Spin-Polarized Current of a Transistor in Single Mn$_{12}$ Molecular Magnets

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Focusing on the framework of how to realize the molecular spintronics in a single molecular magnet, we present theoretical studies on the spin-polarized quantum transport behavior through a single Mn$_{12}$ molecular magnet. Our theoretical results were obtained by carrying out density functional theoretical calculation within the Keldysh nonequilibrium Green function formalism. The ultimate goal of the molecular spintronics is to develop single molecule transistors which generate spin-polarized currents through the molecular magnet. We obtained the density of states, the transmission coefficients and the characteristic features of the current–voltage (I–V) on the spin-polarized transport properties of Mn$_{12}$ by the theoretical calculation. These results show the possibility for the realization of molecular spintronics using single molecular magnets.

**Keywords:** Molecular Spintronics, Single Molecular Transistors, Single Molecular Magnets.

1. INTRODUCTION

Recently there have been very much interests in a single molecule as an active electronic component in single molecule transistors.$^{1}$ When electrons flow through a single molecule transistor geometry (SMTG), their behaviors can be affected by interactions between electron transport and the molecular degrees of freedom in the single molecule. The intramolecular forces in the molecule have to interact strongly with the spin of the electrons, resulting in new mechanisms and transport measurements for observing the electron flow and nanoscale magnetic excitations. The interesting systems of single molecules for such observations are single molecular magnets (SMMs) in the single molecule transistor geometry.$^{2}$

Having focussed on the macroscopic quantum tunneling, the SMMs such as Mn$_{12}$ and Fe$_3$ are characterized as a single large spin with large anisotropy barrier.$^{3,4}$ Due to the large spin and high anisotropy barrier, electron transport through the SMM provides unique physical properties which render them a potential candidate for future applications in quantum information storage and information processing as well as a variety of molecular spintronics. It has been shown that electrons transport through the single molecule transistors in which Tsukagoshi and collaborators injected spin-polarized electrons into the carbon-based materials.$^{5}$ Recently Mn$_{12}$ molecular transistors have been fabricated by both Heersche et al.$^6$ and Jo et al.$^7$ independently. They made different kinds of Mn$_{12}$-derivatives whose molecular formulas can be written as [Mn$_{12}$(H$_2$)$_{2}$(O$_2$)C$_6$(H$_2$)$_2$]$^+$, where R = [C$_6$H$_5$SAc, C$_6$H$_5$SHAc, CH$_3$, CHCl$_3$], Ac being acetate. Hereafter we denote all the kinds of Mn$_{12}$-derivatives as Mn$_{12}$. The single molecular transistors are composed of source and drain electrodes together with the gate electrode connected to the molecule. The schematic representation of molecular transistor is shown in Figure 1(a). It was remarkable that they observed some evidences of electron transport through the SMMs in the SMTG. And in theoretical studies, Rocha et al.$^8$ and D. Waldron et al.$^9$ investigated I–V characteristic and tunneling magnetoresistance for the single molecular transistors with ferromagnetic leads.

In this paper we perform theoretical calculation on the properties associated with the electron transport through the SMM, Mn$_{12}$. More specifically, we study spin-polarized quantum transport through single molecular transistor in which the SMM is contacted with gold wire. The gold–Mn–gold (GMG) structure depicted in Figure 1(b) is a general setup representing the SMTG, in which the Mn$_{12}$ is weakly coupled to two semi-infinite gold wires. We seek for the behavior of spin-polarized electron transport using the Keldysh nonequilibrium Green's function (NEGF) formalism with standard density functional theory (DFT). This formulation has been realized and well equipped in

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the Atomistix software.\textsuperscript{10} We exploit a theoretical method of a self-consistent NEGF-DFT which accounts for all the atomic details and open boundaries of the transistor, and the physics of nonequilibrium transport driven by an external bias.

