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Magnetic crossover realized by electrical methods

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Abstract. Electrical control of molecular-scale magnetisms is a greatly important topic in molecular spintronics. This enables the ultimate-limit manipulation of magnetisms, and has the potential to revolutionize computer technologies. Two mechanisms related to electrical control of molecular-scale magnetisms are concerned in this review. One is the magnetic crossover realized by the electrostatic Stark effect. The other is the magnetic crossover induced by the electron tunneling through the lowest unoccupied molecular orbital under bias voltages or one added electron under gate voltages.

1. Introduction

Over the past few decades, traditional transistors have shrunk dramatically and their dimensions are now less than 10 nm in research [1, 2]. Further miniaturization of transistors is however greatly challenging, due to technique limitations and lack of fundamental transport mechanisms [3]. On this issue, it is worth noting that organic molecules, with sizes of ca. 1 nm, can be synthesized in bulk while accomplishing a variety of electronic tasks, such as rectification, memory, and switching. These materials have the potential to replace some traditional solid-state device counterparts in the future, which gives birth to a new field called *molecular electronics* [4, 5, 6, 7]. The molecular electronics is conceptually fabricating electrical circuits using properties of individual organic molecules. Such circuits have three notable advantages: i) they can be manufactured with room-temperature low-cost chemical methods, instead of expensive high-temperature solid-state growth (e.g. molecular beam epitaxy) and pattering (lithography) techniques; ii) the extremely reduced size enables higher capacity and faster performance, and the limit of conventional silicon circuit integration can be surpassed; iii) the diversity of molecular structures probably brings some novel effects that are not accessible using traditional materials or approaches.

Among organic molecules, the ones with magnetic ions are exceptional objects for electronic devices, since the electrical resistance of devices with individual magnetic organic molecules can be modified by changing the magnetic texture. This has been effectively demonstrated by the giant magneto-resistance (GMR) effect in magnetic multilayers [8, 9]. The superiority of magnetic organic molecules over other organic molecules for electronic devices is that the energy scale relevant for manipulating the spin is orders of magnitude smaller than that involved in manipulating the electron charge in standard transistors. This can translate to molecular devices exhibiting ultra-low power consumption and high speed. Moreover, the powerless non-volatility becomes possible solely in magnetic materials with high Curie temperature. Therefore, an

important branch is evoked and called as *Molecular Spintronics* [10, 11, 12], in which spin effects on electron transport properties are studied and molecular devices are proposed and designed using magnetic organic molecules.

As indicated above, in molecular spintronics the function of a device (e.g. rectification, memory, switching, etc.) is designed to be relied on magnetic textures of magnetic molecules. Thus it is most important to change the magnetic texture of a magnetic molecule in this branch. Moreover, for electronic applications it is desirable to accomplish changes of magnetic textures simply by applying an electric field. This would enable the ultimate-limit manipulation of magnetic textures and open a new pathway to spin-based quantum information processing [13], which have the potential to revolutionize computer technologies. Therefore, we will focus on two mechanisms related to the electrically-induced magnetic crossover in this review. One is based on the effect of electrostatic fields or the Stark effect. The other is closely associated with the electron tunneling through the lowest unoccupied molecular orbital (LUMO) under bias voltages or one added electron on magnetic molecules under gate voltages. Greater details are in the following.

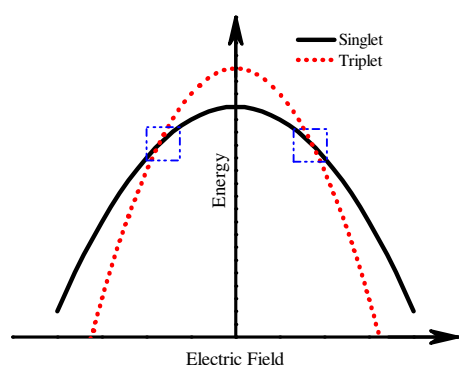## 2. Magnetic crossover achieved by electrostatic Stark effect

Figure 1. (color online). Schematic show for the electric-field induced spin crossover from singlet to triplet based on the second-order Stark effect. The squares mark the crossover points.
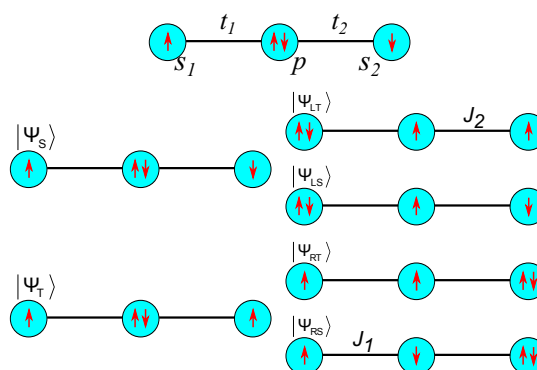

Figure 2. (color online). Schematic illustration of the three-center four-electron model for super-exchange. Reproduced with permission from Ref [15]. Copyright © 2009 Nature Publishing Group.

