

# Theoretical study of molecule mediated spin-polarized electron tunneling between magnetic materials

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## Abstract

Spin-polarized electron tunneling between a Ni tip and a self-assembled monolayer, consisting of  $\sigma$ -bonded bicyclo[2.2.2]octane-1,4-dithiol molecules, deposited on Ni(1 1 1) surface is calculated by density functional approach within Bardeen, Tersoff, and Hamann formalism. The magnitude of the tunneling current is predicted to depend on the spin alignments of the probe tip and the substrate. Comparison with a similar study involving benzene-dithiol, a  $\pi$ -conjugated molecule, suggests that the magnitude of the tunnel current as well as the spin-dependent current is strongly influenced by the nature of the chemical bonds in the molecular structure.

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## 1. Introduction

Organic molecule-mediated electron tunneling between metals has been a subject of intense investigation in the recent years [1–5] due to its potential application in molecular-scale electronics. Very recently, there has also been interest in organic molecule-mediated ‘spin-dependent tunneling’ [6–11]. Although studies of molecule-mediated spin-dependent electron tunneling are often motivated by a need to understand the underlying physics and utilizing molecular tunnel barriers in spin-mediated electronics, such studies also provide useful information on the three-dimensional structure and magnetic properties of the molecular self-assembled monolayers [12].

In a recent article, we reported a density functional theory investigation of spin-dependent tunneling between a magnetic tip and a self-assembled organic monolayer-magnetic substrate [13] with a goal to understand the role of the

organic molecules on electron transport. Our results suggested that the magnitude of the tunnel current sensitively depended on the (a) geometrical features of the cap of the tip and (b) the relative orientation of magnetization at the magnetic tip and the substrate. A self-assembled monolayer (SAM) composed of benzene-1-4-dithiol (BDT), a prototypical  $\pi$ -electron conjugated molecule, was used to investigate electron transport in molecular systems. Since electronic transport characteristics of molecular systems are determined by their electronic and geometrical structures represented by the electron charge distribution, chemical bonding, the molecular orbital energies, it is of interest to examine the effect of a SAM of  $\sigma$ -bonded molecules on spin-dependent electron tunneling between two magnetic electrodes. Here we report the results of such a study, where the SAM consists of, bicyclo[2.2.2]octane-1,4-dithiol (BCODT) molecule, a  $\sigma$ -bonded cage system that has been predicted to have a very small electron transfer coefficient [14,15] due to highly confined electrons and strained chemical bonds. The molecular length of the BDT and the BCODT SAMs are the same ( $\sim 12$  Å), which allows us to compare the results of the two systems focusing on the electronic structure difference.

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## 2. Theory and calculations

The approach for the spin-dependent electron transport calculations were the same as in our previous study [13]. Briefly, Bardeen, Tersoff, and Hamann (BTH) formalism of electron tunneling within the pseudopotential plane wave density functional theory (DFT) approach is used to calculate the spin polarized current in a *tip-vacuum-sample* architecture.

In the BTH approach, the spin-dependent tunneling current  $I^{\uparrow(\downarrow)}$  in low bias limit, can be calculated as [16,17]

$$I^{\uparrow(\downarrow)} = \frac{2\pi e}{\hbar} \times \gamma \int_{-\frac{eV}{2}}^{\frac{eV}{2}} \rho_s^{\uparrow(\downarrow)} \left( \varepsilon + \frac{eV}{2} \right) \times \rho_t^{\uparrow(\downarrow)} \left( \varepsilon - \frac{eV}{2} \right) \times e^{-2d\sqrt{\frac{2m_e}{\hbar^2}(\Phi_{av}-\varepsilon)}} \times \left\{ \left( f \left( \varepsilon - \frac{eV}{2} \right) \right) \times \left( 1 - f \left( \varepsilon + \frac{eV}{2} \right) \right) - \left( f \left( \varepsilon + \frac{eV}{2} \right) \right) \times \left( 1 - f \left( \varepsilon - \frac{eV}{2} \right) \right) \right\} \times d\varepsilon \quad (1)$$

Essentially, the tunneling current represents the integral of convolution of the *projected* density of states of the tip cap  $\rho_t^{\uparrow(\downarrow)}$  with that of the SAM  $\rho_s^{\uparrow(\downarrow)}$  at the tip position. The total current in such a system can be obtained by a summation of the contributions from both the spin-up ( $I^{\uparrow}$ ) and the spin-down ( $I^{\downarrow}$ ) electrons.

