Conductance of carbon atomic wire in the environment of H_2O molecules

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Abstract. The conductance of carbon atomic wire in the environment of H_2O molecules is studied by the non-equilibrium Green function method based on density functional theory. In particular, the carbon wire with seven atoms sandwiched between the Al(100) electrodes is considered. It is found that the transport properties are sensitive to the variation of the number and the position of the H_2O molecule adsorbed on the carbon wire. To our surprise, with different positions of a single H_2O molecule on the carbon wire, the equilibrium conductance shows an evident odd-even oscillatory behavior. For example, the equilibrium conductance of the carbon wire becomes bigger when the H_2O is adsorbed on the odd-numbered carbon atoms; an opposite conclusion is obtained for the H_2O adsorbed on the even-numbered carbon atoms. For the cases of two H_2O molecules, the equilibrium conductance varies largely and the contribution of the third eigenchannel becomes larger in some special configurations. The above behavior is analyzed via the charge transfer and the density of states (DOS). Reasonable explanations are presented.

1 Introduction

In recent years, electronic transport properties of single molecule junctions have gained tremendous interest since they may have wide variety of important applications in future electronic components such as transistors, diodes and switches [1–4]. With the advantages of experimental techniques, for example, scanning tunneling microscope and mechanically controllable break junction [5–7], measurement of current through nanoscale systems is now allowed. And a lot of interesting behaviors, such as highly nonlinear

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I-V characteristics, negative differential resistance (NDR) and electric switching behavior, are found in various systems such as organics [8], carbon nanotubes [9], DNA [10], etc. Meanwhile, considerable amounts of theoretical work have been performed to study transport properties of molecular devices [11, 12]. Among them, atomic nanowires has been an active research area for a decade in experiment and theory studies for them are the ultimate size limit of functional nanodevices. And lots of valuable and interesting results have been found from atomic wires. For example, an even-odd oscillatory conductance behavior was shown in metal [13,14], Au [15] and Pt [15] atomic wires, and also the *I-V* curves through atomic wires were strongly nonlinear. In a recent work, things were very different for the Al atomic wires [16]. For the Al atomic wires , the equilibrium conductance oscillates with a period of four atoms for wires with a typical interatomic spacing of 2.39 Å, but with another period of six atoms for the wires with the interatomic spacing of bulk fcc aluminum, 2.86 Å. A systematic study of equilibrium conductance of C and Si atomic wires was done in our recent work and some unexpected results were found [17]. Though the conductance for both of them oscillates with the number of atoms N, for the C atomic wire the conductance differences between the wires with odd number atoms and that with even number atoms becomes smaller and smaller, and saturates to a constant at last, and for the Si atomic wire, the conductance shows an even-odd oscillatory with a period of "*M*" shape.

Linear atomic chains made of carbon atoms are well known chemical species usually referred to as cumulenes. They are ideal one-dimensional molecular wires, which has long been advocated and they have been the subjects of many studies [18]. However, evidences for it are controversial and its properties are not completely known [19]. The reason may be that transport properties of a molecular devices depend not only on the characteristics of the functional molecules, but also on many other factors, for example, the contact geometry and the gate voltage. In addition, the transport properties of the system are sensitive to its surrounding environment such as the gas molecules and the H_2O molecules and in experiment this is hard to avoid. This issue has rarely been investigated theoretically, and therefore, we study the transport properties of carbon atomic wire in the environment of H_2O molecules in this paper. In particular we take the carbon wire with seven atoms sandwiched between the Al(100) electrodes as an example to find out how the transport properties change with the variation of the number and the position of the H_2O molecule on the carbon wire.

The paper is organized in the following way: the computational method and the device model are presented in Section 2. The results and discussions are given in Section 3, and a short summary is provided in Section 4.

2   Simulation model and computational method

The calculations for equilibrium conductance and Current-Voltage (*I-V*) characteristics have been performed using a recently developed first-principles package TranSIESTA-C

