All-electric-controlled spin current switching in single-molecule magnet-tunnel junctions*

Zhang Zheng-Zhong(张正中)[a], Shen Rui(沈 瑞)[a]†, Sheng Li(盛 利)[a], Wang Rui-Qiang(王瑞强)[b], Wang Bai-Gen(王伯根)[a], and Xing Ding-Yu(邢定钰)[a]

[a] *National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing* 210093, *China*

[b] *Laboratory of Quantum Information Technology, ICMP and SPTE, South China Normal University, Guangzhou* 510006, *China*

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A single-molecule magnet (SMM) coupled to two normal metallic electrodes can both switch spin-up and spin-down electronic currents within two different windows of SMM gate voltage. Such spin current switching in the SMM tunnel junction arises from spin-selected single electron resonant tunneling via the lowest unoccupied molecular orbit of the SMM. Since it is not magnetically controlled but all-electrically controlled, the proposed spin current switching effect may have potential applications in future spintronics.

Keywords: molecular magnets, spin polarized transport, single-electron tunneling

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1. Introduction

Due to the development of material science and technology, molecular-electronic devices have been extensively studied in the past several decades for their potential applications in molecular electronics and spintronics.[1,2] With their small size and low power consumption, many basic molecular devices have been shown to exhibit interesting properties including molecular tunnel junctions with negative differential resistance,[3,4] rectifiers,[5] amplifiers[6] and data storage cells.[7] Unlike conventional semiconductor devices, the conductance of a single molecular device can be more easily controlled, making it function as a controllable switch.[8] To date, the successful measurement of the electronic current through individual molecules leads to various switching effects,[9−12] which can shift molecular devices between the on and off conductance states well. However, all of these switching schemes only depend on the electronic charge degree of freedom and a spin-dependent molecular counterpart remains challenging to produce.

Very recently, a sort of new molecular material, the single-molecule magnet (SMM), has been demonstrated as an appropriate candidate for the basic components of the molecule-based spintronic devices.[13] The SMM is a molecule with a relatively large net spin moment (corresponding to the spin number S) and significant uniaxial magnetic anisotropy.[14] At low temperatures, it is trapped in one of the two metastable spin states $|\pm S\rangle$.[15] This bistability causes the SMM to be a suitable base for memory cells[16] and has stimulated many efforts to investigate the other physical properties of SMMs. So far, electronic tunneling spectra through the SMM have been experimentally demonstrated,[17−19] and the project of writing information onto the SMM was theoretically suggested via an electrical reversion of magnetization.[20,21] In addition, the Kondo effect[22−24] and the Berry phase[25] of a large spin system have also been studied in order to probe the quantum tunneling of magnetization.

In this paper we put forward a new type of spin current switching effect in SMM tunnel junctions, which can switch pure spin-up and spin-down electronic currents, respectively, within two different windows of gate voltage applied to the SMM. The clear advantage is that spin current switching can then op-

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†Corresponding author. E-mail: shen@nju.edu.cn

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erate in a full-electric manner, and needs neither ferromagnetic leads nor an external magnetic field.

2. Model and formulation

The device structure under consideration consists of an SMM connected to two normal-metallic electrodes, as illustrated in Fig. 1(a). This type of metal–SMM–metal junction has been achieved in recent experiments.[17−19,26] A bias voltage V is applied symmetrically to two leads, so that the chemical potentials of the left and right leads are given by $\mu_{\rm L} = eV/2$ and $\mu_{\rm R} = -eV/2$, respectively; and a gate voltage $V_{\rm g}$ is used to adjust the single-electron orbital level ε of the SMM, in which only the lowest unoccupied molecular orbit (LUMO) is relevant to the electronic transport. The Hamiltonian of the system is written as[21]

$$H = \varepsilon_0 \sum_{\sigma} c_{\sigma}^{\dagger} c_{\sigma} + U c_{\uparrow}^{\dagger} c_{\uparrow} c_{\downarrow}^{\dagger} c_{\downarrow} - J \boldsymbol{s} \cdot \boldsymbol{S} - K S_z^2 + \sum_{k,\sigma,\alpha} [\varepsilon_{k\sigma} a_{\alpha k\sigma}^{\dagger} a_{\alpha k\sigma} + (T_{\alpha} a_{\alpha k\sigma}^{\dagger} c_{\sigma} + \text{h.c})], \quad (1)$$