In this approach, an elastic scattering is assumed, and spin-flip scattering and spin precession in the tunneling process are not accounted. This approach views electron transport in terms of electron transitions between weakly coupled reservoirs, i.e. the magnetic tip, and the sample separated by a large insulating barrier provided by the vacuum. The molecular layer then can be viewed as a part of the sample, which is always in equilibrium with the underlying substrate, regardless of the applied bias [18].

In order to match the respective electrochemical potentials at zero bias, the Fermi energy of the molecular monolayer on Ni and the probe *tip* is aligned and taken to be the reference energy in Eq. (1). The work function of the SAM ( $\Phi_{\text{SAM}}$ ), which describes how easily an electron can tunnel out of the SAM surface, is obtained from the energy difference between the vacuum-level potential and the Fermi energy level  $E_F$  of its surface. The work function of monolayers of BCODT and BDT is calculated to be 4.77 and 4.54 eV, respectively [19].

Since nickel is a ferromagnetic material having unbalanced spin-up ( $\uparrow$ ) and spin-down ( $\downarrow$ ) electrons near its Fermi level, the tunneling channels for spin-up and spin-down electrons are explicitly separated. The electrons with magnetic moment parallel to the magnetization are electrons of majority-spin, and with magnetic moment anti-parallel to the magnetization are electrons of minority-spin. More specifically, in parallel spin configuration, the majority spin is spin-up and the minority spin is spin-down for both electrodes; whereas in anti-parallel configuration, the majority spin is spin-up on one electrode and spin-down on the other.

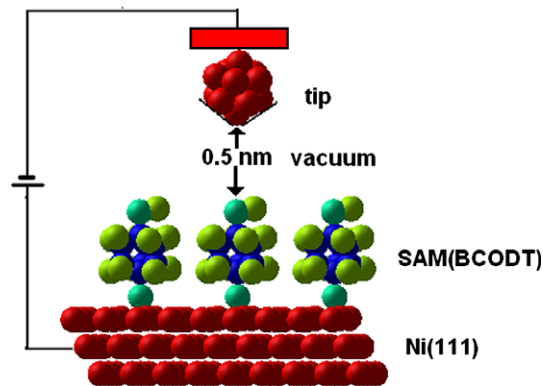


Fig. 1. A schematic illustration of the self-assembled BCODT monolayer on the Ni(111) substrate and the Ni probe *tip* separated by vacuum. The tip cap is represented by a Ni<sub>13</sub> atomic cluster. Notation of symbols: red (dark gray) – Ni; cyan (light gray) – S; blue (black) – C; green (white) – H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A  $3 \times 3$   $R60^\circ$ , 9 Ni atoms/layer supercell is used in the calculation. The magnetic probe tip, separated  $5 \text{ \AA}$  from the SAM, was modeled by the Ni<sub>13</sub> cluster, and the semi-infinite nature of the tip was accounted by introducing broadening of width 0.2 eV ( $\sim$  a few  $k_B T$  at room temperature) in the density of state spectrum of the tip. Considering that the interaction between the magnetic substrate and the non-bonded magnetic tip is negligibly small, the probe tip and the substrate were treated as two separate entities in terms of a single magnetic domain in the computational model. The spin-unrestricted density functional calculations were carried out using the VASP electronic structure program package [13]. The BCODT molecule was taken to be adsorbed at the threefold fcc site of Ni(111) surface. The geometrical configuration considered for calculations is shown in Fig. 1 and is similar to the experimental setup employed in spin-polarized STM studies [20,21].

