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Effect of intermolecular distance and contact hollow-type on the transport properties of parallel atomic wires

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ABSTRACT

We use non-equilibrium Green's function combined with density functional theory to investigate the electronic transport properties of two parallel molecular wires made of carbon atomic chains (triynes) capped with thiol. The results show that the transport behaviors clearly depend on the intermolecular distance when the two wires are separated by a relatively small distance. However, with increasing the wire spacing, the transport properties are dramatically affected by the molecule–electrode contact hollow-type and insensitive to the intermolecular distance. A quantum interference mechanism is proposed to interpret the contact hollow-type dependence of transport properties at large intermolecular distance.

1. Introduction

In recent years there has been increasing interest in investigating the electronic transport properties of individual molecules and atomic wires both theoretically and experimentally [1–7]. These studies are motivated by their exotic physical properties and potential use in molecular electronic devices, such as single-electron characteristic [1], negative differential resistance [2], molecular rectification [3], and electrostatic current switching [4], etc. Although reliable and reproducible experiments [8–10] have been reported recently, serious problems still remain to be resolved, including uncertainty of the number of molecules sandwiched between two bulk electrodes and the lack of precise information of metal–molecule contact structures. Irrespective of this, future electronic applications of molecular devices will require an ensemble of many components with intermolecular distance at the nanometer scale, and quantum interference between electron waves traveling in neighboring molecules is less to neglect. Therefore, the transport properties of two parallel molecules may not be simple superposition of the transport behaviors of each isolated one. Thus, a detailed and quantitative method to accurately determine the transport behaviors from quantum mechanical principles may be a good complement to prediction and interpretation of experimental results. Past theoretical work has indeed addressed these issues [11–17]. Lang and Avouris [11] had shown that the low bias conductance for two parallel cumulenes system was intensively dependent on the wire separation. The range of intermolecular distance considered was 3.5–6.5 a.u. (1.85–3.44 Å). They attributed the large variations of the conductance to both a direct bonding between the wires and an indirect interaction through the bulk electrodes. For bimolecular wires that bridge the electrodes, indirect interaction was found by Yaliraki and Ratner [12]. They set the interwire hopping to zero, and observed an increase in conductance, in the absence of any coupling between two molecules. Liu et al. [13] found that lateral interaction of two parallel benzylmercaptanes separated by 9.4 a.u. (4.97 Å) occurred indirectly through the Au electrodes and led to an increase in conductance. Kondo and co-workers [14] calculated the transport properties of benzene dithiolate single-molecule connect to Au atomic electrodes for the hollow, bridge, and on-top contact structures. They ob-

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served that the currents were clearly dependent on the strength of the molecule–electrode interaction caused by a change of the contact structures. Nevertheless, the effect of contact geometries between molecules and electrodes interfaces of bimolecular junctions on the device behavior is still not fully understood.

One of the most important goals in the engineering of molecular devices is to diminish the size of the electronic components, since with the development of nanofabrication technology we wish to assemble as many electronic building blocks as possible in integrated circuits with a small size. The smallest size is an atomic chain. The transport properties of atomic chains have been studied quite extensively and a number of useful properties have been revealed, such as length dependent conductance oscillation [18] and conductance quantization [19]. Recently, polyyne atomic wires, formed as a linear chain of carbon atom pair $(CC)_n$ with alternating single and triple bonds, end bonded to gold leads by sulfur atoms were predicted to have a high length-independent conductance in a wide range of biases voltages [20]. In this Letter, we examine the electronic transport properties of two parallel polyynes capped with thiol for $n = 3$ (triynes) coupled to Au bulk leads. The results show that in the bimolecular devices, the transport properties depend on the intermolecular distance as well as the molecule–electrode contact hollow-type. We further propose that the quantum interference between electron waves plays an important part in the conducting behavior at comparatively large wire spacing.

2. Model and computational method

Fig. 1(a) shows a schematic illustration of molecular junction for two parallel triynes sandwiched between two Au (111) electrodes. The sulfur atoms, adopted as the alligator clips to provide chemical and geometrical stability between the wires and Au electrodes, are chosen to adsorb symmetrically on the gold surfaces at hollow sites due to the strongest molecule–electrode interaction [14,15]. The Au (111) surfaces have two kinds of hollow sites — fcc and hcp hollow [13], as denoted by A and B in Fig. 1(b5). Figs. 1(b1)–(b3) show bimolecular structures $M1$–$M3$ with contact hollow-type AA, i.e., two triynes couple to the electrodes at the site of A. Figs. 1(b4)–(b6) show $M4$–$M6$ with contact hollow-type AB, and two molecules contact the Au surface at A and B, respectively.