Diefenbach and Kim [14] firstly proposed that the Stark effect can be concerned to accomplish the spin-state crossover by an electric field. In their opinion, an external electrical field perturbs the electronic structure of a molecule. The effect of such a perturbation can be simply associated with the polarizability of the molecule and hence with the Stark effect. For a molecule with no permanent electric dipole, the linear (first-order) Stark effect vanishes, and the correction to the energy is given by the second-order Stark effect, which is proportional to the polarizability α of the molecule and to the square of the electric field $\mathbf{E}$ strength, i.e. $E_{el} = -\frac{1}{2}\alpha\mathbf{E}^2$. This relation applies to the ground spin states as well as to excited spin states, whereby each spin state responds differently to the perturbation and the spin-state crossover could be realized by an external electric field. As an example, their first-principles studies demonstrate that the ground state of the complex $Ba_2(C_6H_6)$ is changed from a nonmagnetic singlet to a magnetic triplet by an uniform external electric field, as shown by Fig. 1. This result lays the basis for the electrically-controlled manipulation of magnetism by means of the Stark effect. In addition, they suggest that a good candidate for a molecular magnetic switch must process the following

conditions: i) the polarizability of the molecule must be high, and correspondingly, the gap between HOMO (highest occupied molecular orbital) and LUMO must be small, such that the electronic structure of the molecule is easily and distinctively perturbed by an external electric field; ii) the molecule must possess a nonmagnetic ground state (GS) with a magnetic excited state (ES) in close proximity (a very low GS-ES gap).

Similarly based on the Stark effect, Sanvito and co-workers [15] demonstrate that the sign of the exchange coupling between the two magnetic centers can be altered by an electric field. In their work, a simple model for super-exchange shown in Fig. 2 is used to illustrate the effect of an electric field on the sign of the exchange coupling between the two magnetic centers. The dependence of the energy gain on the electric field is accordingly depicted by

$$\Delta E_{GS}^{S/T} \sim \Delta E_{GS}^{S/T}(0) + \frac{1}{2a_0}p_{GS}^{S/T}V + \frac{1}{4a_0}\alpha_{GS}^{S/T}V^2, \tag{1}$$

and the electrical dipole moment and the polarizability are respectively defined as

$$p_{GS}^{S/T} = \frac{ea_0}{4}\left(\frac{t_1^2}{(\delta_{12}^{\pm})^2} + \frac{t_2^2}{(\delta_{21}^{\pm})^2}\right), \tag{2}$$

$$\alpha_{GS}^{S/T} = \frac{e^2a_0}{4}\left(\frac{t_1^2}{(\delta_{12}^{\pm})^3} + \frac{t_2^2}{(\delta_{21}^{\pm})^3}\right). \tag{3}$$

Here, a_0 is the distance between the magnetic centers and the bridge, and the quantities $\delta_{ij}^{\pm} = E_i \pm J_j$ are the energies of the four excited states $|\Psi_{\alpha\beta}\rangle$ measured with respect to the energy of $|\Psi_S\rangle$ or $|\Psi_T\rangle$. E_i equals to $\Delta_{s_i} + U_{s_i} - U_p$, with U_{s_i} and U_p being the Coulomb charging energies of the s_i magnetic center and the bridge; Δ_{s_i} being the difference of their on-site energies. The four excited states $|\Psi_{\alpha\beta}\rangle$ depend on whether the hopping is to the left or to the right center (α=L, R), and whether the final molecular state is in an overall singlet or triplet state (β=S, T). The hopping integrals t, from the bridge to the magnetic center, differ for the two centers (i.e. t_1 and t_2), since this model is assumed to be generally asymmetric. As an example, their density-functional studies clearly show that a crossover of the magnetic coupling is accomplished by an uniform external electric field in the complex $MeO-CoCp_2-Ac-CoCp_2$ with a large permanent electric dipole. Moreover, they show that the critical field for the magnetic crossover can be engineered by using an appropriate choice of substituents to attach to the basic magnetic molecule. Such a strategy for the synthesis seems much simpler than the one needed for making the molecules with large electron density necessary for a crossover driven by the second-order Stark shift.

