Conductance of an Ensemble of Molecular Wires: A Statistical Analysis

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We report on a first principles analysis of quantum transport through molecular wires made of 4,4'bipyridine and 6-alkanedithiol contacted by Au electrodes. We investigate how charge transport is altered due to small structure changes at the molecule-electrode contacts. These changes include distance between the molecule and the contact, extra metal atoms at the Au surface, binding sites, molecular orientation, and bias voltages. By investigating hundreds of wires we extract a statistical picture on transport properties of the two different molecules. We compare quantitatively with the corresponding experimental data.

One of the most important problems in molecular electronics [1] is to understand the effects of molecule-metal contacts and learn how to control them. This, however, has proved to be exceedingly difficult to achieve experimentally [2–6]. Indeed, existing data suggested [7] that at nanoscale even a single impurity at the contact region can have a substantial influence on charge transport. It is therefore not surprising that theoretical analysis on just one or a few molecular devices, even using highly sophisticated first principles methods, can hardly capture the vast microscopic details of an experimental device and obtain quantitative comparison with experimental data. Such a problem has existed for many years and is still not resolved; for example, experimental [2] data and theoretical calculation [8] differed by several orders of magnitude on electric current flowing through a benzene molecule.

There are numerous microscopic details of a metal-molecule contact during device operation: where the molecule is bonded on the metal surface, what the metal-molecule distance at the anchoring is, the presence or absence of an impurity atom, the orientation angle of the molecule, the effect of bias, thermal fluctuations, etc. Importantly, these factors can dynamically vary during current flow, therefore a *theoretical* atomic structure of a device may differ from reality. Hence, until good atomic control of contacts can be achieved experimentally, a most meaningful theoretical approach is to examine a statistical ensemble of devices so as to cover as many microscopic details as possible, and to obtain an *average* physical picture.

The statistical approach to quantum transport has been widely applied in experimental measurements [9,10]. Cui *et al.* [9] measured over four thousand current-voltage (*I-V*) curves of octanedithiol wires contacted by Au leads. They found that all the *I-V* curves produce only five distinct families of low voltage conductance, and conductances are all roughly integer multiples of a basic value. The basic value therefore gives a good indication on the conductance of a single Au-octanedithiol-Au wire. Similarly, Xu *et al.* reported measurements of single mole-

cule conductance by repeatedly forming over one thousand break junctions in a gold scanning tunneling microscope [10]. Importantly, in such statistical analysis the uncontrollable experimental factors are washed out in the average conductance, while the fluctuation around the average provides information on whether or not the conductance is sensitive to microscopic details.

It is the purpose of this Letter to report first principles calculations of quantum transport properties for an ensemble of molecular wires whose molecule-metal contacts differ in their structural details: contact distance, binding site, impurity metal atom, orientation angle, and voltage. We imagine that these structural differences are caused by instabilities and/or fluctuations, and the device ensemble provides a statistical picture of charge transport in these wires. We focus on two kinds of prototypical molecular wires, one involves 4,4'bipyridine molecule and the other 6-alkanedithiol, contacted by gold leads. The bipyridine molecule is conductive due to the π channel along the molecule, while the alkanedithiol has much greater resistance [3,11]. We use the first principles electronic packages TRANSIESTAC [12] and MCDCAL [13] in the calculation which is based on carrying out density functional theory (DFT) atomistic analysis within the nonequilibrium Green's function framework, as documented in Refs. [13,14].

Binding sites and molecule orientation.—For a thiol group there are several likely binding sites on the Au surface [15,16], namely, the top, bridge, and hollow sites. The molecule also has some freedom to rotate around its axis. As suggested by DFT calculations [17], these degrees of freedom allow several local energy minimum in the configurational space. As shown in the inset of Fig. 1(c), the top four atoms on the Au(100) surface are meshed with a 3×3 grid, corresponding to the hollow, bridge, and top sites. To simulate the large number of configurational degrees of freedom, we allow each end of a molecule to bind to one of these likely sites, then further generate configurations by rotating the molecule along its axis at integer multiples of $\pi/8$. This way, there are

$9 \times 9 \times 16 = 1296$ atomic configurations for the wire. We further assume that the statistical weight of each configuration is equal: this is a plausible assumption if the different configurations are due to random fluctuations. We take this as a practical way for computing the average conductance of the ensemble.