where $\varepsilon_0 \equiv \varepsilon - eV_{\rm g}$, and $c_{\sigma}^{\dagger}$ (c_{σ}) is the relevant electron creation (annihilation) operator with σ as the Pauli spin index. U denotes the Coulomb repulsion and J is the exchange interaction between the electron spin in the LUMO, $\boldsymbol{s} = \sum_{\sigma\sigma'} c_{\sigma}^{\dagger} \sigma_{\sigma\sigma'} c_{\sigma'}/2$, and the giant spin $\boldsymbol{S}$ of the SMM. The parameter K is the uniaxial anisotropy constant of a free molecule and we neglect the electron correction to the magnetic anisotropy. $a_{\alpha k\sigma}^{\dagger}$ ($a_{\alpha k\sigma}$) is the creation (annihilation) operator for the electron with momentum k, spin σ, and energy $\varepsilon_{k\sigma}$ in lead α. The tunnel-coupling strength between the SMM and the normal metallic leads is described by T_{α}, which is assumed to be independent of momentum k and spin σ.

It is easy to diagonalize the Hamiltonian $H_{\rm mol}$ of the isolated SMM, i.e., the first four terms in Eq. (1). If we define $\boldsymbol{S}_{\rm T} = \boldsymbol{s} + \boldsymbol{S}$, it can be shown that the eigenvalue m of $S_{\rm T}^z$ is a good quantum number due to commutation relation $[S_{\rm T}^z, H_{\rm mol}] = 0$. By defining $n = 0, 1, 2$ as the electron number in the LUMO, the eigen-energies can be obtained as:[16,21] $\varepsilon_{|0,m\rangle} = -Km^2$ for eigen-states $|0, m\rangle = |0\rangle_{\rm L} \otimes |m\rangle_{\rm mol}$, $\varepsilon_{|1,m\rangle^{\pm}} = \varepsilon_0 + J/4 - K(m^2 + 1/4) \pm \Delta\varepsilon(m)$ for eigen-states $|1, m\rangle^{\pm} = C_1^{\pm} |\downarrow\rangle_{\rm L} \otimes |m + 1/2\rangle_{\rm mol} + C_2^{\pm} ||\uparrow\rangle_{\rm L} \otimes |m - 1/2\rangle_{\rm mol}$, and $\varepsilon_{|2,m\rangle} = 2\varepsilon_0 + U - m^2$ for eigen-states $|2, m\rangle = |\uparrow\downarrow\rangle_{\rm L} \otimes |m\rangle_{\rm mol}$. Here $\Delta\varepsilon(m) = \sqrt{K(K - J)m^2 + (J/4)^2(2S + 1)^2}$, and $C_1^{\pm}$ and $C_2^{\pm}$ act as effective Clebsch–Gordan coefficients, which are given by

$$C_1^{\pm} = \mp \frac{[2\Delta\varepsilon(m) \pm (2K - J)m]^{1/2}}{2[\Delta\varepsilon(m)]^{1/2}}, \quad (2)$$

and

$$C_2^{\pm} = \frac{J[S(S + 1) - m^2 + 1/4]^{1/2}}{2[\Delta\varepsilon(m)]^{1/2}[2\Delta\varepsilon(m) \pm (2K - J)m]^{1/2}}. \quad (3)$$

In the above expressions $|\bullet\rangle_{\rm L(mol)}$ represents the spin state of the LUMO (SMM).

