Effects of intrinsic spin-relaxation in molecular magnets on current-induced magnetic switching

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Current-induced magnetic switching of a single magnetic molecule attached to two ferromagnetic contacts is considered theoretically, with the main emphasis put on the role of intrinsic spin-relaxation processes. It is shown that spin-polarized current can switch magnetic moment of the molecule, despite the intrinsic spin-relaxation in the molecule. The latter processes increase the threshold voltage (current) above which the switching takes place.

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Single-molecule magnets (SMMs)[1,2] attract much attention due to their unique properties and possible applications in quantum information processing[3] and information storage technology.[1,4] Apart from this, SMMs are promising as key elements of novel spintronics devices.[5] Therefore, an important question is how to manipulate the SMM in order to write a bit of information on it. One possibility relies on the application of an external magnetic field. In this paper, however, we consider another possibility, i.e., the current-induced magnetic switching (CIMS).[6–8] The phenomenon of CIMS[9] is well known in the case of artificial layered nanostructures. Since present-day technology allows one to attach a SMM to electronic contacts,[10] CIMS of a SMM is an alternative way of writing information in SMM-based memory elements.

There are several challenging aspects of the current-induced manipulation of SMM's spin. First, the up-to-date experimental techniques offer only limited control of the relative orientation of the molecule's easy axis and leads' magnetizations.[11] Second, intrinsic spin-relaxation time of the molecule[12] has a significant influence on the switching parameters and is hardly controllable externally. Finally, the efficiency of spin injection from ferromagnetic leads to molecules is the subject of intense technological efforts. The main objective of this paper is to provide a detailed analysis of the second point, i.e., of the influence of intrinsic spin-relaxation on the CIMS of a SMM.

It is only very recently, that the switching of SMM's spin due to spin-polarized current has been proposed.[6–8] However, the intrinsic spin-relaxation in the molecule has not been taken into account. When the energy ε of the lowest unoccupied orbital (LUMO) level of the molecule is sufficiently low, electronic transport takes place owing to tunneling between the electrodes and the LUMO level. The CIMS can then occur when the LUMO level is exchange coupled to the SMM's spin. The corresponding Hamiltonian of the molecule can be written in the form

$$\mathcal{H}_{SMM} = -\left(D + \sum_{\sigma} D_1 c_{\sigma}^{\dagger} c_{\sigma} + D_2 c_{\uparrow}^{\dagger} c_{\uparrow} c_{\downarrow}^{\dagger} c_{\downarrow}\right) S_z^2 + \sum_{\sigma} \varepsilon c_{\sigma}^{\dagger} c_{\sigma} + U c_{\uparrow}^{\dagger} c_{\uparrow} c_{\downarrow}^{\dagger} c_{\downarrow} - \frac{1}{2} \sum_{\sigma\sigma'} J \boldsymbol{\sigma}_{\sigma\sigma'} \cdot \boldsymbol{S} c_{\sigma}^{\dagger} c_{\sigma'}, \quad (1)$$

where $\boldsymbol{\sigma}$ is the Pauli spin operator for electrons in the LUMO level, $\boldsymbol{S}$ is the molecule's spin, $c_{\sigma}^{\dagger}$ (c_{σ}) is the relevant creation (annihilation) operator, and U is the Coulomb energy of two electrons of opposite spins in the LUMO level. The first term of $\mathcal{H}_{SMM}$ describes the anisotropy of a SMM, whereas the final one accounts for the exchange interaction between the SMM's core and the LUMO level, with J being the relevant exchange parameter. The influence of the molecule's oxidation state on the anisotropy[14] is taken into account by the terms linear in D_1 and D_2. The above Hamiltonian applies to molecules that can be described by the uniaxial anisotropy term (such as approximately the Mn_{12} molecule). For nonuniaxial systems, e.g., for the Fe_8 molecule,[1,2] the transverse anisotropy term $\mathcal{H}_{\perp}^{an} = E(S_x^2 - S_y^2)$ with E denoting the corresponding transverse anisotropy constant, has to be included into consideration. The transverse anisotropy modifies the energy spectrum, and thus can also indirectly affect the switching parameters. In this paper the transverse anisotropy is assumed to be small and therefore neglected. Its role, however, is effectively taken into account as a contribution to the phenomenological relaxation time. The tunneling processes between the molecule and leads are described by $\mathcal{H}_T$, $\mathcal{H}_T = \Sigma_q \Sigma_{\mathbf{k}\sigma} [T_q a_{\mathbf{k}\sigma}^{q\dagger} c_{\sigma} + T_q^* c_{\sigma}^{\dagger} a_{\mathbf{k}\sigma}^{q}]$, where T_q is the tunneling matrix element between the SMM and the qth lead [$q = L$ (R) for the left (right) electrode], and $a_{k\sigma}^{q}$ ($a_{k\sigma}^{q\dagger}$) is the annihilation (creation) operator of an electron with the wave vector $\boldsymbol{k}$ and spin σ in the qth electrode. The system is shown schematically in Fig. 1(a).