method, which is based on the non-equilibrium Green's function (NEGF) technique. The TranSIESTA-C, which is implemented in the well tested SIESTA method, is capable of fully self-consistently modeling the electrical properties of nanoscale devices that consist of an atomic scale system coupling with two semi-infinite electrodes as shown in Fig. 1. Such nanoscale devices are divided into three parts: left and right electrodes, and a central scattering region. In fact, the central region includes a portion of the semi-infinite electrodes. The external potential bias takes part in the self-consistent calculation directly. Therefore, the effects of the bias voltage on the electronic structure of the system can be fully considered. Details of the method and relevant references can be obtained elsewhere [20,21]. In our calculation, the convergence criterion for the Hamiltonian, charge density, and band structure energy is 10^{-4} and the atomic cores are described by normconserving persudopotentials.
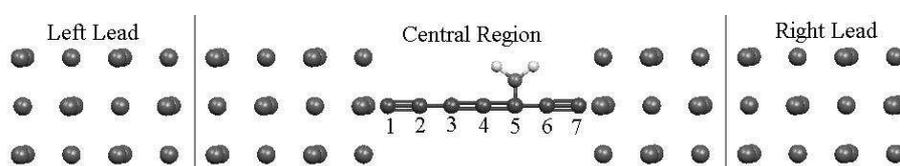
Figure 1: (color online) Model structure of an atomic wire in the environment of one H_2O molecule sandwiched between two Al(100) nanoscale electrodes with finite cross section.

The model structure for our theoretical analysis is illustrated in Fig. 1, a carbon atomic wire with seven carbon atoms in the environment of one H_2O molecule sandwiched between two Al(100) nanoscale electrodes with semi-infinite cross section. We have chosen a suppercell with a large enough vacuum layer in the x and y directions so that the device has no interaction with its mirror images. Specifically the electrode is chosen from the perfect Al crystal along the (100) direction, and the number of atoms in each atomic layer is arranged as 5, 4, 5, 4, ... Four Al atomic layers (5, 4, 5, 4) are selected for the electrode cell. The carbon atomic wire with H_2O molecules together with four surface atomic layers in the left electrode and three surface atomic layers in the right electrode is chosen as the central scattering region, as indicated by two vertical lines. The terminate atoms of the wires are positioned symmetrically above the Al(100) hollow sites. Without specializing, the contacts distance between the carbon wire and electrode is fixed at d=1.9 a.u. and 2.0 a.u. between the carbon atom and oxygen atom. The distances between carbon atoms are equal to that from Ref. [22], i.e., 2.5 a.u.. Details about it will be given in the following.

3   Results and discussion

For the convenience of description, seven carbon atoms of the wire are numbered from left to right $C_1 \sim C_7$. Fig. 3(a) shows the zero bias transmission spectra of the carbon wire in the absence of H_2O molecules. There are two significant energy regions, [-1.7, 0.7 eV]

and [1.4, 2 eV], where the incident electrons in these regions contribute most significantly to the transmission spectra. The equilibrium conductance of the system is $1.06G_0$, as can be seen from Fig. 3(a). The above results are consistent with the literature provided by Lang and Avouris [23]. When one H_2O molecule is adsorbed in turn on the position $C_2 \sim C_6$ of the carbon wire, we get an evident even-odd oscillatory conductance, as shown in Fig. 2(a). The equilibrium conductance of the carbon chain decreases to 0.76, 0.61, 0.76 G_0 respectively when the H_2O molecule is adsorbed in turn on the C_2, C_4 or C_6, while it increases to $1.73G_0$ when on the C_3 or C_5. Thus the equilibrium conductance of the carbon wire becomes bigger when the H_2O is adsorbed on the odd-numbered carbon atoms, an opposite conclusion is obtained when the H_2O on the even-numbered carbon atoms.
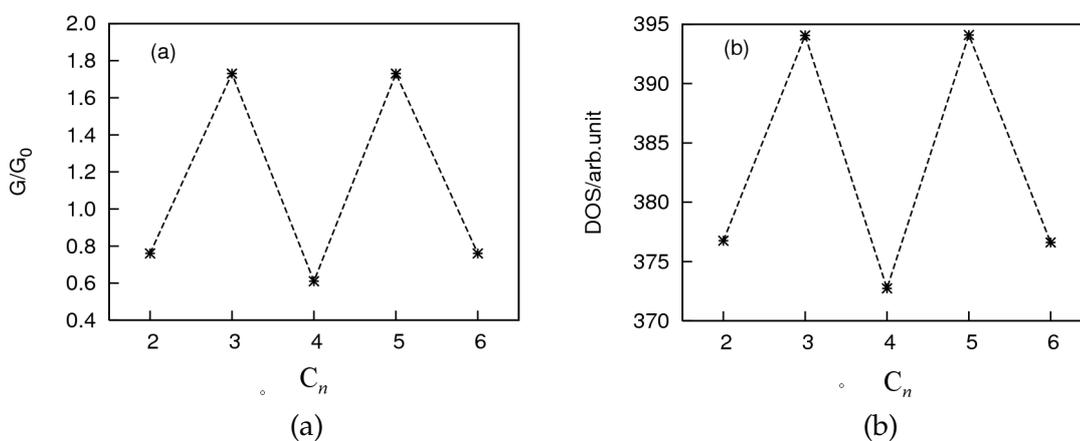
Figure 2: (a) The equilibrium conductance and (b) the DOS at the Fermi level as a function of the position, where the one H_2O molecule is adsorbed on the carbon wire.

