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Quantum transport of the single metallocene molecule

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HIGHLIGHTS

- The metallocene molecules structure become stretched along the transport direction.
- The nickelocene molecule have a larger conductance.
- Negative differential resistance is found in the ferrocene, cobaltocene molecules.

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ABSTRACT

The Quantum transport of three single metallocene molecule is investigated by performing theoretical calculations using the non-equilibrium Green's function method combined with density functional theory. We find that the three metallocene molecules structure become stretched along the transport direction, the distance between two C_p rings longer than the other theory and experiment results. The larger conductance is found in nickelocene molecule, the main transmission channel is the electron coupling between molecule and the electrodes is through the Ni d_{xz} and d_{yz} orbitals and the s , d_{xz} , d_{yz} of gold. This is also confirmed by the highest occupied molecular orbital resonance at Fermi level. In addition, negative differential resistance effect is found in the ferrocene, cobaltocene molecules, this is also closely related with the evolution of the transmission spectrum under applied bias.

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1. Introduction

The possibility of trapping single molecules in between metal electrodes have been envisioned both experimentally and theoretically since the early seventies [1–3]. Then the practical realization of such a concept became possible by establishing stable and reproducible contacts between the molecules and the metallic electrodes. Very recently, a single-molecule diode is the first to developed that may have the real-world technological applications for nanoscale devices [4].

Single metallocene molecules, which have a unique sandwich structure, are considered to be promising candidates in the field of molecular electronic devices, because they can stay stable even after repeated oxidation/reduction steps [5]. Experiment show that metallocene molecule has been shown to be suitable for deposition on the metallic surface without giving rise to dissociation [6]. It also provides an ideal system to investigate the adsorption and the nature of the interaction between metallocene molecules and metallic surface. Exploiting the interesting properties of

organic molecules a wide range of applications have been devised, among which one can mention molecular rotors, spin filters, giant magnetoresistance and current rectifiers, et al. [7–18]. For example, many ferrocene-based molecular devices have been studied, including terahertz oscillator [7], molecular wires [12], transistors [13,14], rectifiers [15,16], and negatively differential resistance devices [17,18].

Recent theoretical studies have developed a first-principles, nonequilibrium Green's function (NEGF) using density functional theory (DFT), and have been extremely useful as the electron transfer process can be correlated directly to the details of the interaction between the molecules and the metals. We report here a study on the electron transport in the three small molecules (ferrocene, cobaltocene, and nickelocene) attached to the Au electrodes, with a particular focus on the effect of the electron transfer process. The molecules are composed of two C_p rings and one transition metal atom, either iron, cobalt, or nickel, respectively. In the gas phase the ground-state is found to be the eclipsed configuration (D_{5h}). In addition, the current vs. voltage behavior of the metallocene molecules were also investigated using a bias between the left and right electrodes.

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2. Model and method

The molecular device is depicted in Fig. 1 in the eclipsed configuration. In this setup, one C_p ring of the small molecules (ferrocene, cobaltocene, and nickelocene) connected to the gold electrodes, respectively. In order to understand the structure, the electronic and the transport properties of small molecules (ferrocene, cobaltocene, and nickelocene), we have performed a complete series of first-principles simulations for metallocene sandwiched between semi-infinite gold electrodes with (100) orientation.

The electronic structure and the transport properties have been calculated with the *ab initio* transport code SMEAGOL [19,20]. SMEAGOL is a fully self-consistent method that combines the non-equilibrium Green's function (NEGF) [21,22] formalism with density functional theory (DFT) [23]. The method uses the single-particle Kohn–Sham Hamiltonian provided by the DFT code SIESTA [24] and calculates the zero-bias electron transmission coefficients and the I - V curves of a two-terminal device. And SMEAGOL is capable of fully self-consistent calculations of the electrical properties of devices formed by an atomic-scale object attached to two semi-infinite current/voltage electrodes, i.e. it calculates the scattering potential at finite bias. All of these properties are calculated in ground-state (GS). Recently liu et al. [25] developed a density functional theory for the steady-state (SS) properties of molecular junctions under a finite bias. Maybe the SS-DFT yields energetically more stable nonequilibrium steady state.

Our DFT calculations use the Perdew–Zunger form [26] of the local-density approximation (LDA) to the exchange–correlation functional and a double-zeta plus polarization basis set for both Fe (Co and Ni) and Au. Scalar-relativistic Troullier–Martins pseudo-potentials [27] in nonlocal form are generated from the $5d^{10}6s^1$ reference configuration for Au, the $3d^64s^2$ configuration for Fe, the $3d^74s^2$ configuration for Co, the $3d^84s^2$ configuration for Ni. Periodic boundary conditions are applied in the basal plane (orthogonal to the transport direction) with four irreducible k -points in the two-dimensional Brillouin zone. A k -grid sampling of $2 \times 2 \times 100$ for the gold electrodes is employed, together with a mesh cut-off of 200 Ry. The same mesh cut-off is used also in the self-consistent transport calculations. We consider 128 real and 50 complex energy points when integrating the Green function.