Tunneling between the leads and molecule gives rise to a finite spin-dependent width Γ_{σ} of the LUMO level, $\Gamma_{\sigma} = \Sigma_q \Gamma_{\sigma}^{q}$, where $\Gamma_{\sigma}^{q} = 2\pi |T_q|^2 D_{\sigma}^{q}$ and D_{σ}^{q} is the spin-dependent density of states (DOS) at the Fermi level in the lead q. The parameters Γ_{σ}^{q} will be used in the following to describe coupling strength between the LUMO level and leads. It is convenient to write Γ_{σ}^{q} as $\Gamma_{\pm}^{q} = \Gamma_q (1 \pm P_q)$, where $\Gamma_q = (\Gamma_+^q + \Gamma_-^q)/2$, and P_q is the polarization of the qth lead, $P_q = (D_+^q - D_-^q)/(D_+^q + D_-^q)$. Here $\sigma = +$ ($-$) corresponds to spin-majority (spin-minority) electrons. In the following, we assume that the couplings are symmetric, $\Gamma_L = \Gamma_R = \Gamma/2$.

When the energy ε of the LUMO level is large enough, electron tunneling to the molecule is energetically forbidden at bias voltages of interest. However, electric current still can flow due to higher order tunneling processes, e.g., cotunneling ones, and CIMS of the molecule's spin is still possible[6] when the electrons virtually entering the molecule couple to

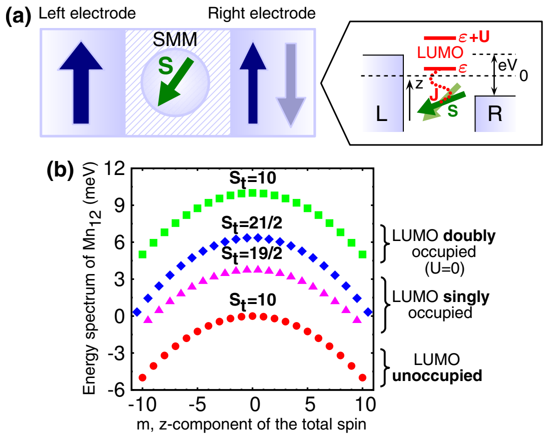

FIG. 1. (Color online) (a) Schematic representation of the system and switching mechanism due to spin-polarized current. (b) Energy levels of the Mn_{12} molecule for the following parameters: $D\approx 0.05$ mV, $D_1\approx -0.006$ meV, $D_2\approx 0.0017$ meV (Ref. 14), $J=0.25$ meV, $\varepsilon=5$ meV, and $U=0$. Different parabolas correspond to indicated values of the SMM's total spin S_t and occupation numbers of the LUMO level.

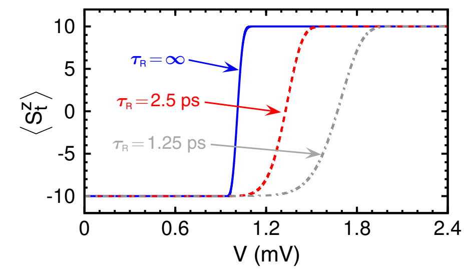

FIG. 2. (Color online) The effect of intrinsic relaxation processes on magnetic switching of the molecule Mn_{12} in the limit of high LUMO level, calculated for indicated values of the relaxation time, τ_R, and for parallel magnetic configuration. The polarization parameters of the electrodes are $P_L=1$ and $P_R=0.5$. The other parameters are $J_\lambda=100$ meV, $D\approx 0.05$ meV (Ref. 14), $T=0.01$ K, and $c=10$ kV/s.