## 3. Results and discussion

### 3.1. Geometry

The calculated bond lengths together with binding energy are listed in Table 1. Also listed in the table for comparison are the corresponding parameters for BDT adsorbed on Ni. The BCODT molecule consists of C–C single bonds with a bond length ( $R_{\text{C-C}}$ ) in the range of 1.54 – 1.57  $\text{\AA}$ , whereas in the BDT molecule three  $\pi$  bonds are shared by the six C atoms in addition to the C–C  $\sigma$  bonds, yielding a shorter bond length ( $R_{\text{C-C}}$ ) of about

Table 1  
Bond lengths ( $R$ ) and binding energy ( $E_b$ ) of bicyclo[2.2.2]octane-1,4-dithiol (BCODT) and benzene-1,4-dithiol (BDT) adsorbed on Ni(111)

Molecule	$R_{\text{C-C}}$ ( $\text{\AA}$ )	$R_{\text{C-S}}$ ( $\text{\AA}$ )	$R_{\text{Ni-S}}$ ( $\text{\AA}$ )	$E_b$ (eV)
BCODT	1.54–1.57	1.84, 1.89	2.18	2.85
BDT	1.41–1.42	1.76, 1.79	2.19	2.24

1.42 Å. The C–S bond length in BCODT is slightly larger than that in BDT implying a relatively smaller overlap of atomic orbitals between C and S atoms in the former. The adsorption of molecules via S–Ni bond on the substrate further stretches the C–S bond by 0.06 and 0.02 Å for BCODT and BDT, respectively. The calculated Ni–S bond length ( $\sim 2.18$  Å) between the two systems remains the same.

The surface binding energy of the molecule is calculated by subtracting the energies of an isolated molecule and the Ni(111) bare surface from the total energy of the combined system. As shown in Table 1, the bulky molecule BCODT appears to form a relatively more stable monolayer on Ni(111) than BDT by 0.61 eV. It is clear that despite the same anchor atom S, the difference in the overall structure of the two molecules plays a significant role on their binding and interaction with the substrate.

### 3.2. Tunneling current

The total tunneling current calculated for the configurations in which the spin orientation of the magnetic tip is aligned either parallel (P) or anti-parallel (AP) to that of the magnetic substrate is shown in Fig. 2. Individual contributions of spin-up and spin-down electrons to the tunneling current are shown in the inset of Fig. 2. It is apparent that at low bias voltage (up to  $\sim 200$  mV), there is practically no effect of the spin orientation at the magnetic tip and SAM–substrate system on the tunneling current. However, as the bias increases, the parallel (P) orientation appears to offer a greater tunneling probability than the anti-parallel (AP) orientation. An important point to note in molecular-mediated tunnel current, as presented here is that, the tunneling current increases with bias in

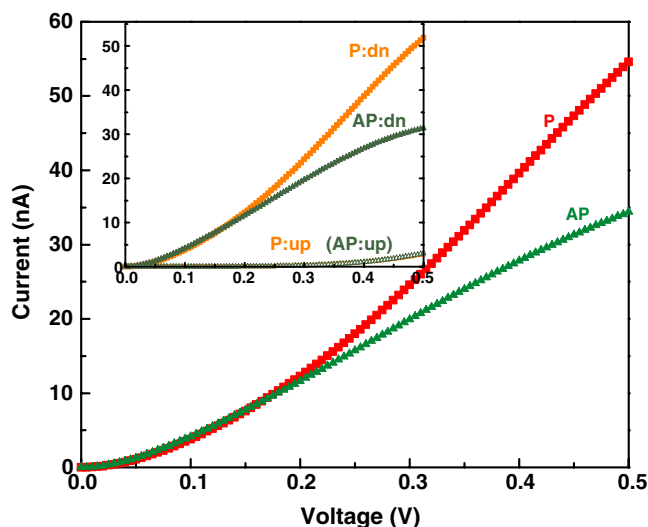


Fig. 2.  $I$ – $V$  curves for the parallel (P) and anti-parallel (AP) spin configurations of the tip–vacuum–SAM–substrate system. The contributions to the total currents from spin-up and spin-down electrons in both parallel and anti-parallel spin configurations are shown in the inset.

both P and AP spin orientation at the magnetic tip and the SAM–substrate complex. This is due to the quantum mechanical nature of electron tunneling, as in the current study, which unlike the giant magnetic resistance (GMR) observed in the solid state, does not vanish and therefore does not switch off the current completely in the AP orientation.

