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Design of nanoswitch based on C_{20}-bowl molecules: A first principles study

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ABSTRACT

We demonstrate theoretically by density functional non-equilibrium Green's function method that a much simplest two-terminal wire can exhibit switching, and we present a realistic theory of its behavior. We consider a C_{20}-bowl molecular wire sandwiched between an Au (1 0 0) substrate and a monatomic Au scanning tunneling microscope (STM) tip. Lateral motion of the tip over the pentagon ring causes it to change from one conformation class to the other and to switch between a strongly and a weakly conducting state. Thus, surprisingly, despite their apparent simplicity, these Au/C_{20}/Au nanowires are shown to be a convenient switch, the simplest two-terminal molecular switches to date. Experiments with a conventional STM are proposed to test these predictions.

1. Introduction

The next generation of electronic devices will undoubtedly be constructed of molecules, or have features of molecular size. The results of recent experimental [1–3] and theoretical studies [4–11] predict a brilliant future for molecular electronics. Among various efforts and activities, several schemes have been proposed to design and construct molecular switches [3,8–11]. The basic idea is to find molecules that have two or more distinct states with vastly different conductance. Switching between *on* and *off* states can be performed by applying an external bias or by using a scanning tunneling microscope (STM) tip to manipulate the system [3,8–11].

The transport properties of carbon-based nanostructures have attracted much attention because of possible applications for nanodevices [12–15]. Several theoretical [13,16–18] and experimental [19–22] studies have elucidated various aspects of electron transport through metal/C-based nanostructures/metal junctions [12–22]. However, the possibility that wires of this type such as C_{20} molecule may be capable of switching is far from obvious a priori and has not been investigated until now.

Thus, as well as identifying the simplest two-terminal molecular switch to date and shedding new light on the mechanisms of molecular switching, the present work reveals an unexpected new dimension of the physics of Au/C_{20}/Au molecular wires.

The molecular switch that we describe should be amenable to experimental study with presently available techniques. Thus, our findings also raise the prospect of bridging the gap that has persisted in this field between theory and experiment, since molecular switching was first observed.

2. Computational details

The calculations have been performed using a recently developed first-principles package SMEAGOL [23,24], which is based on the combination of DFT (as implemented in the well-tested SIESTA method [25]) with the NEGF technique [26,27]. SMEAGOL is capable of fully self-consistently modeling the electrical properties of nano-scale devices that consist of an atomic scale system coupling with two semi-infinite electrodes. Such nano-scale devices are referred to as two-probe systems and they are divided into three parts for theoretical calculations: left and right electrodes, and a central scattering region. The scattering region actually includes a portion of the semi-infinite

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electrodes. The simulation procedure of such two-probe systems can be described briefly as follows.

Firstly, the electronic structure of two electrodes is calculated only once by SMEAGOL to get a self-consistent potential. This potential will be shifted rigidly relative to each other by the external potential bias and provides natural real space boundary conditions for the Kohn–Sham (K–S) effective potential of the central scattering region. Then from the Green's function of the central scattering region, we can obtain the density matrix and thereby the electron density. Once the electron density is known, the DFT Hamiltonian matrix, which is used to evaluate the Green's function, can be computed using the above boundary conditions by means of standard methods:

$$\hat{G} = \lim_{\delta \to 0}[(E + \mathrm{i}\delta)\hat{S} - \hat{H}_{S[\rho]} - \hat{\Sigma}_{\mathrm{L}} - \hat{\Sigma}_{\mathrm{R}}]^{-1} \tag{1}$$

where $\hat{H}_{s[\rho]}$ is DFT Hamiltonian and $\hat{\Sigma}_{\mathrm{L}}$ and $\hat{\Sigma}_{\mathrm{R}}$ are the self-energies, respectively, for the left and right lead. This procedure is iterated until self-consistency is achieved. Moreover, the current through the atomic scale system can be calculated from the corresponding Green's function and self-energies using Landauer–Buttiker formula [28]

$$I(V) = \frac{2e}{h}\int_{-\infty}^{+\infty} \mathrm{d}E[f_{\mathrm{l}}(E - \mu_{\mathrm{l}}) - f_{\mathrm{r}}(E - \mu_{\mathrm{r}})]T(E, V) \tag{2}$$

where μ_{l} and μ_{r} are the electrochemical potentials of the left and right electrodes, respectively, i.e.,

$$\mu_{\mathrm{L}} - \mu_{\mathrm{R}} = eV_{\mathrm{b}} \tag{3}$$

and f_{r}, f_{l} are the corresponding electron distributions of the two electrodes. $T(E, V)$ is the transmission coefficient at energy E and bias voltage V, which is given by

$$T(E, V) = \mathrm{Tr}[\mathrm{Im}\Sigma_{\mathrm{l}}(E)G^{\mathrm{R}}(E)\mathrm{Im}\Sigma_{\mathrm{r}}(E)G^{\mathrm{A}}(E)] \tag{4}$$

where $G^{\mathrm{R}}(E)$ and $G^{\mathrm{A}}(E)$ are the retarded and the advanced Green's function of the central region. Based on the eigenchannel decomposition of the conductance, this total transmission $T(E)$ can be decomposed into nonmixing eigenchannels $T_n(E)$ [29] as

$$T(E) = \sum_n T_n(E) \tag{5}$$

In our DFT calculation, the local-density approximation (LDA) to the exchange-correlation potential [30] is used. Only valence electrons are considered in the calculation, and the wave functions are expanded by localized numerical (pseudo)atom orbitals (PAOs) [31]. The atomic cores are described by norm-conserving pseudo potentials [32].