3. Results and discussion

In order to calculate the most stable structures for the metallocene configuration, we perform geometry relaxation by keeping fixed the bulk Au leads and relaxing the apexes of the point contact [28]. The structural data are summarized in Table 1. Following relaxations, the apexes structure becomes contracted along the transport directions, i.e. the distance becomes $d_L = 1.65 \text{ \AA}$ (between the two layers on the left) and $d_R = 1.64 \text{ \AA}$ (between the two layers on the right), which is all smaller than half of the bulk lattice constant 2.04 \AA . Due to the under-coordinated atoms of the atomic sized nanoscale devices, local strain is induced and the bonds become shorter and stronger. And the metallocene molecule

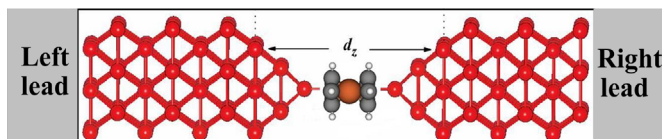


Fig. 1. The configuration connecting (100) oriented fcc Au leads and metallocene molecule: the C atoms is the minimum, the Fe, Co, Ni atom in the middle and the rest is H atom.

Table 1

Optimized structural parameters of ferrocene, cobaltocene and nickelocene molecule.

		Cp–Cp (Å)	C–C (Å)	C–H (Å)
FeCp ₂	SIESTA	4.734	1.447	1.099
	SIESTA ^a	3.335	1.450	1.096
	Exp. ^b	3.322	1.440	1.140
CoCp ₂	SIESTA	4.776	1.444	1.097
NiCp ₂	SIESTA	4.912	1.442	1.099

^a Reference [30].

^b Reference [31].

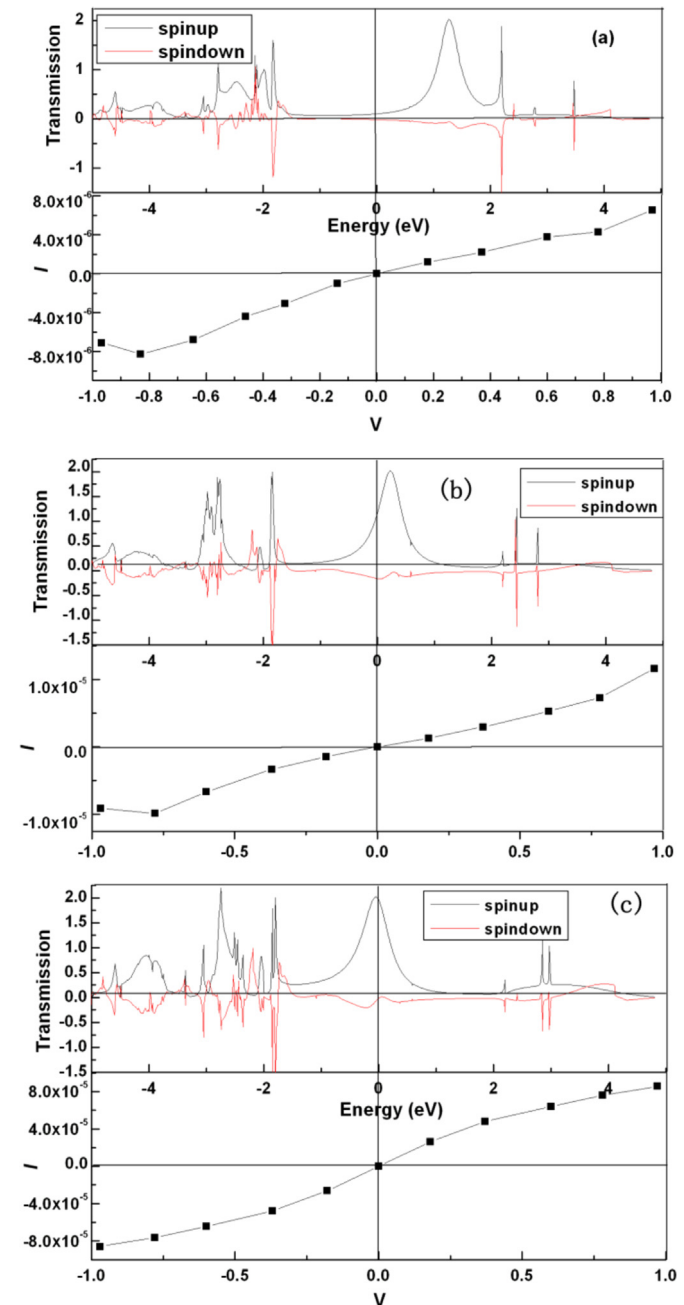


Fig. 2. The transmission coefficients as a function of energy at zero bias, $T(E;V)$, and the I - V characteristics of three metallocene molecules: (a) the ferrocene molecule; (b) the cobaltocene molecule and (c) the nickelocene molecule.

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