and kinetic stability of the Si–C bond.[17,18] Second, the presence of alkane helps to speed up the convergence of the self-consistent cycle in the *ab initio* calculation. Note that this system is equivalent to a classical RC circuit as shown in the lower panel of Fig. 1. Our nanocapacitor can be divided into two regions. Region one is the capped CNT with a carbon atom while region two is the alkane with bulk Si. Since DOS of the bulk silicon is very large, the charge relaxation resistance R_2 in region two can be neglected.

To calculate the charge relaxation resistance of the nanocapacitor, we used the first principles quantum transport package MatDcal[15,19] which is based on the Keldysh nonequilibrium Green function (NEGF). The basic principle and practical implementation of the NEGF-DFT formalism can be found in Ref. 15. A linear combination of the atomic orbitals(LCAO) basis set[20] was employed to solve the Kohn–Sham (K-S) equations numerically. The exchange-correlation was treated at the LSDA level[21] and a nonlocal norm conserving pseudopotential[22] was used to define the atomic core. The density matrix was constructed in orbital space and the effective potential was solved in real space. In our calculation, the NEGF-DFT self-consistency was carried out until the numerical tolerance was less than 10^{-4} eV.

According to Ref. 1, for a two plate quantum capacitor similar to that of the experiment by Gabelli *et al.*,[11] the dynamical electrochemical capacitance $C_\mu(\omega)$ is related to the dynamical conductance through the relation $G(\omega)=-i\omega C_\mu(\omega)$ and can be derived as:[13]

$$\frac{e^2}{C_\mu(\omega)} = \frac{e^2}{C_0} + \frac{1}{dN_L(\omega)/dE} + \frac{1}{dN_R(\omega)/dE}. \tag{3}$$

Here, C_0 is the usual electrostatic geometric capacitance and $dN_L(\omega)/dE$ and $dN_R(\omega)/dE$ represent the frequency dependent global DOS of left plate and right plate, respectively. In the low-frequency limit, the real part of the quantum capacitance $C_\mu(\omega)$ corresponds to the static electrochemical capacitance and its imaginary part is proportional to the charge relaxation resistance. Here, $dN_\alpha(\omega)/dE$ can be expressed using the nonequilibrium Green functions:[12,13]

$$\frac{dN_\alpha(\omega)}{dE} = \mathrm{Tr}\int \frac{dE}{2\pi}\frac{f-\bar{f}}{\hbar\omega}[\bar{G}^r\Gamma_\alpha G^a] \tag{4}$$

where f is the Fermi distribution function and $\bar{f}\equiv f(E_+)$ with $E_+\equiv E+\hbar\omega$; $G^{r,a}=G^{r,a}(E)$ is the retarded (advanced) Green function and $\bar{G}^{r,a}\equiv G^{r,a}(E+\hbar\omega)$; Γ_α is the linewidth function describing the coupling between the α plate to the reservoir. Since the dN_R/dE is much larger than dN_L/dE due to the bulk structure of Si, the third term of right hand side of Eq. (3) can be safely neglected. Expanding the dynamic conductance $G(\omega)$ to the second order in frequency, the charge relaxation resistance at zero temperature is given by:[12]

$$R_q = \frac{h}{2e^2}\frac{\mathrm{Tr}[G^r\Gamma_L G^a]^2}{[\mathrm{Tr}(G^r\Gamma_L G^a)]^2}. \tag{5}$$

Note that in the limit ω goes to zero, the zero temperature partial DOS is given by $dN_\alpha/dE=\mathrm{Tr}[G^r\Gamma_\alpha G^a]$. If we diagonalize the matrix $G^r\Gamma_\alpha G^a$, the number of eigenstates gives the number of transmission channels and the corresponding eigenvalues are the partial DOS denoted as $dN_{\alpha,n}/dE$ contributed from nth eigenchannel. Clearly, we have $dN_\alpha/dE=\Sigma_n dN_{\alpha,n}/dE$ where Σ_n is over all the eigenchannels of DOS. Hence, Eq. (5) can be written as

$$R_q = \frac{h}{2e^2}\frac{\sum_n [dN_{L,n}/dE]^2}{\left[\sum_n dN_{L,n}/dE\right]^2}. \tag{6}$$

One important consequence of this equation is that the charge relaxation resistance is equal to half of the resistance quantum $h/2e^2$ if there is only one eigenchannel.[1]