The structural model for our theoretical analysis is illustrated in Fig. 1. In this two-probe system, C_{20} couples with two atomic scale Au (1 0 0) electrodes, which extend to reservoirs at $\pm\infty$, where the current is collected. Three Au atomic layers have been chosen for the electrode cell in the *z*-direction. In the central scattering region, the C_{20} couples with three atomic layers to the bottom side and with the STM tip, which was represented by a tetrahedron of Au atoms, to the *top* side. These atomic layers in the central scattering region are large enough [33], so that the perturbation effect from the scattering region is screened and they are denoted as surface-atomic layers.

In order to investigate the switching behavior of the C_{20} molecular wire, we consider two conformations for the C_{20}-wire attached to the Au electrodes. In the first conformation, the STM tip was placed above the carbon atom of the pentagon ring of the C_{20} (Fig. 1(a)); this is referred as a *top* conformation. In the second conformation, on the other hand, the Au tip atom is over the *hollow* site of the pentagon plane of the C_{20}, as depicted in Fig. 1(b); this is referred as a *hollow* conformation.

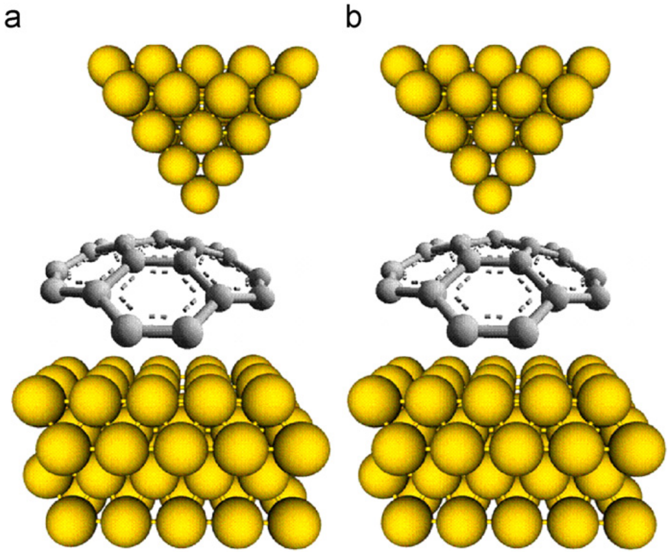

Fig. 1. A schematic of a C_{20}-bowl molecular wire sandwiched between the two Au (1 0 0) electrodes according to the STM technique. (a) The *top* conformation and (b) *hollow* conformation.

3. Results and discussion

In recent years, much progress has been made in developing theories of electron transport through molecules [34–44]. An important conclusion has been that the current at low bias is carried by molecular orbitals. The overlap between the orbitals and the states of the contacts is sensitive to the orientation of the molecule relative to the contacts, which implies a strong orientation-dependence of the molecular wire's conductance [11,40]. Such overlap effects have been found in semi-empirical [36,41] and density functional [11,38] transport calculations.

Thus, it is reasonable to expect them to result in a significant change in conductance when an Au/C_{20}/Au wire switches between a *top* and a *hollow* conformation, and our calculations show this to be the case. Since density functional non-equilibrium Green's function calculations have been successful in explaining the experimental current–voltage (*I–V*) characteristics of a variety of molecular wires consisting of organic molecules bonded to gold electrodes [13,41,42,44] we adopted this approach here. In Fig. 2, we show the calculated current of the C_{20} in its ground state conformation for two positions of the STM tip along a linear trajectory over the C_{20} that passes through the locations that the tip occupies in Fig. 1.

When the tip is furthest from the center of the C_{20} ring where the C_{20} bonds to the Au tip atom, the C_{20} in its ground state is in the *top* conformation and has low current intensity at a source-drain bias around 3.0 V. When the tip moves towards the center, the C_{20}'s ground state switches to the *hollow* conformation, which is seen to be much high conducting in the same range of bias. Thus, whenever the C_{20} is made to flip from a *hollow* conformation to a *top* conformation, by displacing the STM tip, the molecule is predicted to switch from a highly conducting to a weakly conducting state, and vice versa.

This large difference in conductance between the *top* and *hollow* conformations can be understood within Landauer theory [28] by considering the transmission probabilities, *T*, for electrons to scatter through the molecular wire, taking account of orientational effects [40].

Fig. 3 shows the zero bias transmission spectra of the two considered conformations. It has a peak of weaker strength below