Figure 1 plots histograms based on the samples of the two molecular wires [18]. Figures 1(a) and 1(c) are histograms of transmission coefficient $T(E)$ at the Fermi energy of the leads (shifted to $E = 0$). Although the ensemble size is not very large, several useful observations can be noted by comparing these figures. (i) The T values of bipyridine wires spread from 0 to 0.9 with the maximum about 0.4. On the other hand, the T values of alkanedithiol wires distribute much more narrowly, from 0.001 to 0.005 with the maximum about 0.002. The distribution for bipyridine wires is clearly more spread out than that for alkanedithiol wires. This means that the conductance of bipyridine is more sensitive than that of alkanedithiol to the molecule configuration. This can be interpreted using the insets in Figs. 1(a) and 1(c): For alkanedithiol wires, the transmission is largely mediated by the tails of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) states. Since these states are mainly localized on the thiol end groups, the conductance is less sensitive to the rotation along the molecule axis. For bipyridine wires, in contrast, the transmission is largely mediated by π states which are extended through the molecule. Therefore, both the orientation and the binding sites have significant effects on the conductance. (ii) The distributions give an *average* equilibrium conductance of $0.39G_0$

and $0.0025G_0$ for bipyridine and alkanedithiol wires, respectively. Namely, they differ by more than 2 orders of magnitude from each other.

To analyze these results further, we define a quantity called "conductibility," which accounts for the total transmission probability in a given energy range:

$$S(E_1, E_2) \equiv \int_{E_1}^{E_2} T(E)dE. \qquad (1)$$

This quantity should be comparable to the charge current:

$$I = \frac{2e}{h} \int T(E, V_b)[f_L(E) - f_R(E + eV_b)]dE, \qquad (2)$$

where f_L and f_R are Fermi functions of the left and right leads. The conductibility $S(E, E')$ therefore provides a measure for the behavior of current at small voltage. Figures 1(b)1, 1(b)2, 1(b)3, and 1(b)4 and 1(d)1, 1(d)2, 1(d)3, and 1(d)4 show conductibility histograms in different energy ranges. As the energy range is made wider and wider, it is interesting to observe that these histograms for the two molecules evolve in different ways. For the bipyridine wires, all the histograms are rather widely spread, and the S values in 1(b)1 are on average smaller than those of 1(b)2, 1(b)3, and 1(b)4. This suggests that the average current does not change drastically above a certain voltage although the current through a single bipyridine wire may vary strongly from one configuration to another. For the alkanedithiol wires, the shape of $S(E, E')$ histograms changes from rather narrow to widespread as the energy range is increased, and the peak height of $S(E, E')$ decreases. This indicates that the currents in alkanedithiol
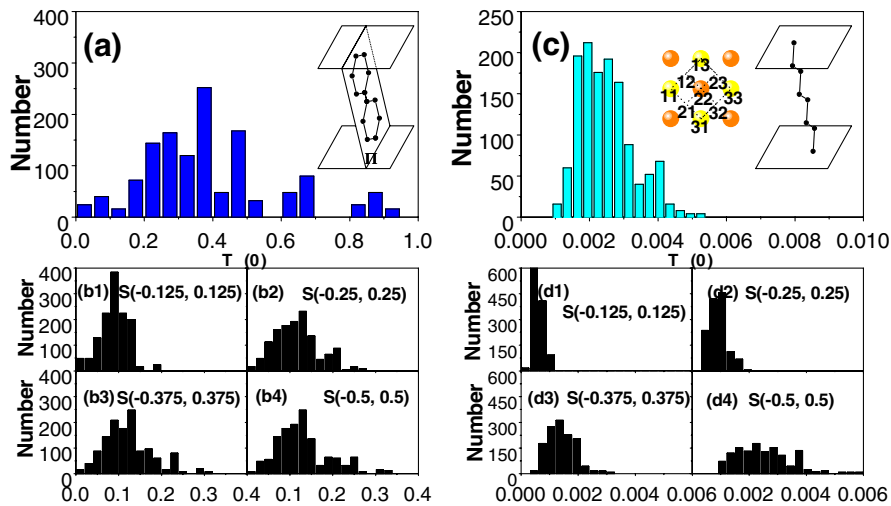

FIG. 1 (color online). Statistic analysis of transport properties for molecular wires with different binding sites and orientations. The distance between the two Au lead surfaces is fixed at 11.38 Å for bipyridine wires and 12.38 Å for alkanedithiol wires. Each N atom in bipyridine and each S atom in alkanedithiol can bind to one of the nine sites marked in the middle inset of (c). (a) Histogram of transmission coefficient at Fermi energy, $T(0)$, for the ensemble of bipyridine wires. Inset: schematic showing an approximate geometry of the bipyridine wires. (b1)–(b4) histograms of the quantity $S(E_1, E_2)$ in different energy ranges for the bipyridine wires. (c) Histogram of $T(0)$ for the ensemble of alkanedithiol wires. Middle inset: the numbers indicate binding sites in the ensemble. Right inset: schematic showing an approximate geometry of the alkanedithiol wires. (d1)–(d4) Histograms of $S(E_1, E_2)$ for the ensemble of alkanedithiol wire.