The electron tunneling probability from the Ni tip to the SAM is determined by a response at the SAM due to the electrical perturbation at the tip, which depends primarily upon the convolution (mixing) of DOS of the tip cap and the SAM at the position of the tip. The larger current in the parallel configuration is therefore due to a stronger mixing of the occupied majority-spin (minority-spin) DOS of the tip with the unoccupied majority-spin (minority-spin) DOS of SAM at the position of the tip. In contrast, the current in the anti-parallel configuration is due to convolution of the occupied majority-spin (minority-spin) DOS of the tip with the unoccupied minority-spin (majority-spin) DOS of the SAM at the tip position.

Under a positive bias, the electron current flows from the occupied 3d orbitals of the Ni tip to the unoccupied orbitals of the SAM adsorbed on the Ni substrate. As shown by the *projected* density of states (PDOS) given in Fig. 3, the spin polarized d-states of the Ni substrate hybridizes with the p-states of the S atom of the BCO molecule, polarizing the spin in the monolayer. We note that a higher spin polarization of the orbitals appears only in the immediate vicinity of the Fermi energy ( $|\Delta E| < 1$  eV). On the other hand, the exchange interaction between the parallel spins of the valence and core states of the Ni atom induces a strong spin polarization in the DOS of the probe tip and the Ni substrate. The spin up and spin down carriers therefore experience different scattering potential because of the spin polarization both at the magnetic substrate and the monolayer, yielding a different spin up and

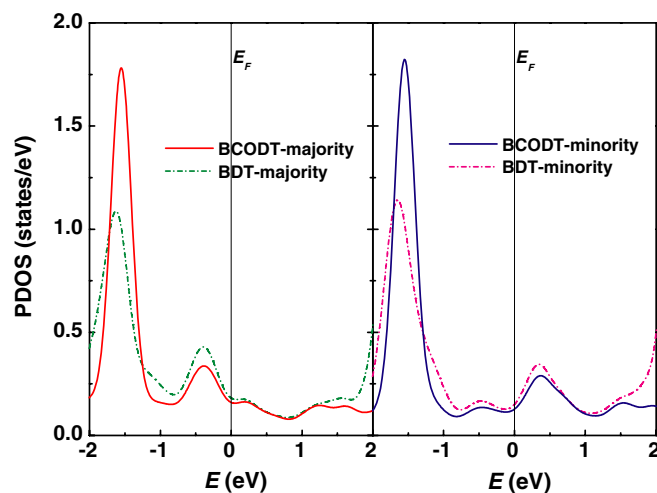


Fig. 3. The projected density of states (PDOS) of the BCODT and BDT monolayers on Ni(111). Zero of the energy is aligned to the Fermi energy.

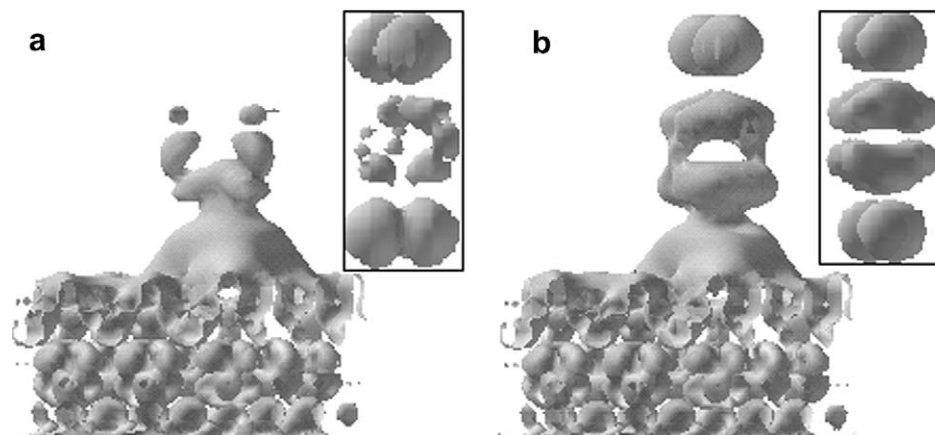


Fig. 4. The spin density isosurface of: (a) BCODT and (b) BDT monolayers deposited on Ni(111) substrate. The charge density of the HOMO of the corresponding molecule is also shown in the inserted box.