Our first principal calculation demonstrates that the oscillatory conductance has close relation to the charge distribution of the system. The charge distributing on each carbon atom in the wire is non-equal (4e as we may believe) when the carbon wire is placed between two electrodes. But in fact, C_1 and C_7 have a higher charge number occupation, 4.567 e; followed by C_3 and C_5, taking the charge number 4.113 e. This nonequal charge distribution is caused by a part of the ionic bond characteristics between the bond of the metal electrode and the carbon chain. When a H_2O molecule is adsorbed on the C_3 or C_5, the coupling between the covalent bond of the carbon atom and oxygen atom is much stronger due to the rather higher charge occupation of C_3 or C_5, while it is weaker when a H_2O molecule is adsorbed on the C_2, C_4 or C_6 for the lower charge occupation of C_2, C_4 or C_6. The Coupling strength determines the density of states(DOS) of the system at Fermi level. The stronger the coupling, the higher the DOS; and for the same reason, the weaker the coupling, the smaller the DOS. So the DOS oscillates with the position change of the H_2O molecule on the carbon wire in turn from left to right, as shown in Fig. 2(b). The DOS at the Fermi level of the system is rather higher when H_2O molecule is adsorbed on the C_3 or C_5, while it is smaller for the H_2O molecule on the C_2, C_4 or C_6. Here, the
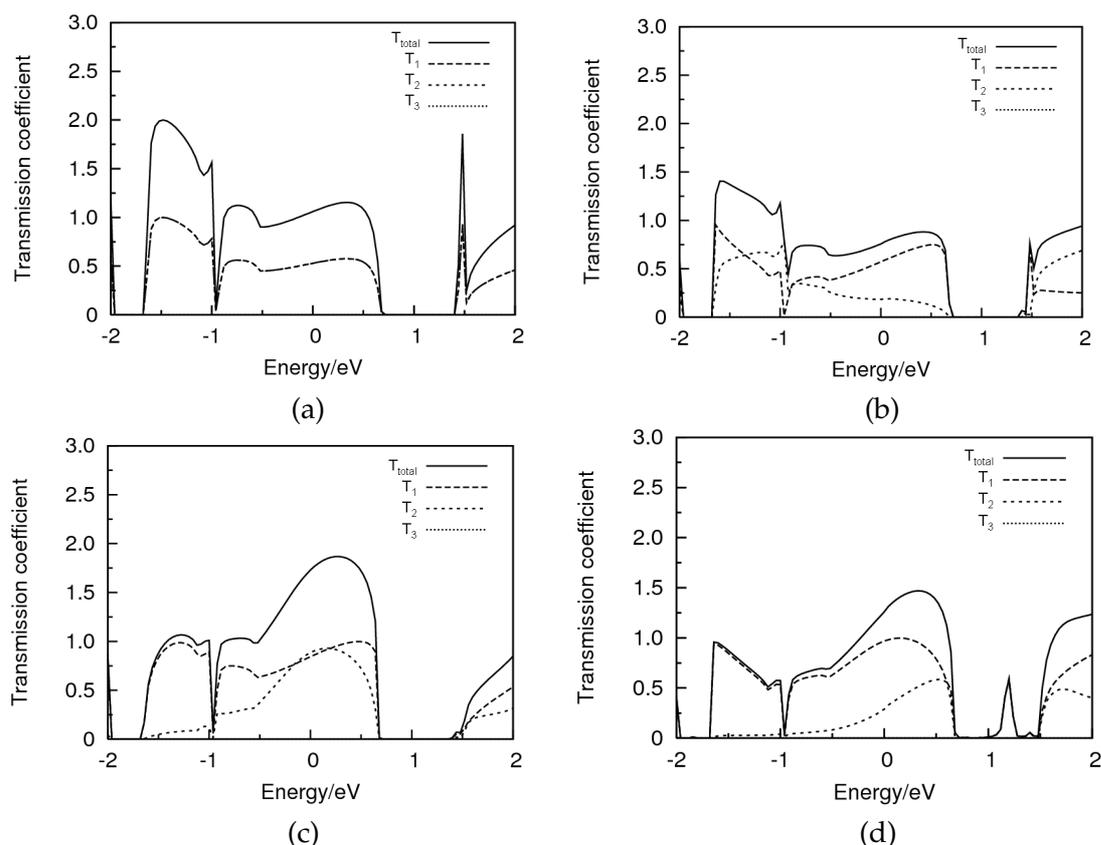
Figure 3: The transmission coefficient as a function of incident electron energy ($T(E)$) for the two-probe system: (a) the system without H_2O molecule absorbed on the carbon atomic wire; (b,c) the system with one H_2O molecule absorbed on C_2 and C_3 respectively; (d) the system with two H_2O molecules absorbed on C_2 and C_5. Here the Fermi energy $E_f = 0$ eV.

change of the density of states is consistent with the transmission coefficients.