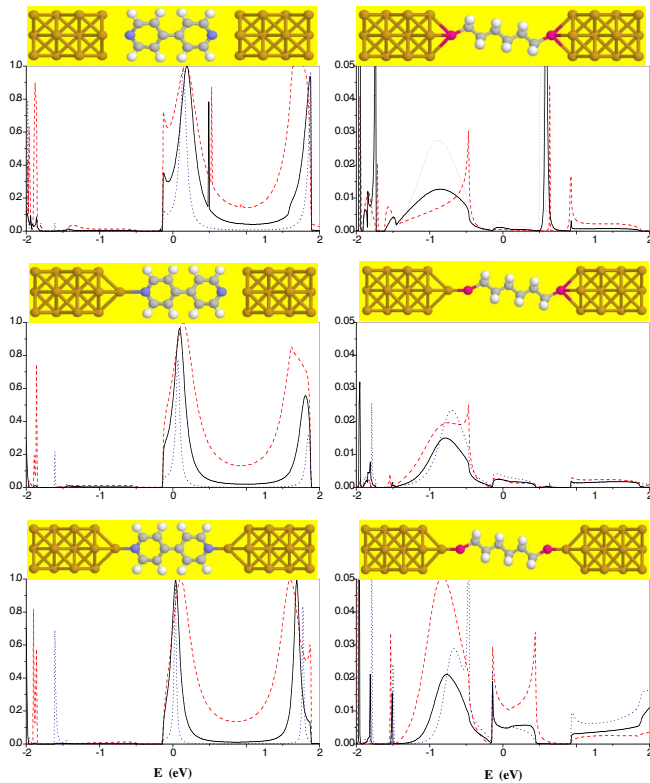FIG. 2 (color online). Transmission coefficients $T = T(E)$ at zero bias versus electron energy for 4,4'bipyridine and 6-alkanedithiol wires with small differences in the contact region. Top row: wires without extra Au atoms extruding from contacts; middle row: with one extruding Au atom; bottom row: with one extruding atom at each surface. Different lines correspond to different contact distances d measured from the nitrogen atom in the bipyridine or S from the alkanedithiol to the Au surface or the extruding atom (same d to both leads). Dashed line (red): $d = 1.5$ Å; solid line (black): $d = 2.0$ Å; dotted line (blue): $d = 2.5$ Å. Fermi energy of the leads is shifted to $E = 0$.

wires are close to each other at small voltage but they diversify gradually with the increase of voltage, and the average current increases monotonously with the bias voltage.

Lead-molecule distance and surface structure.—Since the contact may not be a perfect crystal surface and the molecule may not bond perfectly at the equilibrium bond length, we investigate three combinations of lead surfaces: (a) two Au(100) surfaces without impurity; (b) one additional Au atom sitting on one of the surfaces; (c) one additional Au atom sitting on each surface (Fig. 2). We start by determining the equilibrium bond distance between the molecule and the lead surface or the extruding surface atom, using *ab initio* total energy relaxation. Afterward, different molecule-surface distances are simulated by simply changing the distance around the equilibrium value.

Each panel in Fig. 2 plots typical transmission coefficients versus electron energy for 4,4'bipyridine or 6-alkanedithiol wires at several different molecule-surface

distances. Several observations are in order. (1) In the plotted energy range, there are two large transport resonances for the bipyridine wire. By examining the scattering states, these transport features are found to come from the lone-pair state and the π state in the ring structures of the molecule. In contrast, there are only tiny features for the alkanedithiol wire whose transmission is very small (note the scale in the figure). (2) Increasing the molecule-surface distance (dashed to solid to dotted lines), transmission features for bipyridine wires becomes sharper because transport is through resonance states whose linewidth becomes narrower when the overlap between these states and states in the leads is reduced. For the alkanedithiol wire, changing the distance causes transmission to change in a complicated manner. This is related to the fact that transport in alkane is nonresonant where the *tail* of the HOMO state dictates conduction [11]. Changing the distance can vary how the Fermi level of the leads is aligned within the HOMO-LUMO gap of the alkane, thereby possibly increasing or decreasing transmission in a complicated fashion. (3) Transmission in bipyridine wire is less sensitive to extruding atoms on the lead surface as compared to that of alkanedithiol wires (compare the three rows of Fig. 2). This is expected because the wave function of bipyridine is more extended in space; hence its transmission is affected by a relatively larger area of electrode surface. For alkanedithiol, the wave functions are more local and directional; hence transmission depends more sensitively on the atomic arrangement at the binding sites.
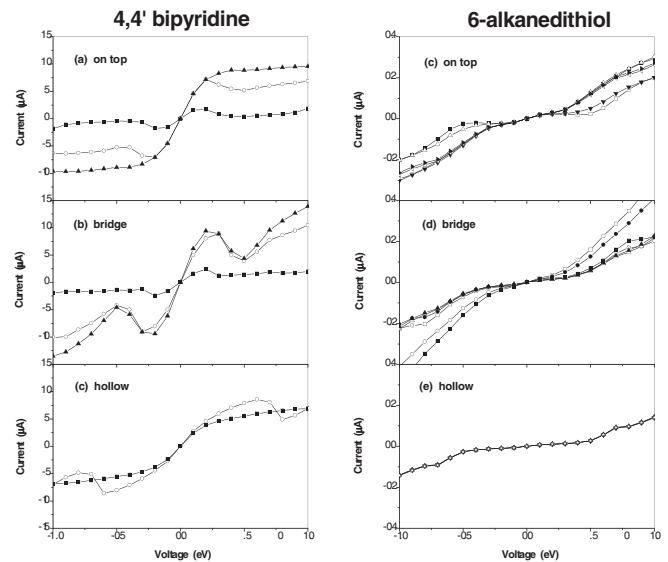