spin down tunneling currents ( $I^{\uparrow(\downarrow)}$ ), as shown in the inset of Fig. 2. In both P and AP spin configurations, spin-down electrons are found to be the major carrier, leading to a much higher current than spin-up electrons.

A comparison of the results of the transport calculations obtained for BCODT with those obtained for BDT shows, as expected, a higher tunneling current in the case of the latter, due to a highly conjugated delocalized electrons. Another striking difference between the two molecular systems (BCODT and BDT) is seen in terms of the change in the magnitude of the tunneling current when the spin alignment of the tip and substrate switches from AP to P. It is attributed to the presence of a higher spin polarization in BDT above  $E_F$  also see Fig. 3. For example, the tunneling current in the P alignment is about 60% higher for the case of BCODT, whereas it is about 80% higher for BDT relative to that in the AP alignment at 0.5 V.

Fig. 4 shows the spin density for molecular SAM on Ni substrate displaying a significant polarization associated with the S atom bonded to three Ni atoms. Comparison of the spin density on the backbone of C atoms, however, reveals a difference between BCODT (SAM)-Ni (substrate) and BDT (SAM)-Ni (substrate). In the case of BDT, the spin polarization is distributed uniformly over the entire molecule, whereas in the case of BCODT it is non-uniform, decreasing rapidly away from the S–Ni bonding site in the molecule. This feature is again strongly correlated with the electronic structure of the molecules: the delocalized electrons in  $\pi$ -bonds in BDT have higher magnetization susceptibility than the localized electrons in  $\sigma$  bonds in BCODT. The spin density distribution is a reminiscence of the highest occupied molecular orbital (HOMO) of the molecule, which is also shown in the inset of Fig. 4 for both BCODT and BDT. The HOMO of BDT is a hybrid state of one of the  $\pi$ -orbitals of six C atoms and the lone pair p-orbitals of two S atoms and highly delocalized. In contrast, the HOMO of BCODT is mainly a combination of p-orbitals of two S atoms without any overlap.

#### 4. Summary

We have investigated the effect of a  $\sigma$ -bonded, electronically ‘rigid’ molecule in mediating spin-dependent tunneling between two magnetic electrodes in the weak coupling regime. The  $\sigma$ -bonded system is represented by thiolated BCO molecules chemically bonded on a Ni substrate. The other magnetic electrode is taken as a probe tip of Ni atoms. Our calculation reveals that at low bias potential there is little or no difference in the tunnel current across the tip–SAM junction. This is due to a very low electron-transfer coefficient of the BCO molecule due to highly confined electrons. At increased bias, both P and AP orientations of electron spin at the tip and SAM–substrate complex yield higher tunnel current. However, the P orientation offers a higher current in comparison with the AP orientation. This is because the spin polarization of DOS (i.e.  $P = (\text{DOS}_{\text{up}} - \text{DOS}_{\text{dn}}) / (\text{DOS}_{\text{up}} + \text{DOS}_{\text{dn}})$ ) induced in the SAM has the same sign as that in the tip as well as in the substrate, thereby a constructive convolution of DOS between the SAM and the tip is generated when the majority spins are aligned in parallel. The calculated spin-dependent electron transport mediated by  $\sigma$ -bonded BCODT SAM on Ni, though qualitatively similar to the  $\pi$ -bonded BDT SAM on Ni, is quantitatively different. The total calculated tunnel current is much lower in the BCODT case than the BDT case. Further the difference in P and AP currents is also smaller by 20% in the BCODT system than that in the case of BDT due to a smaller and more localized spin polarization in DOS which mimics its intrinsic chemical bonding features.

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