Compared with the transmission spectrum of the carbon atomic wire without H_2O molecule (in Fig. 3(a)), the basic outline of the transmission spectrums of the wire with one H_2O molecule stays unchanged, as is shown in Figs. 3(b) and 3(c). A H_2O molecule's intervention in the carbon wire doesn't lead to the emergence of a new eigenchannel; only the eigenchannels T_1 and T_2 making contribution to the total transmission coefficient change. Then we can conclude from above that the stronger coupling between the oxygen atom and the carbon atom when the H_2O molecule is adsorbed on the C_3 or C_5 of wire increases the density of states of the system near the Fermi surface, which causes to the increase of the transmission coefficient.

Based on the above analysis of the cases with one H_2O molecule, we studied the three cases with two H_2O molecules adsorbed on C_2-C_4, C_2-C_5, and C_3-C_5 respectively, here the transmission spectrums for the cases of C_2-C_5 and C_3-C_5 are shown in Fig. 3(d) and
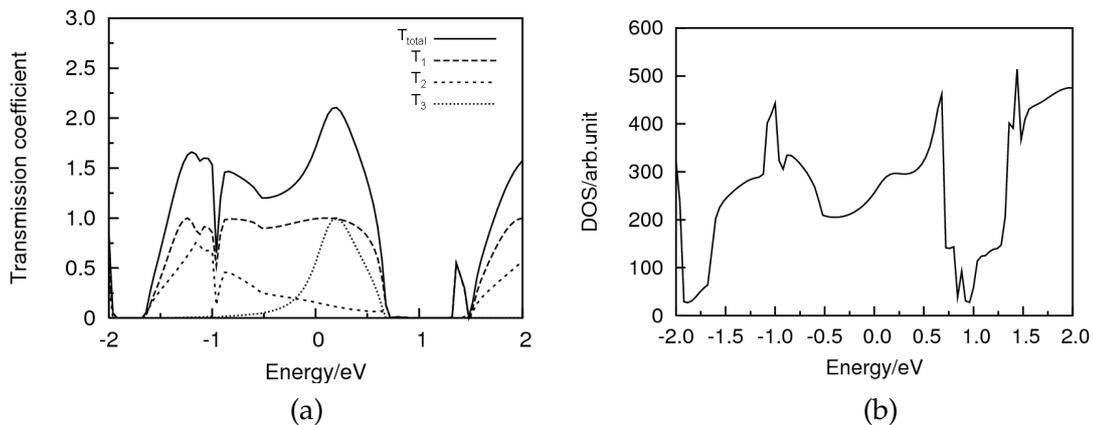
Figure 4: (a) The T(E) and (b) the DOS for two-probe system with two H_2O molecules absorbed on C_3 and C_5. The Fermi energy $E_f = 0$ eV.

Fig. 4(a). When the two H_2O molecules are adsorbed on C_2-C_4 and C_2-C_5, the equilibrium conductances of the systems are 0.77 G_0 and 1.26 G_0 respectively. There are still again two eigenchannels T_1 and T_2 contributing to the total transmission coefficient. When the two H_2O molecules are adsorbed on the special position C_3-C_5, the equilibrium conductance of the system increases up to 1.71 G_0, about equal to that of one H_2O molecule adsorbed on C_3 or C_5. But we find in the transmission spectrum that the value of the T_3 eigenchannel which is being suppressed previously now increases by a substantial amount (Fig. 4(a)).

4   Conclusion

We study the transport properties of a carbon atomic wire in the environment of H_2O molecules by the first principals. Some interesting results are gained. The equilibrium conductance shows an evident odd-even oscillatory behavior with different position of a single H_2O molecule absorbed on the carbon wire. This odd-even oscillatory behavior is induced by the nonequal charge distributing on each carbon atom in the wire when the carbon wire placed between two electrodes. For the case of two H_2O molecules, the equilibrium conductance varies largely and the contribution of the third eigenchannel which is inhabited becomes much larger in some special configuration.

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