FIG. 3. Current-voltage characteristics for Au-4,4'bipyridine-Au wires (left panel) and Au-alkanedithiol-Au wires (right panel) on different binding sites. The molecule is set perpendicular to the electrode surface, and rotated for multiples of $\frac{\pi}{4}$ along its axis. Different symbols correspond to rotations along the molecular axis for every $\frac{\pi}{4}$ (equivalent configurations are not included).

The bias voltage.—To obtain insight to the contact effect on current-voltage (*I-V*) characteristics, we investigate wires with contacts at the top, bridge, and hollow sites when the molecule is allowed to rotate along its axis for multiples of $\frac{\pi}{4}$. Figure 3 plots the *I-V* curves of the two molecular wires at these situations. Each curve corresponds to a different rotational angle. For bipyridine wires, the *I-V* curves increase monotonously when $V_b < 0.1$ V. Some *I-V* curves develop negative differential resistance when $V_b \approx 0.25$ V, and the reason can be traced to the quasi-1D nature of the Au electrodes [19]. One can also observe that *I-V* curves with top and bridge binding sites are more sensitive than that of the hollow site to rotation of the molecule. For alkanedithiol wires, the *I-V* curves increase linearly at a small voltage (less than 0.1 V) and develop nonlinear characteristics about 0.25 V. The current through alkanedithiol wires is also much smaller than that through the bipyridine, consistent with the transmission function of Fig. 1. The top and bridge sites give more sensitivity on alkanedithiol rotation than the hollow site, and the average current over rotation is greater for top and bridge sites than that for the hollow site.

Comparison to experimental data.—The average conductance for the ensemble of alkanedithiol wires studied here is $0.0025G_0$. This is to be compared with the reported experimental value [10] of $0.0012G_0$. Considering the relatively small ensemble size, the fact that only the simplest geometries are sampled, as well as many other unknowns in the experimental break junctions [10], this level of quantitative comparison between *ab initio* calculations and experimental data is, indeed, satisfactory.

On the other hand, the average conductance for the ensemble of 4,4'-bipyridine wires is found to be $0.39G_0$, this is about 40 times larger than the experimentally reported value of $0.01G_0$ [20]. As we have shown, the bipyridine wires have sensitive dependence on contact details as the transmission coefficients spread widely [Fig. 1(a)], due to π channels in the molecule which give good transparency to charge flow. Naively, if such a molecule is well connected to the leads, its π channel could contribute a quanta G_0 to the total conductance. In other words, the current should be of the order of 1 μA at 0.1 V, which is what we found for many wire configurations in the ensemble (Fig. 3). Nevertheless, there are other configurations in the ensemble which do give much smaller conductance [see Fig. 1(a)] that would compare much better to the experimental value, although their statistical weight is not large enough to tip the balance [21]. These results show that computing a single configuration may not give a satisfactory comparison with experiments, and the average over an ensemble may provide a better prediction.

In summary, by analyzing an ensemble of samples, we have obtained a statistical picture on charge transport through molecular wires that differ by structural details. It is found that contact effects on 4,4'-bipyridine wires are dramatically different from that on alkanedithiol, and all

the differences can be attributed to a different conducting mechanism: the conduction of bipyridine is through resonant states (the π channel) while that for alkanedithiol is through nonresonant tunneling. The ensemble average conductance is consistent with the experimental data for the alkanedithiol wires, but is 40 times larger for the bipyridine wires.

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