III. NUMERICAL RESULTS

Using Eq. (5), we calculated the charge relaxation resistance R_q of the nanocapacitor shown in Fig. 1 by varying the number of the carbon atoms and the distance between the carbon atom and the cap of CNT. Figure 2 shows the global DOS dN_L/dE at zero frequency and the corresponding charge relaxation resistance R_q of CNT-C-Alk-Si versus Fermi energy with C-C distance equal to 2.45 a.u. (1.297 Å). As shown in Fig. 2(a), DOS is flat and small for most of energies except that three sharp resonant peaks occur

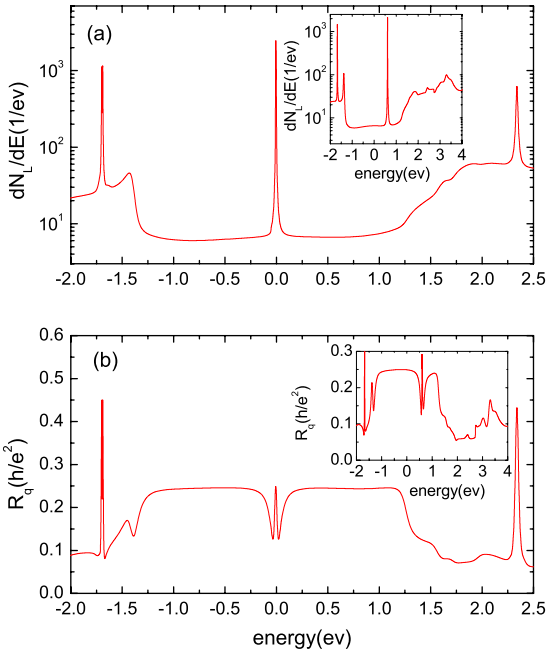

FIG. 2. (Color online) (a) dN_L/dE vs energy (eV) in logarithmic scale for the CNT-C-Alk-Si capacitor with C-C distance equal to 2.45 a.u. (b) R_q against the energy. Insets are that of the CNT-Alk-Si capacitor.

at $E=0$, $E=2.35$ eV, and $E=-1.7$ eV. Comparing with the result from CNT-Alk-Si structure (shown in the inset), we found that the effect of the carbon atom is twofold. It gives rise to a resonant state at $E=2.35$ eV and shifts the resonant level at $E=0.55$ eV down to $E=0$. Figure 2(b) shows the calculated R_q versus energy using Eq. (5). We see that R_q shows a plateau region with a value equal to 0.25 in the unit of resistance quantum. This plateau region is well correlated with the corresponding flat region in DOS. At the position of the first resonant peak at $E=0$, R_q also shows a small peak with peak value approximately equal to 0.25. While for the second and third resonant peaks with $E=2.35$ eV and -1.7 eV, R_q are close to 0.5, which is half of resistance quantum. In order to understand this behavior, we plot the eigenchannels of partial DOS $dN_{L,n}/dE$ against energy in Fig. 3. We found that in the energy range $E=[-1.2,1.2]$ eV, the partial DOS dN_L/dE is dominated by four eigenchannels for the system of Cap-CNT with one carbon atom. These four eigenchannels can be divided into two groups according to their contributions to the charge relaxation resistance. One group consists of two degenerate eigenchannels and the other contains two nearly degenerate eigenchannels. In the energy range $E=[-1.2,1.2]$ eV except near $E=0$, there are only two nearly degenerate eigenchannels (the second group) contributing equally to the transport. Therefore, R_q is close to 0.25 according to Eq. (6). When energy is close to $E=0$, the other two degenerate eigenchannels (the first group) give rise to a sharp peak in DOS that is much larger than the contribution from the second group. Therefore R_q is exactly 0.25 due to the degenerate peak in DOS. In addition, the competition between these two groups gives rise to the valleys of R_q close to $E=0$. When the energy is greater than 1.2 eV, three additional double degenerate

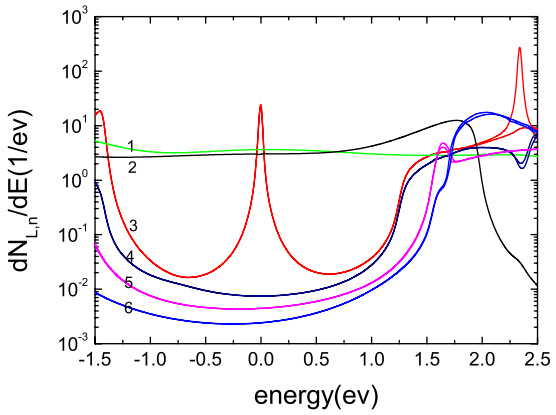

FIG. 3. (Color online) The eigenchannels of dN_L/dE in logarithmic scale of the CNT-C-Alk-Si capacitor with C-C distance equal to 2.45 a.u. Only dominated eigenchannels are shown. Apart from two channels labeled by 1 and 2 which are nondegenerate, all the other channels (3, 4, 5, 6) are double degenerate when $E=[-1.5,1.5]$ eV.