the molecule's spin via the exchange interaction. The total Hamiltonian $\mathcal{H}$ (including the molecule's and tunneling parts) can be then effectively reduced to $\mathcal{H}=-DS_z^2+\frac{1}{2}\Sigma_{qq'}\Sigma_{\sigma\sigma'\mathbf{k}\mathbf{k}'}(J_\lambda\boldsymbol{\sigma}_{\sigma\sigma'}\cdot\boldsymbol{S}+\delta)a_{\mathbf{k}\sigma}^{q\dagger}a_{\mathbf{k}'\sigma'}^{q'}$, where $J_\lambda=J\lambda$, with λ representing an effective parameter that accounts for the cotunneling probability. Additionally, δ takes into account those tunneling processes between the leads that are not included in the exchange term. These, however, are irrelevant from the point of view of switching process and can be neglected ($\delta=0$).

Switching of the SMM's spin takes place consecutively via the magnetic states of the molecule, Fig. 1(b). These states are described by the eigenvalue m of the z component of the molecule's total spin, $S_t^z\equiv S_z+\frac{1}{2}(c_\uparrow^\dagger c_\uparrow-c_\downarrow^\dagger c_\downarrow)$ (where the second term represents the contribution from electrons in the LUMO level), and the corresponding occupation number n of the LUMO level, i.e., $|n,m\rangle$. Transitions between neighboring molecular states, due to tunneling through the LUMO level, are governed by the following selection rules: $|\Delta S_t^z|=1/2$ and $|\Delta n|=1$. The relevant description of how to obtain the set of molecular magnetic states in question and selection rules can be found in Refs. 7 and 8.

To analyze the magnetic switching of a SMM, it is convenient to consider the mean value of the z component of the total molecule's spin,

$$\langle S_t^z\rangle=\sum_{n,m} mP_{|n,m\rangle}, \tag{2}$$

where $P_{|n,m\rangle}$ is the probability of finding the molecule in the state $|n,m\rangle$. This probability can be determined from the relevant master equations and the corresponding transition rates between the molecular states. The key point is that these transition rates must include also the effects due to intrinsic spin-relaxation.

Generally, in the systems under consideration one can distinguish two classes of SMM's spin-relaxation processes. The first class is associated with the coupling of the molecule to ferromagnetic leads,[6–8,15] and the other one includes all intrinsic spin-relaxation processes.[2,12] The role of the latter processes in the CIMS of the SMM's spin is the main objective of this paper. It is important to note that even at low temperatures the molecule's spin is subject to decoherence due to interaction with its environment. A SMM in an excited molecular spin level can undergo transitions to neighboring levels of lower energy, which is accompanied by emission of a phonon. As a consequence, excited molecular spin states have a finite lifetime, and it has been shown that this time for Fe_8 is of the order of 10^{-6} s.[12] Furthermore, coherence of the SMM's spin can also be lost due to various forms of magnetic interactions with the environment, e.g., due to the hyperfine interaction with nuclear moments of protons in the vicinity of the molecule.[2,12]

To include the intrinsic spin-relaxation processes, we introduce the relaxation rate γ_R in addition to the rates $\gamma^{|n,m\rangle|n',m'\rangle}$ describing current-induced transitions between the molecular states $|n,m\rangle$ and $|n',m'\rangle$. The latter ones can be calculated from the Fermi golden rule [Eqs. (8) in Refs. 6 and 7]. In turn, intrinsic relaxation of the molecule's spin occurs as transitions between neighboring molecular states of the same spin multiplet, Fig. 1(b), i.e., the occupation of the LUMO level is not changed by these processes. Furthermore, we assume that all contributions to the spin-relaxation are fully characterized by a single phenomenological relaxation time τ_R. Such a description, though simplified, allows one to capture the basic features of how relaxation processes influence the CIMS of a SMM. Assuming that the transition from a given state $|n,m\rangle$ takes place only to the neighboring states $|n,m\pm 1\rangle$ of the same multiplet,[13] the relaxation rate can be then written in the form

$$\gamma_R^{|n,m\rangle|n,m\pm 1\rangle}=\frac{1}{\tau_R}\frac{\exp\left[\frac{\Delta}{2k_BT}\right]}{2\cosh\left[\frac{\Delta}{2k_BT}\right]}. \tag{3}$$

Here, $\epsilon_{|n,m\rangle}$ denotes the energy of the molecular state $|n,m\rangle$, k_B is the Boltzmann constant, T is the temperature of the system, and $\Delta=\epsilon_{|n,m\rangle}-\epsilon_{|n,m\pm 1\rangle}$. The Boltzmann factor in Eq.