The transport process is dominated by sequential tunneling through the SMM level, while the cotunneling and direct tunneling are very weak and can be neglected safely. For the weak coupling between the SMM and leads, the master equation approach holds. The total spin-σ current flowing through the SMM can be written as $I_{\sigma} = (I_{L\sigma} - I_{\rm R\sigma})/2$, where $I_{\rm L\sigma}$ ($I_{\rm R\sigma}$) stands for the spin-σ current flowing from the left (right) lead to the SMM, yielding

$$I_{\alpha\sigma} = -(e/h) \sum_{i,f} (n_i - n_f) R_{\alpha\sigma}^{f \to i} P_f, \quad (4)$$

where $P_{i(f)}$ describes the probability of finding the SMM in state $|i(f)\rangle$, and $R_{\alpha\sigma}^{f \to i}$ denotes the rate of transition between the states $|i\rangle$ and $|f\rangle$, reading as $R_{\alpha\sigma}^{f \to i} = \Gamma_{\alpha\sigma}[f(\varepsilon_i - \varepsilon_f - \mu_{\alpha})|\langle i|c_{\sigma}^{\dagger}|f\rangle|^2 + f(\varepsilon_i - \varepsilon_f + \mu_{\alpha})|\langle f|c_{\sigma}^{\dagger}|i\rangle|^2]$. $\Gamma_{\alpha\sigma} = 2\pi D_{\alpha\sigma}|T_{\alpha}|^2$ is the line-width function with $D_{\alpha\sigma}$ the density of states at Fermi level of lead α and $f(\varepsilon_i - \varepsilon_f \pm \mu_{\alpha})$ are Fermi–Dirac distribution functions. We denote $R_{f \to i} = \sum_{\alpha\sigma} R_{\alpha\sigma}^{f \to i}$ and the steady state solution P_i for the occupation probability can be obtained by solving a set of rate equations:[16,21] $\dot{P}_i = \sum_{f \neq i} P_f R_{f \to i} - P_i \sum_{f \neq i} R_{i \to f} = 0$ with $\sum_i P_i = 1$. From the factor $\langle i|c_{\sigma}^{\dagger}|f\rangle^2$ in $R_{\alpha\sigma}^{f \to i}$, it follows that the transition between the eigen-states of the SMM satisfies two basic selection rules: $|\Delta n| = 1$ and $|\Delta m| = 1/2$.

3. Results and discussion

In what follows numerical calculations are performed for the Mn_{12}–Ac molecule[17,27−29] with spin number $S = 10$, $K = 0.06$ meV, $J = 3.92$ meV, $U = 25$ meV and the applied bias voltage $V = 0.5$ mV. As the electrodes under consideration are made of the normal metal, the line-width functions $\Gamma_{\alpha\sigma}$ are free from spin index. Because of a high anisotropy barrier (KS^2), one may expect that at low temperatures

and a small bias voltage, the SMM cannot reverse its giant spin. In this case, the SMM is assumed to be initially saturated in state $|0, S\rangle$, and characterized by a spin number S and an additional unoccupied orbital (LUMO). From the expressions for $\varepsilon_{|0,S\rangle}$, $\varepsilon_{|1,S+1/2\rangle^-}$, and $\varepsilon_{|2,S\rangle}$, it is found that the LUMO has two spin-split levels with an energy interval of $\Delta E = 2\varepsilon_r + U$ where $\varepsilon_r = K(S+1/2) + \Delta\varepsilon(S+1/2) - J/4$. The electron occupation configurations for the $|0, S\rangle$, $|1, S+1/2\rangle^-$, and $|2, S\rangle$ states are plotted in Fig. 1(b).

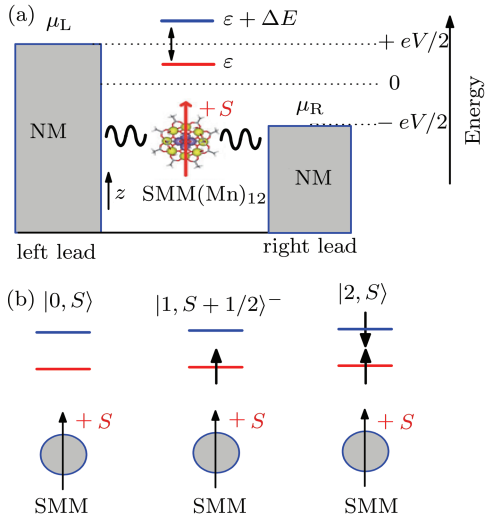


Fig. 1. (a) Schematic representation of the SMM tunnel junction. A finite bias voltage V is applied, $eV = \mu_L - \mu_R$, where μ_L and μ_R denotes the electrochemical potential of the left (right) electrode, and the SMM is characterized by a spin number S and two LUMO levels. (b) Schematic illustration of electron occupation on two energy levels of the LUMO for the $|0, S\rangle$, $|1, S+1/2\rangle^-$, and $|2, S\rangle$ states.