eigenchannels become important and the charge relaxation resistance decreases quickly. As one further increases energy to 2.2 eV, one of the eigenchannels in the first group splits and starts to dominate. When energy E is equal to 2.35 eV, contribution to DOS due to this eigenchannel is much larger than the rest making R_q close to $h/2e^2$ as predicted in Ref. 1.

In Fig. 4(a), we plot the charge relaxation resistance R_q of CNT-C-Alk-Si nanocapacitor as a function of Fermi energies when the C-C distance d varies from 2.45 to 5.45 a.u. with 47 data points. Following observations are in order. (1) We see from the figure that for most energies in the range between -1.2 to 1.2 eV, we have $R_q \simeq h/4e^2$ mainly due to two nearly degenerate eigenchannels as we have analyzed in Fig. 3 at short C-C distances. Out of this energy range, there are more eigenchannels of dN_L/dE that contribute to R_q giving rise to a much smaller value according to Eq. (6). (2) With the increasing of C-C distance, the resonant peak that is due to the single carbon atom moves from $E=2.35$ eV when $d=2.45$ a.u. to $E=0.6$ eV when $d=5.45$ a.u. At the same time, the peak height decreased from $R_q \sim 0.5$ and eventually vanishes at $d=3$ a.u. indicating that other transmission channels become equally important. This peak re-emerges at $d=3.5$ a.u. with peak height gradually increased to $R_q \sim 0.3$ at $d=5.45$ a.u. In the meantime, a broad peak of R_q appears at $E \sim 1.2$ eV when $d=3.2$ a.u. Upon further increasing the distance, the height of this broad peak increases with its width decreasing. In addition, the location of the peak moves toward $E=0$. When the C-C distance is equal to 5.25 a.u., the peak height of R_q is larger than $0.4h/e^2$. (3) Near $E=0$, the charge relaxation resistance also changes as one increases the distance d. When $d=5.25$ a.u., we have $R_q \sim h/2e^2$ as shown in Fig. 4(b). To understand this, we plot the eigenchannels of dN_L/dE as a function of energy in Fig. 4(c). We see that there is one eigenchannel (curve 2) with very large DOS peaked near $E=0$ that dominates the transport. It is this channel that leads to the half of resistance quantum. At $E=0.6$ eV, the major contribution to R_q comes from two double degenerate transmission channels. Finally, in Fig. 5(a), we show the charge relaxation resistance R_q of

