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Ab initio investigation of the I–V characteristics of the butadiene nano-molecular wires: A light-driven molecular switch

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Abstract

We apply a first-principles computational approach to study a light-sensitive molecular switch. The molecule that comprises the switch can convert between a *trans* and a *cis* configuration upon photoexcitation. We find that the conductance of the two isomers varies dramatically, which suggests that this system has potential application as a molecular device. A detailed analysis of the projection of the density of states (PDOS) and the transmission coefficients $T(E)$ of the system reveals the mechanism of the switch.

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1. Introduction

Electronic devices that switch between high and low resistance states are at the heart of the modern information technology. As miniaturization of this technology continues to progress the long-standing fundamental problem of identifying and understanding the smallest physical systems that are capable of switching behavior is attracting growing interest [1–5]. The results of recent experimental [6] and theoretical studies [5,7] predict a brilliant future for molecular electronics. Among various efforts and activities, several schemes have been proposed to design and construct molecular switches [6,7].

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 tip to manipulate the system [6–8].

However, these methods are not ideal since they impose severe limitations in device applications. Alternative methods, such as those based on fast, light-driven processes, are therefore highly desirable. The photosensitive butadiene molecule discussed in this Letter is one such candidate for an optoelectronic device. In the ground electronic state, the butadiene has two conformations, *trans* and *cis*. The molecule can switch reversibly from one structure to another under photoexcitation, with the structural change occurring on an electronically excited state.

In this Letter, we investigate the electron transport through the molecular wire, Au-S-butadiene-S-Au, which consists of a single butadiene molecule, *cis*/*trans* isomers, which has been functionalized by replacing a hydrogen ended atom with an S group to provide a good contact with gold (111), and two semi-infinite gold leads.

To contribute to the knowledge about the mechanism of switching behaviour in single molecular devices, in the current research we present a detailed first-principles analysis of the I–V characteristics of the butadiene sandwiched between two Au (111) electrodes. Our results suggest that switching behav-

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iour is mainly attributed to the changes of the coupling between the molecular orbitals in the butadiene and the incident states of the electrodes under external bias.

We will use density functional non-equilibrium Green's function, DFT-NEGF, method via the newly developed method, SMEAGOL [9,10], to calculate the $(I–V)$ characteristics of butadiene coupled to two Au (111) surfaces via thiol bonds. With this method, it is possible to make a full self-consistent description of a nanostructure coupled to two electrodes with different electro-chemical potentials. A virtue of the method is that it employs the same level of approximation for the electrodes and the nanostructure.

The organization of the Letter is as follows. We start with a brief description of the density functional based non-equilibrium Green's function method (Section 2), and in Section 3 we report our main results for the transmission functions of the different structures and discuss their implications, together with an analysis of the molecular levels important for electron transmission. In Section 4, the results are summarized.

2. Computational details

The calculations have been performed using a recently developed first-principles package SMEAGOL [9,10], which is based on the combination of DFT (as implemented in the well-tested SIESTA method [11]) with the NEGF technique [12,13]. 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 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, it 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.

$$\hat{G} = \lim_{\delta \to 0} \left[(E + i\delta)\hat{S} - \hat{H}_{S[\rho]} - \hat{\Sigma}_L - \hat{\Sigma}_R \right]^{-1} \tag{1}$$

where $\hat{H}_{S[\rho]}$ is DFT Hamiltonian and $\hat{\Sigma}_L$ and $\hat{\Sigma}_R$ 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 [14]

$$I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} dE \left[f_l(E - \mu_l) - f_r(E - \mu_r) \right] T(E, V) \tag{2}$$

where μ_l and μ_r are the electrochemical potentials of the left and right electrodes respectively, i.e.,

$$\mu_L - \mu_R = eV_b \tag{3}$$

and f_r, f_l are the corresponding electron distribution of the two electrodes. $T(E, V)$ is the transmission coefficient at energy E and bias voltage V, which is given by

$$T(E, V) = \mathrm{Tr}\left[\mathrm{Im}\, \Sigma_l(E) G^R(E)\, \mathrm{Im}\, \Sigma_r(E) G^A(E) \right] \tag{4}$$

where $G^R(E)$ and $G^A(E)$ are the retarded and 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 $T_n(E)$ [15] as

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

In our DFT calculation, the local-density approximation (LDA) to the exchange-correlation potential [16] is used. Only valence electrons are considered in the calculation, and the wave functions are expanded by localized numerical (pseudo)atom orbitals (PAOs) [17]. The atomic cores are described by norm-conserving pseudo potentials [18]. We use a DZP basis set for the organic molecule and a SZP basis set for the gold atoms in the transport calculations. The k-grid sampling of $2 \times 2 \times 30$ for the gold electrodes and a $2 \times 2 \times 1$ k-grid sampling for the two probe system, together with the meshcutoff of 200 Ry for both of them, was implemented.

The structural model for our theoretical analysis is illustrated in Fig. 1. In this two-probe system, butadiene molecule couples with two atomic scale Au (111) 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 butadiene molecule couples with three atomic layers to both the left and right electrodes. These atomic layers in the central scattering region are large enough [19] so that the perturbation effect from the scattering region is screened and they are denoted as surface-atomic layers.

As we know, the distance between the molecule and electrodes is an important parameter, but it is difficult to precisely measure and control in the present experiments related to the molecular conductance, for example, the separation between the tip and the surface in STM experiments [20] and the molecule-metal separation in the mechanically controllable break-junction (MCB) experiments, etc.

Since there is no direct experimental information regarding the geometry of the butadiene molecule and its attachment to the leads, thus the structural optimizations were performed for scattering region using the conjugate gradient (CG) algorithm until the maximum residual forces were smaller than 0.04 (eV/Å).