The above two works prove that electrical manipulations of magnetic textures can be realized by means of the Stark effect. However, such magnetic crossovers are just achieved in isolated molecules. In molecular devices or molecular junctions, the performance of the Stark effect is possibly different from that in isolated molecules, due to the presence of the metallic electrodes and the coupling of the molecule with the electrodes. Particularly, the condition for magnetic crossovers in molecular junctions may be greatly different from that in isolated molecules. To explicitly clarify the effect of the electrodes, we build a model junction [16], where a single magnetic molecule $Fe_2(acpypentO)(NCO)_3$ is sandwiched between two Au(100) nanoelectrodes [see Fig. 3 (a)]. Our investigations by density-functional theory plus the Keldysh nonequilibrium Green's function method demonstrate that the energy of this system is almost symmetrically raised as the bias voltage increases, which is displayed in Fig. 3 (b). This indicates a negative effective polarizability of the molecular junction, opposite to the positive polarizability of an isolated molecule. More importantly, there are some energy crosspoints between the ferromagnetic (FM) configuration and the antiferromagnetic (AFM) configuration around 0.4
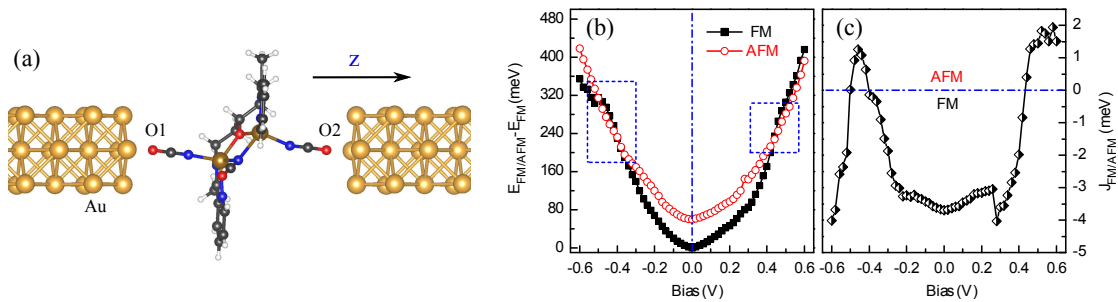
Figure 3. (color online). (a) the model molecular junction of $Fe_2(acpypentO)(NCO)_3$; (b) the relative energy $[E_{FM/AFM} - E_{FM}(V_B = 0)]$ as the function of the bias voltage; (c) the magnetic-coupling constant $[J_{FM/AFM} = (E_{FM} - E_{AFM})/S_{max}^2]$ as the function of the bias voltage. S_{max} is the maximum total spin of the molecule. Reproduced with permission from Ref [16]. Copyright © 2012 American Physical Society.

V [see Fig. 3 (c)] because of $\alpha_{FM} < \alpha_{AF} < 0$. In other words, the magnetic crossover from FM to AFM is realized by applying a certain bias voltage in our built molecular junction. On the contrary, in the isolated $Fe_2(acpypentO)(NCO)_3$ molecule no energy crosspoints are observed between the ground-state (GS) FM configuration and the excited-state (ES) AFM configuration due to $\alpha_{FM} > \alpha_{AF} > 0$. From these results, the electrodes and the molecule-electrode couplings indeed have great impact on the Stark effect in a molecular junction, and the sign of the effective polarizability in molecular junctions can be opposite to that in the isolated molecules. Moreover, the crossover from the GS magnetic configuration to the ES magnetic configuration is never observed when electric fields are applied to isolated molecules of $|\alpha_{GS}| > |\alpha_{ES}|$, but it can be realized if electric fields (or bias voltages) are applied to molecular junctions of these molecules sandwiched between two electrodes.

Finally, it is necessary to point out that the prediction of a magnetic crossover is just based on the relative energies of the two magnetic textures in the above description. In practice, the magnetic crossover also depends on the transition probabilities from one magnetic texture to another. An indication for this probability is related to the off-diagonal elements of the spin-orbital coupling matrix [14] or a non-spin-conversing interaction such as hyperfine interaction with nuclear spins [15].

3. Magnetic transition associated with one added electron on molecules

Recently, three well-established experiments report that the transition between low spin and high spin can be realized just by applying bias voltages to molecular junctions with an individual SCO molecule sandwiched between two metallic surfaces [17, 18, 19], which is a great advance in molecular spintronics. To explain these bias-induced spin transitions from low spin to high spin, several possible mechanisms have been suggested. For example, local resistive heating due to inelastic scattering of tunneling electrons or Joule effect may trigger this spin transition [17, 18]; the stability of the two spin states may be influenced by Stark effect [14, 15, 16] or other electrostatic field effects; electron-induced excited spin state trapping may play a key role in this spin transition, analogous to light-induced excited spin state trapping [19, 20]. As a matter of fact, the spin transition from low spin to high spin is only observed by applying a certain negative bias voltage in the two experiments [17, 19], but not by any positive bias voltage. Due to this feature, the Joule-effect mechanism could not be the underlying cause of these two bias-induced spin transitions, because inelastic scattering of tunneling electrons is present at both bias polarities. On the other hand, electrostatic field effects could also be hardly responsible for these bias-induced spin transitions, which has been directly confirmed by