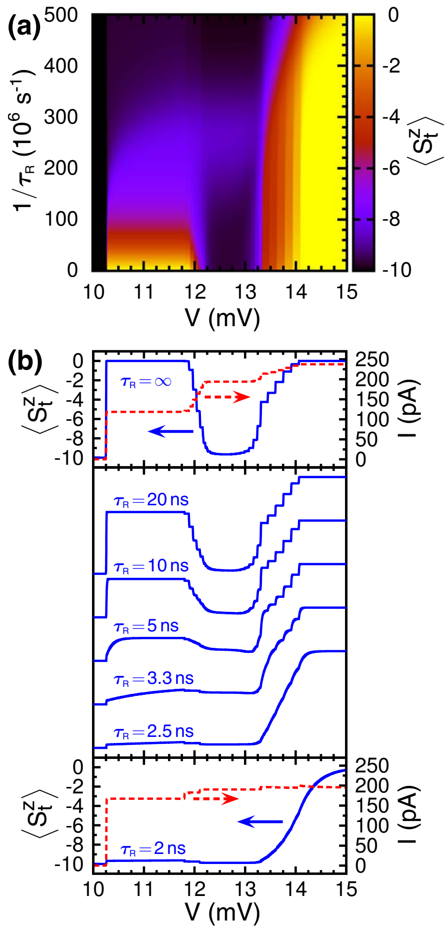

FIG. 3. (Color online) (a) The mean value of the total spin $\langle S_t^z \rangle$ for different values of the inverse relaxation time, τ_R^{-1}, in the case of parallel configuration of the electrodes' magnetic moments, calculated for $P_L = P_R = 0.5$. Solid lines in part (b) represent cross sections of the plot (a) for several values of τ_R, whereas the dashed lines correspond to the current flowing through the system. The other parameters are as in Fig. 1, and $T = 0.01$ K, $c = 1$ V/s, and the coupling parameter $\Gamma = 0.001$ meV.

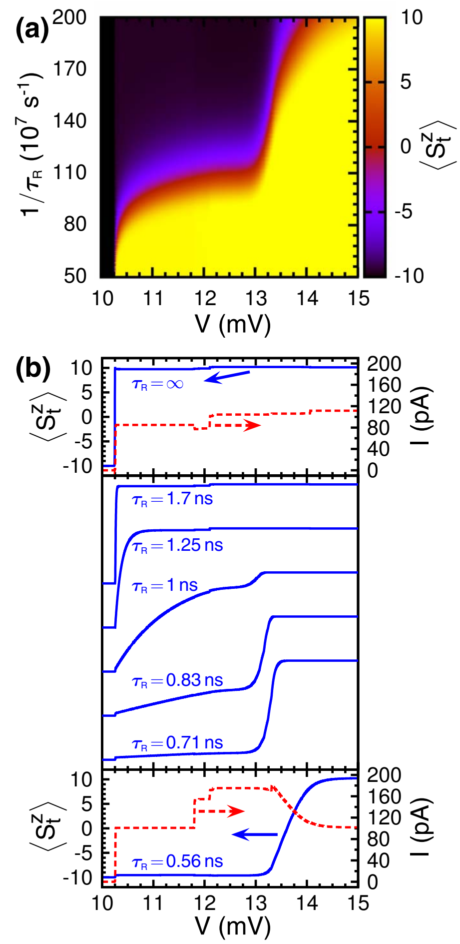

FIG. 4. (Color online) The same as in Fig. 3 but for antiparallel alignment of the electrodes' magnetic moments.

(3) assures that the intrinsic spin-relaxation drives the SMM's spin to a state of lower energy.