The calculated results for the spin-up current $I_\uparrow$ and spin-down current $I_\downarrow$ (scaled by $e\Gamma/2h$) are plotted as functions of the gate voltage in Fig. 2(a). At zero temperature, two 100% spin-polarized electronic currents are switched for two gate-voltage windows, respectively: pure spin-up current switching for $19.35 < \varepsilon_0 < 19.85$ and pure spin-down current switching for $-44.85 < \varepsilon_0 < -44.35$; while $I_\uparrow = I_\downarrow = 0$ out of the two windows. Such an SMM junction is an all-electric controlled switching device, having two spin-selected "on" states and one "off" state. It can also be used as a perfect spin filter device. For an injection of spin-unpolarized electronic current from the normal source into drain via the SMM, either a pure $I_\uparrow$ or a pure $I_\downarrow$ can pass through the SMM junction, if ε_0 is just in the corresponding gate-voltage window.

At finite temperatures, the switching plateaus evolve into two peaks of $I_\uparrow$ and $I_\downarrow$; with increasing T, the peaks become lower and broaden, but the switching retains a high spin-polarized current at low temperatures, as shown in Fig. 2(a). As the temperature increases, the difference between the two occupation probabilities P_i and P_f decreases. The difference between the two transition rates $R^{f\to i}_{\alpha\sigma}$ and $R^{i\to f}_{\alpha\sigma}$ also become small at high temperature. From Eq. (4), one can find that the decrease of I_σ shown in Fig. 2(a) stems from the decrease of the difference in the occupation probabilities and that in the transition rates with increasing temperature. If the spin polarization of switching current is defined as $\eta = |(I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)|$, it is found that η can remain almostly 100% for $T \leq 2$ K.

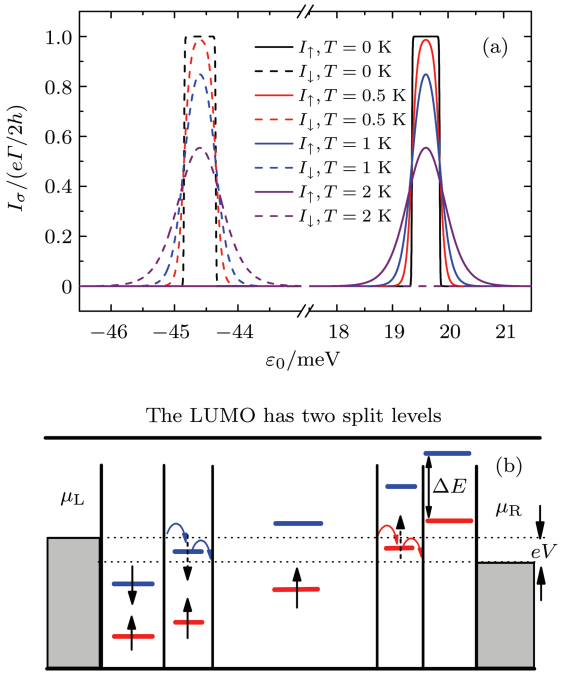


Fig. 2. (a) Spin polarized currents $I_\uparrow$ (solid line) and $I_\downarrow$ (dashed line) as a function of gate voltage at low temperatures with $U = 25$ meV and $J = 3.92$ meV; (b) The location of the LUMO levels in the spin-up and spin-down "on" and "off" regions.