In the self-consistent NEGF-DFT, we want to understand the characteristic features of spin-polarized current through a single molecular transistor in terms of controlling the bias voltage. It is shown that the spin-polarized currents flow through the spin channels of the SMM in the GMG transistor, which enables us to propose the possibility for the realization of molecular spintronics in single molecule magnets.

The paper is organized as follows. In the Section 2 we give a brief explanation on the computational method for the calculation of nonequilibrium transport through molecular spintronics. Numerical results for the density of states (DOSs), transmission spectra, and the spin-polarized electric currents are presented and discussed in Section 3. The conclusion follows in Section 4.

2. THEORETICAL METHOD

Let us review the theoretical approach in order to study spin-polarized transport properties on the typical model of Gold-Mn-Gold transistor shown schematically in Figure 1. We have performed a self-consistent ab-initio technique in which the density functional theory is exploited within the NEGF formulation.\textsuperscript{11,12} The density matrix of the molecular device is constructed by means of NEGF within the standard local spin density approximation (LSDA). Using the NEGF formulation nonequilibrium density can be calculated by means of the lesser Green function\textsuperscript{13-18}

\[
\rho = \frac{1}{2\pi} \int dE G^R_M(E) \tag{1}
\]

where M stands for the extended molecule part of the device. In the NEGF let us consider the effect of an external bias, \(V_b\). Then the density matrix is described by a function of \(V_b\). The lesser Green function is expressed by

\[
G^R_M(E) = i [G^R_M(E)[\Gamma_{LR}^f(E - \mu_L) + \Gamma_{LR}^\alpha(E - \mu_R)]G^R_M(E) \tag{2}
\]

where \(G^R_M\) is the retarded green function of the extended molecule. \(\mu_{L/R} = \mu \pm eV/2\) are the chemical potential of both leads and \(\mu\) is a chemical potential without bias.

In both leads \(\Gamma_{L/R}\) matrices are defined by self-energies as follows,

\[
\Gamma_{L/R}(E) = i[\Sigma^R_{L/R}(E) - \Sigma^{R}_{L/R}(E)] \tag{3}
\]

And the retarded green function, \(G^R_M\) also incorporates the self-energies of the both leads

\[
G^R_M(E) = [\epsilon^+ S_M - H_M - \Sigma^R_M(E) - \Sigma^{R}_{M}(E)]^{-1} \tag{4}
\]

The molecular Hamiltonian in Eq. (4) is constructed by the input density matrix in the steady state finite bias voltage. After including effect of the external bias, the Hamiltonian is described by

\[
\hat{H}_M = -\frac{1}{2} \hat{\nabla}^2 + V_{xc}[\rho] + J[\rho] + V_{xc}[\rho] + V_b(r) \tag{5}
\]

where the right hand side of Eq. (5) is translational energy, ionic, Coulombic, exchange-correlational, and bias potential, respectively. In the procedure of calculating the electronic molecular Hamiltonian of the device, we take pseudo atomic orbitals of the valence shell as basis functions.\textsuperscript{19}

After making convergence of the self-consistent NEGF-DFT by iteration, we obtain spin dependent transmission coefficient

\[
T_\sigma(E, V_b) = \sum_{\epsilon}^\uparrow \sum_{\epsilon}^\downarrow T^\sigma_{\epsilon}\epsilon(E, V_b) \tag{6}
\]

in terms of the Green function. In Eq. (6)\textsuperscript{16}

\[
T^\sigma_{\epsilon} = Tr[\Gamma^\dagger G^R_M \Gamma^\dagger G^R_M] \tag{7}
\]

is the spin dependent transmission coefficient of the longitudinal momentum. We take a single k-point along the traverse surface and several \(k\)-points along the z-axis since we use the gold wire as the electrode. All physical quantities in Eq. (6) are regarded as functions of the longitudinal momentum. \(\sigma \uparrow \downarrow\) denotes spin index. \(T_\sigma(E, V_b)\) is dependent on \(V_b\) and self consistent Korn-Sham potential which has spin dependence. Finally spin polarized current can be obtained in the form

\[
I_\sigma(V_b) = e \int_{\mu_L}^{\mu_R} dE \sum_{\epsilon}^\uparrow \sum_{\epsilon}^\downarrow f_\epsilon(E - \mu_L) - f_\epsilon(E - \mu_R) \tag{8}
\]