In the present Letter, the structures of $M1$–$M6$ have been optimized[1] and the quantum transport calculations have been carried out by an *ab initio* code package, ATK 2008.10.0, which is based on the combination of density-functional theory (DFT) with non-equilibrium Green's functions [21] (NEGF) technique, and the method has been used to simulate or explain the novel properties of the electronic devices and has reasonably reproduced experimental data [22–24]. The local density approximation is used in the self-consistent DFT electronic structure description. The core electrons are modeled with Troullier–Martins [25] no-local pseudopotentials, while valence electrons are expanded in a SIESTA localized basis set. We use a double ζ + polarization (DZP) basis set for molecules, and a single ζ + polarization (SZP) for gold atoms. In this approach, we have assumed that the electron transport through the device is so quick that there is no time for the molecules to deform.

3. Results and discussion

As shown in Fig. 2(a), the I–V characteristic curves for the two-probe systems given in Fig. 1 have been plotted in the range of 0 to 2.0 V. From the figure, as expected, we can see that the currents of $M1$–$M6$ are larger than that of $M0$ at the same bias. It indicates that the intermolecular interaction can enhance electronic transport evidently [12–17]. Particularly, the current of $M1$ is clearly larger than that of $M4$ (the difference value of their intermolecular separation is only 0.45 Å), which means the transport properties are obviously dependent on the intermolecular distance at relatively small wire spacing. With respect to the contact hollow-type AB, the smallest wire spacing is 1.67 Å. We neglect to consider this structure, since the intermolecular separation is sufficiently small, the pairing wires will be degenerated to the narrowest graphene nanoribbon showing edge effect: the edge states, firmed mainly by the nonbonding π-electrons, are almost massless with 1/300 group velocity of that of light in vacuum [26]. From the figure, interestingly, we also find that the I–V curve of $M2$ coincides with $M3$, and $M5$ coincides with $M6$.[2] However, the I–V curve of $M2$ ($M3$) is clearly different from that of $M5$ ($M6$). This reveals that

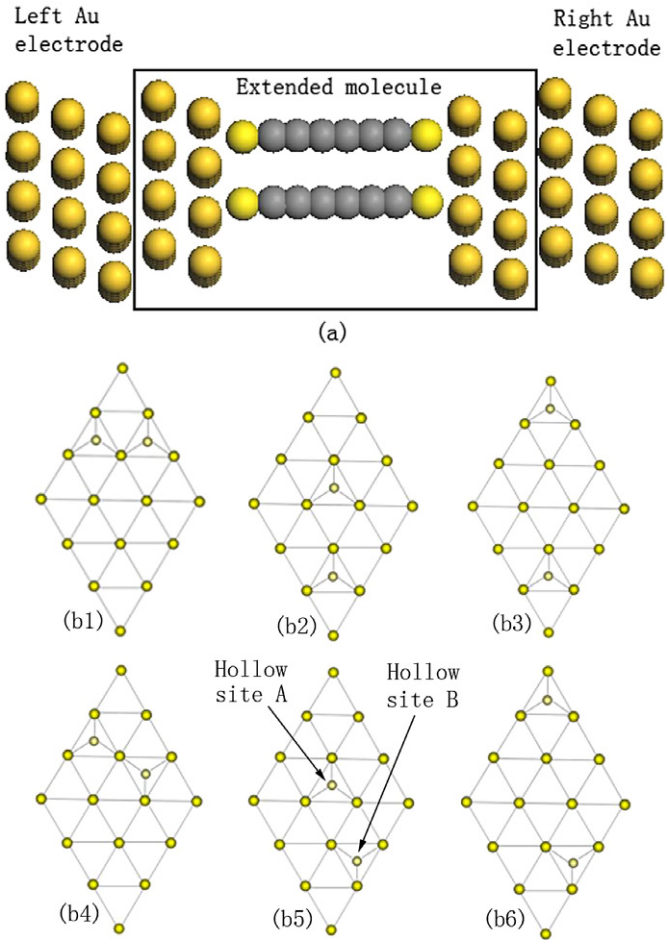

Fig. 1. (a) Schematic illustration of the molecular junction in our simulation. The gold electrodes form a (4×4) structure of the (111) surface, with 16 atoms in each layer. The extended molecular consists of two layers Au slice both in the left and right electrodes, and the two parallel triynes capped with thiol. The complete two-probe structure has the geometry, (ABC)AB-molecules-BC(ABC), which allows the molecules to connect to the same slice on both sides and ensures they are vertical to the Au leads. (b1)–(b6) correspond to molecular structures $M1$–$M6$ with different intermolecular distance 2.88, 4.99, 9.98, 3.33, 4.40, and 9.27 Å, respectively. The S atoms sit on the hollow site of the gold triangles and the Au–S distance is 1.87 Å, which is a typical Au–S distance.

[1] The geometry of the two wires in the bimolecular junction is assumed to be the sameness.

[2] Results of the other bimolecular structures separated between 4.40 and 9.98 Å with two kinds of electrode–molecule contact hollow site (not shown here) fit the curves.