At low temperatures, the tunneling processes through the SMM with a high anisotropy barrier take place between the three lowest energy states which are characterized by a saturated spin S and a spin-split LUMO with three occupation configurations as shown in Fig. 1(b). In order to understand the underlying physics of the switching effect, we plot the location of the LUMO levels within and without the spin-selected switching windows in Fig. 2(b). For the

separation of the two levels greater than the bias voltage of the junction, i.e., $2\varepsilon_r + U > eV$, there is at most one level (ε_r or $-\varepsilon_r - U$) in the bias window $[\mu_{\rm R}, \mu_{\rm L}]$ with $\mu_{\rm L} - \mu_{\rm R} = eV$. From Fig. 2(b), it is seen that in the "off" states there is no LUMO level within the bias window so that no electron can tunnel via the SMM. In this case, both levels are above $\mu_{\rm L}$ for $\varepsilon_0 > \varepsilon_r + eV/2$, or both levels are below $\mu_{\rm R}$ for $\varepsilon_0 < -\varepsilon_r - U - eV/2$, or one level is above $\mu_{\rm L}$ and the other is below $\mu_{\rm R}$ for $-\varepsilon_r - U + eV/2 < \varepsilon_0 < \varepsilon_r - eV/2$. In the ε_0 window $[\varepsilon_r - eV/2, \varepsilon_r + eV/2]$, the spin-up level of the LUMO is just between $\mu_{\rm L}$ and $\mu_{\rm R}$ so that only the spin-up electron can pass through the SMM, giving rise to spin-up current switching. From Eq. (4), the spin-up tunneling current is obtained as

$$I_\uparrow = \frac{e\Gamma P_{|0,S\rangle}}{h} |\langle 0, S|c_\uparrow|1, S+1/2\rangle^-|^2 = e\Gamma/2h, \quad (5)$$

where $P_{|0,S\rangle} = 1/2$, and the factor $\langle 0, S|c_\uparrow|1, S+1/2\rangle^-$ selects only spin-up electrons to tunnel through the SMM. Similarly, in the ε_0 window of $[-\varepsilon_r - U - eV/2, -\varepsilon_r - U + eV/2]$, the spin-down level of the LUMO is just between $\mu_{\rm L}$ and $\mu_{\rm R}$ so that only the spin-down electron can pass through the SMM, leading to spin-down current switching. In this case, the spin-down tunneling current, corresponding to the left switching plateau in Fig. 2(a), yields,

$$\begin{aligned} I_\downarrow &= \frac{e\Gamma P_{|1,S+1/2\rangle^-}}{h} |^-\langle 1, S+1/2|c_\downarrow|2, S\rangle|^2 \\ &= e\Gamma/2h. \end{aligned} \quad (6)$$

In Fig. 2(a) the centres of two switching windows are located at $-\varepsilon_r - U$ and ε_r, respectively, the distance between them being just equal to the separation of the two LUMO levels, and the width of each window is the bias voltage eV. It then follows that $2\varepsilon_r + U > eV$ is the necessary condition of forming 100% spin-polarized switching. If this condition is not satisfied, the two LUMO levels may simultaneously enter into the bias voltage window $[\mu_{\rm R}, \mu_{\rm L}]$. In this case, there is a charge current switching, but no spin-current switching. In the absence of Coulomb interaction ($U = 0$), $I_\uparrow$ and $I_\downarrow$ are exactly symmetric with respect to $\varepsilon_0 = 0$. The presence of U shifts the ε_0 window for the spin-down current $I_\uparrow$ towards a lower gate voltage, while that for the spin-up current $I_\uparrow$ remains unchanged. In addition to the U effect, a larger spin S, a larger uniaxial anisotropy constant K, and/or a larger exchange energy J can result in a larger ε_r so as to enlarge the distance between two spin-current switching windows, favorable to a high spin polarization of switching currents.

4. Conclusion

We have proposed a three-state switching effect with two "on" states for spin-up and spin-down current switching as well as a current "off" state. Such fully spin-polarized current switching can be realized in an SMM (e.g., Mn_{12}–Ac) tunnel junction and arises from the spin-selected single electron resonant tunneling via the LUMO of the SMM. The present three-state switching can be controlled in a full-electric manner without spin–orbit interaction and external magnetic field, and is a good candidate for spin-current switching and filter devices in future spintronic circuits.

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