In order to calculate \(I_\sigma(V_b)\) on the base of density functional theory we use standard norm-conserving pseudo potential. In particular, on the self-consistent NEGF-DFT calculation about the density matrix we performed complex contour energy integration with 30 points and additionally at least 8 points along real energy axis in the bias spectrum provided that the \(V_b\) is non zero. For simulation of the two-probe GMG, we took 10 \(k\)-points which are sufficient to sample the longitudinal Brillouin zone for convergent the density matrix.

3. RESULTS AND DISCUSSION

In this section using fully self-consistent ab-initio DFT code installed in the Atomistix software\textsuperscript{7} we calculated the density of states (DOS) of the isolated Mn\textsubscript{2}Ac molecule, simply Mn\textsubscript{12}. In the calculation for the exchange correlation energy, we used the functional of Ceperley-Alder known as the LSDA with the Perdew-Zunger parameterization. And we took into account the valence electrons explicitly by using pseudo atomic orbitals. Their interactions with core electrons were modeled as norm-conserving pseudo potentials including nonlinear partial-core corrections. In particular on the GMG transistor we calculated transmission coefficients and spin-polarized currents through the method explained in Section 2.

The three dimensional structure of Mn\textsubscript{12} is obtained from X-ray crystallographic data by Lis et al.\textsuperscript{8} in Figure 2(a). The electronic structure and distribution of the spin density of isolated Mn\textsubscript{12} were obtained in the DFT self-consistent calculation. It is confirmed that the increase to double zeta (DZ) from single zeta (SZ) basis set does not show any noticeable improvement. So we adopted single zeta basis set for all calculations to save computational time. The structure of Mn\textsubscript{12} and its Mn skeleton are represented in Figures 2(a) and (b).

Composed of four Mn atoms, the spin configurations of inner sublattice are mutually parallel while those of outer sublattice composed of eight Mn atoms are mutually parallel also in Figure 2(b). It has been known that these two sublattices of spins are antiparallel each other\textsuperscript{21} to make total spin quantum number \( S = 10 \). As for the structure of Mn\textsubscript{12} the 12 Mn atoms are divided into four equivalent subunits due to \( S_4 \) symmetry.\textsuperscript{20} Each subunit is composed of 3 Mn atoms, among which Mn-1 denotes the atom located in inner sublattice while Mn-2 and Mn-3 are placed in the outer sublattice as shown in Figure 2(b). Here are two possible initial conditions for the spin configuration: one is parallel spin configuration between two sublattices and the other is antiparallel one. Our calculation shows that the antiparallel spin configuration is 1.5 eV more stable than the parallel configuration.

![Fig. 2. (a) The overall structure of a single Mn\textsubscript{12} molecular magnet composed of Mn (violet), O (red), C (black), and H (white). (b) A basic skeleton of the Mn\textsubscript{12} which is composed of the three kinds of Mn-1, Mn-2, and Mn-3.](image)

<table>
<thead>
<tr>
<th>Density</th>
<th>Mn-1</th>
<th>Mn-2</th>
<th>Mn-3</th>
<th>Net spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>+1.2</td>
<td>+1.3</td>
<td>+1.3</td>
<td>( S = 9.52 ) (( S = 10 ), SM)</td>
</tr>
<tr>
<td>Spin</td>
<td>-2.4</td>
<td>+3.58</td>
<td>+3.59</td>
<td></td>
</tr>
</tbody>
</table>