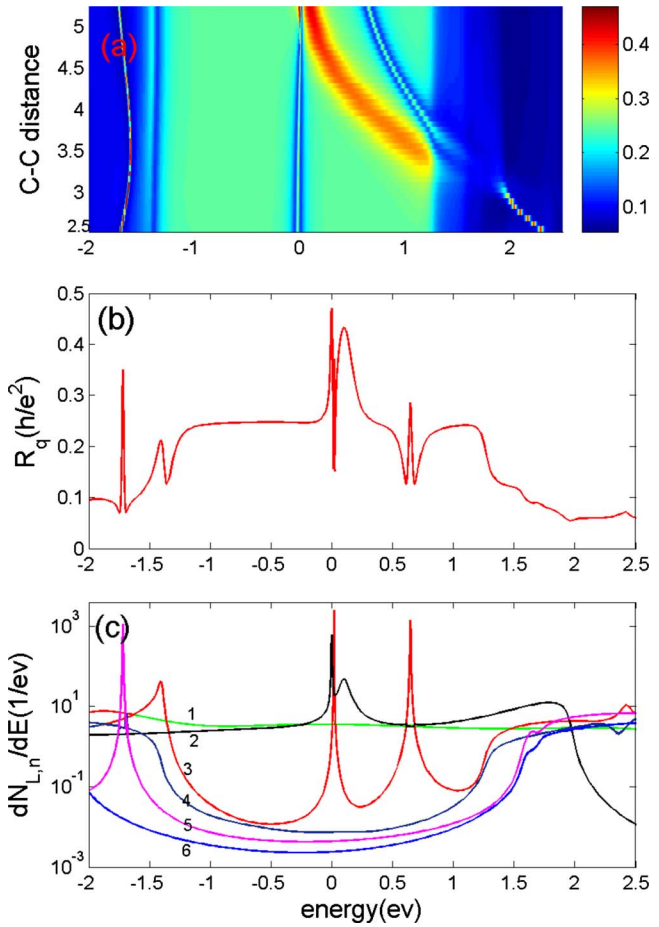

FIG. 4. (Color online) (a) The charge relaxation resistance R_q as a function of energy and the C-C distance in unit a.u. of the nanocapacitor CNT-C-Alk-Si. (b) R_q vs energy when d=5.25 a.u. (c) The dominating eigenchannels of dN_L/dE as a function of energy when d=5.25 a.u. Similar to Fig. 2, channels 1 and 2 are nondegenerate while channels 3, 4, 5, 6 are double degenerate.

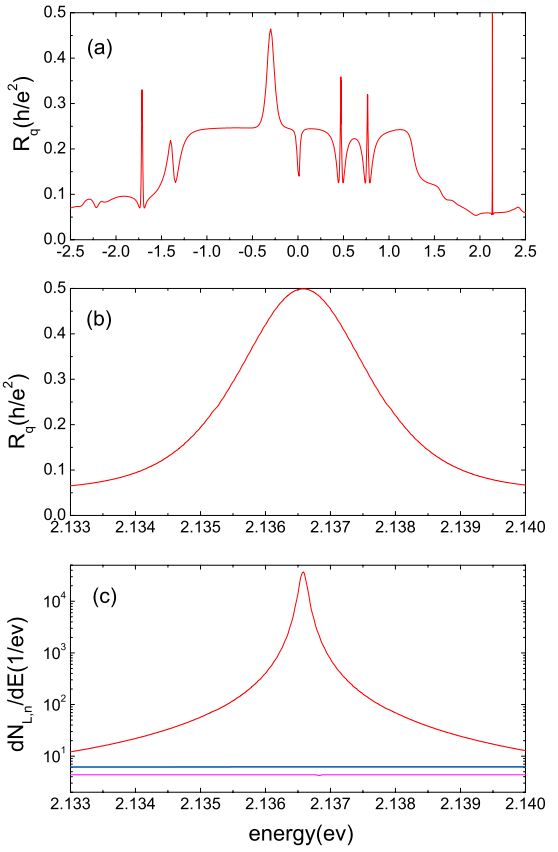

FIG. 5. (Color online) (a) and (b) R_q vs energy of CNT-C-C-Alk-Si capacitor with the distance between the cap of CNT and the first C atom as well as the distance between the first C atom and the second C atom equal to 5.45 a.u. and 5.0 a.u., respectively. (c) eigenchannels of dN_L/dE in logarithmic scale as a function of energy.

the CNT-C-C-Alk-Si capacitor, in which the distance between the cap of CNT and the first carbon atom and the distance between the first and the second carbon atom are fixed to be 5.45 and 5.0 a.u., respectively. We see several plateau regions with $R_q \sim h/4e^2$ showing the signature of double degenerate eigenchannels. In particular, there is a sharp peak at E=2.136 eV which is zoomed in Fig. 5(b). Here, R_q is exactly half resistance quantum $h/2e^2$ at the resonant energy. According to Eq. (5), we expect that it must belong to the single-channel transport. Indeed, as shown in Fig. 5(c), there is only one eigenchannel that completely dominates the DOS. Finally, our predictions can be checked experimentally using a similar setup of Ref. 7 where a STM tip is used to measure the electrochemical capacitance of nanojunctions as a function of distance.

In summary, we have investigated the low-frequency response of the CNT-C-Alk-Si capacitor using the first principle calculation method within the nonequilibrium Green's function formalism. By changing the C-C distance and the number of carbon atoms of CNT-C-Alk-Si nanocapacitor, we have calculated the charge relaxation resistance R_q using Eq. (5). Resonant behaviors are found as we vary the C-C distance. Our results show that R_q is approximately equal to a quarter of resistance quantum for two nearly degenerate transmission channels. While for a single-channel transmission, R_q is exactly equal to $h/2e^2$. This shows that the theory of charge relaxation resistance developed by Büttiker *et al.* applies at atomic scale. Finally, it would be interesting to numerically check the charge relation theory in the presence of dephasing.[23]

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