Gopakumar *et al* [19]. For the last possibility, its details have been far from clear, such as the information of excited states, its definite effect on the spin transition, and the explanation for the dependence of spin transition on the bias polarity, etc.
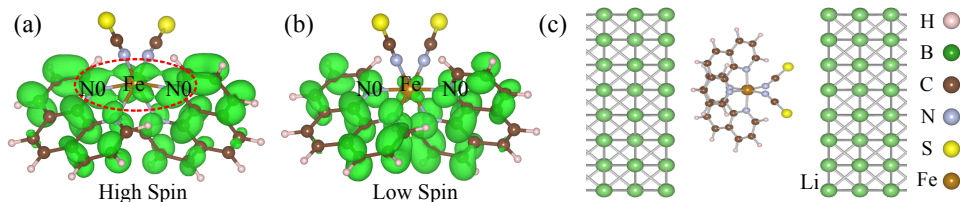

Figure 4. (color online). (a) and (b) the real-space distributions of the added electron in the high-spin and low-spin phases of $Fe(phen)_2(NCS)_2$. The circle marks the p-d hybridization between N0 and Fe. (c) the molecular junction of $Fe(phen)_2(NCS)_2$ sandwiched between two metallic leads. The 'phen' and 'NCS' groups are respectively connected to the left and right electrodes. Reproduced with permission from Ref [21].

Our latest work has explicitly revealed the mechanism for the bias-induced spin transition from low spin to high spin [21]. In this work, we propose that the bias-induced spin transition from low spin to high spin is associated with the electron tunneling through the LUMO of SCO molecules or one added electron on these molecules. To prove such a proposal, two steps are required: i) one added electron on the SCO molecule can accomplish the spin transition from low spin to high spin; ii) one electron can be added to the SCO molecule when a certain bias voltage is applied to a molecular device. Firstly, our density-functional studies show that the spin transition from low spin to high spin is indeed accomplished by adding one electron to the SCO molecule (e.g. $Fe(phen)_2(NCS)_2$). Moreover, by analyzing the related data, this one electron induced spin transition is ascribed to the respective occupations of a p-d bonding and a p-d non-bonding states in the high-spin and low-spin phases, as displayed in Fig. 4 (a) and (b). Secondly, our electron transport studies prove that one electron can be added to the central SCO3 molecule by applying negative bias voltages to our built molecular junction of an individual $Fe(phen)_2(NCS)_2$ [see Fig. 4(c)], but one added electron is hardly realized under positive bias voltages. That is to say, one added electron on the central SCO3 molecule is determined by the bias polarity in this junction. This fact is directly related to the inherently unequal couplings of the molecule with the two electrodes, indicated by that different groups of the molecule are contacted with the left and right electrodes. Here, it is pointed out that our built junction is similar to the experimental junction [17], and the left (right) electrode can be equivalent to the STM tip (substrate). Negative (positive) bias voltages are defined to raise the electrochemical potential of the left (right) electrode with respect to the right (left) electrode, which is equivalently the same with the definition of the bias polarity in this experiment as well. Based on such two-step studies, one can easily appreciate the spin transition from low spin to high spin induced by bias voltages, especially the dependence of spin transition on bias polarity in the experiment.

4. Conclusions
In this review for electrical control of molecular-scale magnetisms, two mechanisms are illustrated: one is based on the electrostatic Stark effect, the other is related to the electron tunneling through the LUMO under bias voltages or one added electron under gate voltages. For the first one, it is emphasized that the electrodes have great impact on the Stark effect in a molecular junction. As a consequence, the magnetic crossover of a molecule, absent (present) in an isolated situation, probably succeeds (fails) in a molecular device. As for the second one,

the fundamental cause for the magnetic crossover is that different p-d states are occupied at different magnetic phases under bias or gate voltages. Based on this mechanism, one can well appreciate the spin transition dependent on the bias polarity. Moreover, it will also facilitates rational and efficient design of molecular devices (e. g. transistors, memories) using SCO molecules. Finally, although some advances have been made in exploring mechanisms related to electrically-induced magnetic transitions, it is still necessary to uncover more other related mechanisms, and particularly, it is more important to design molecular spin devices by taking full advantage of these mechanisms in experiments.

Acknowledgments

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