The values of charge and spin density of each Mn atom are presented in the Table 1. The charge densities of Mn atoms are +1.2 for Mn-1 and +1.3 for Mn-2, 3, respectively, in the unit of electron number. Even though the charge densities of Mn atoms are nearly same between two sublattices, their spin magnetic moments have a noticeable difference such as -2.4 for Mn-1 and about +3.6 for Mn-2, Mn-3. This means that the charge distribution of up spin and down spin is different between two sublattices. So, the resultant net spin quantum number is \( S = 9.52 \). Moreover when we consider the extra net magnetization of the oxygen atoms, the total magnetization of the single molecule gives exactly \( S = 10 \) which shows great consistency with experimental value.\textsuperscript{21,22}

The DOSs and the charge density isosurfaces of the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) states for the isolated molecule are presented in Figures 3 and 4. The Fermi energy is indicated by the straight line at \( E = 0.0 \) eV. In this figure each state in the DOSs was displayed on Gaussian form with width of 0.14 eV since the state of the isolated molecule is actually represented by a delta function with the same intensity. In the case of the up spin states the HOMO-LUMO gap is 0.5 eV while it is 1.5 eV in the expression of the down spin states. Besides their difference in the HOMO-LUMO gaps, both the HOMO and LUMO of the

![Fig. 3. Densities of states (DOSs) of the up and down spin channels for a single Mn\textsubscript{12} molecular magnet. The deep dashed straight line stands for Fermi energy, the solid line for DOSs of the up spin channel and the dotted line for the down spin channel. Note that since each state behaves like a delta function, the DOSs have been broadened by 0.17 eV on purpose for the display.](image)
up spin states are more delocalized throughout the whole molecule as compared with those of down spin states. Such structural and electronic properties allow Mn$_{12}$ to play the role of molecular spintronics by generating spin polarized current.

The structure of SMM transistor using Mn$_{12}$ can be realized by connecting gold wires through sulfur atoms attached to the Mn$_{12}$ along the direction of an easy axis with length of 1.3 nm (see Fig. 1).

The zero-bias transmission coefficients and current-voltage (I-V) characteristics of the spin up and down electrons, respectively, are presented in Figures 5 and 6. These physical quantities are agreed with the transport properties in the molecular transistors of one dimensional (1D) leads. It is shown that $T_s(E, V_b)$ has a series of sharp peaks which are consistent with previous studies in the 1D leads. The series of peaks are caused by quantized subbands in the cross section of the 1D leads. The behavior of the transmission coefficients can result in understanding voltage dependence of spin-polarized current. Figure 5 shows that $T_s(E, V_b)$ curves become dominant by the series of resonance features. Among these resonance features a sharp resonance of transmission coefficient gives a rise to the largest contribution to the current near the Fermi level. When we apply positive bias $V_b$ to the molecular device, the current is mainly carried by the up spin channels while it is strongly suppressed through the down spin ones as shown in Figure 6. Therefore the characteristics of the spin-polarized currents are mainly determined by the behavior of the transmission coefficients near the Fermi energy. The behaviors of the spin-polarized currents depending on the bias-voltage are entirely consistent with the features of the DOSs and transmission coefficients. It is clearly shown that dominant contribution of the current is given by spin up electrons for the bias voltage up to 0.16 eV in Figure 6.

4. CONCLUSION AND SUMMARY

We have exploited a first principle calculation for carrying out NEGF-DFT atomistic analysis of spin-polarized quantum transport through a single Mn$_{12}$ molecular magnet. On the base of the Gold-Mn-Gold model, we have investigated the densities of states, the transmission coefficients and the characteristic features of the spin-polarized current of the SMM. It has been shown that the transmission coefficients have a series of sharp peaks in the one dimensional leads.
Our findings are that the spin-polarized current is dominantly carried by the up spin electrons. The transmission coefficients of the up spin electrons result in the current of spin-polarized electron transport. The current is largely enhanced by the up spin electrons while it is strongly suppressed through the down spin electrons up to 0.16 bias voltages. We propose that these results provide the possibility for realizing the molecular spintronics using single molecular magnets.

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References and Notes


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