Taking into account the relaxation processes discussed above, the master equations for the probabilities $P_{|n,m\rangle}$ take the form

$$c\frac{dP_{|n,m\rangle}}{dV} = -(\gamma_R^{|n,m\rangle|n,m-1\rangle} + \gamma_R^{|n,m\rangle|n,m+1\rangle})P_{|n,m\rangle} + \gamma_R^{|n,m-1\rangle|n,m\rangle}P_{|n,m-1\rangle} + \gamma_R^{|n,m+1\rangle|n,m\rangle}P_{|n,m+1\rangle} + \sum_{n',m'}[\gamma^{|n',m'\rangle|n,m\rangle}P_{|n',m'\rangle} - \gamma^{|n,m\rangle|n',m'\rangle}P_{|n,m\rangle}]. \quad (4)$$

In the following we assume that initially the molecule is saturated in the state $|0,-10\rangle$, and then voltage growing linearly in time is applied, $V = ct$, with c denoting the speed at which the voltage is augmented. It means that for the molecule of the spin $S = 10$, like the molecule Mn_{12} or Fe_8, one has to solve the set of 21 coupled differential equations for the situation of high LUMO level and 84 equations in the general case.

In Fig. 2 we show evolution of the z component of the molecule's spin in the case of parallel magnetic configuration and high LUMO level (current flows then due to higher order processes). The results clearly show that the molecule's spin becomes switched when the voltage exceeds some critical value, which is determined by the magnetic anisotropy (energy gap between the states corresponding to $m = -10$ and $m = -9$) and the intrinsic relaxation time. Since the intrinsic spin-flip relaxation processes tend to restore the initial state, the lowest threshold voltage occurs in the absence of intrinsic spin-relaxation. The switching also takes place in the presence of intrinsic spin-relaxation processes, although the threshold voltage becomes increased. However, it transpires that the relaxation times observed in molecular magnets[2,12] are far too long to have a measurable effect on the CIMS for the parameters assumed in Fig. 2. Similar behavior also occurs in the case when magnetic moments of the leads are antiparallel.

The parameters assumed in Fig. 2 correspond to half-metallic ferromagnetic left electrode ($P_L = 1$), and typical $3d$ ferromagnetic metallic right electrode. For simplicity the positive bias corresponds to electrons flowing from left to right ($e>0$), i.e., from half-metallic ferromagnetic electrode to the $3d$ one. Spin-up electrons leaving the half-metallic electrode can change its spin orientation when interacting via exchange coupling with the molecule's spin, and this way can increase the spin number m of the molecule's spin. Intrinsic relaxation processes tend to restore the initial state. When the current exceeds some critical value, the competition of intrinsic spin-relaxation (lowering the quantum number m) and current-induced processes (increasing the number m) leads to spin reversal of the molecule. This takes place in both, parallel and antiparallel (with magnetic moment of the right electrode being reversed) magnetic configurations. For reversed bias polarization only switching from the state $|0,10\rangle$ to the state $|0,-10\rangle$ is possible.

In Figs. 3 and 4 we show the average value of the total spin $\langle S_t^z\rangle$ and current flowing in a biased system in the case when switching occurs due to sequential tunneling of electrons through the molecule's LUMO level. These two figures correspond to parallel (Fig. 3) and antiparallel (Fig. 4) magnetic configurations. Clearly, there is no switching in the parallel configuration. Instead of this, current excites the molecule to higher states and the average spin becomes zero (see Fig. 3). The situation is different in the antiparallel configuration, where there is a clear switching from the state $|0,-10\rangle$ to the state $|0,10\rangle$. To understand this behavior one should note that in Figs. 3 and 4 the spin polarization of both electrodes is the same. Consequently, the current-induced processes increasing the number m and those decreasing m occur with the same rate in the parallel configuration. Accordingly, none of the molecule's spin states is stabilized by the current. In contrast, in the antiparallel configuration the processes increasing the number m start to dominate over those decreasing m above a certain threshold voltage, and the switching to the state $|0,10\rangle$ takes place. Current-induced switching of the molecules's spin may be possible also in the parallel configuration, provided spin polarizations of the electrodes are different.

In conclusion, we have shown that spin-polarized current flowing through the molecule can switch its magnetic moment despite intrinsic spin-relaxation processes in the molecule. The latter processes increase the threshold voltage (current) and switching time. If for a certain bias polarization current stabilizes the state $|0,-10\rangle$ (or $|0,10\rangle$), then the opposite current stabilizes the state $|0,10\rangle$ (or $|0,-10\rangle$).

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