Switching of a quantum dot spin valve by single molecule magnets

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We explore theoretically the spin transport in nanostructures consisting of a gold quantum dot bridging nonmagnetic electrodes and two Mn12-Ph single molecule magnets (SMMs) that are thiol bonded to the dot but are not in direct contact with the electrodes. We find that reversal of the magnetic moment of either SMM by the application of a magnetic field leads to a large change in the resistance of the dot, i.e., a strong spin-valve effect.

We show that this phenomenon arises from the following physical principle: The spin-dependent molecular orbitals that extend over the dot and both SMMs change drastically when the magnetic moment of either SMM is reversed, resulting in a large change in the conduction via those orbitals. The same physics may also be responsible for the spin-valve phenomena discovered recently in carbon nanotube quantum dots with rare-earth SMMs [M. Urdampilleta et al., Nat. Mater. 10, 502 (2011)].

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Molecular spintronics combines two active fields of study: molecular electronics and spintronics. The ultimate goal of this field is to control the electronic spin and charge on the molecular scale where quantum effects emerge. In the search for new molecular spintronic nanodevices, single molecule magnets (SMMs) appear to be natural candidates. A SMM is a molecular-size nanomagnet that exhibits quantum behavior such as quantum tunneling of the magnetization (QTM), Berry phase interference, and magnetoresistance phenomena. Spin-valve-like effects have also been predicted in SMMs with magnetic electrodes. In a recent advance, experimental detection of spin-valve-like behavior has been reported in a system with nonmagnetic electrodes and SMMs coupled to a (nonmagnetic) carbon nanotube quantum dot. It was suggested that this behavior was due to the magnetic moments of individual SMMs bound to the dot reversing at different values of the applied magnetic field as the field was swept. It was proposed that this would result in changes in the resistance of the dot due to modulation of the spin transport through the dot, i.e., a spin-valve effect. However, to our knowledge, a relevant quantitative theory has been lacking. Thus the physics responsible for the observed behavior has not been definitively identified.

Here we explore spin-valve phenomena in devices with a pair of SMMs bound to a nonmagnetic quantum dot bridging nonmagnetic electrodes theoretically. Our results reveal that spin-valve functionality in such devices can arise from current carrying electronic resonant states that extend over the whole device, including the quantum dot and both SMMs that are bound to it. When the magnetic moment of one of the SMMs is reversed, these states, being spin dependent, are strongly modified. Consequently the resistance of the device changes. Thus the system exhibits a spin-valve effect. Thus our findings demonstrate a principle for spin-valve operation that differs fundamentally from that based on exchange-modulated tunnel barriers that was put forward in Ref. 6. We also show that this spin-valve phenomenon is not limited to devices with carbon quantum dots and rare-earth-based SMMs as in the recent experiment. We predict such spin-valve behavior also in other devices having different properties. These include, for example, the much better electronic transport characteristics (absence of Coulomb blockade) exhibited by spin valves with gold quantum dots and some transition-metal-based single molecule magnets.

We consider SMMs based on Mn12. Mn12 contains four Mn4+ ions surrounded by a nonplanar ring of eight Mn3+ ions. The large spin S = 10 and magnetic anisotropy barrier (up to ~6.1 meV along the easy axis) lead to high blocking temperatures (~3.5 K) and long relaxation times. These properties make the Mn12 family promising candidates for molecular spintronics. However, Mn12 deposition on different surfaces has met with varying degrees of success. Nevertheless, Mn12 has been chosen to explore the spintronics of SMM transistors experimentally and signatures of magnetic states were observed.

We present quantum transport calculations that demonstrate a spin-valve effect in nanodevices that consist of two Mn12O12(CO2C6H4SH3)16 (henceforth Mn12-Ph) SMMs coupled to a small gold quantum dot containing 15 gold atoms, as shown in Figs. 1(a) and 1(b). Although the SMMs do not lie directly in the current path in these devices, we shall show that the relative orientation of their magnetic moments can strongly influence the electric current passing through the device. Thus, we predict these systems to exhibit a strong spin-valve effect. We also found similar results for other gold nanocluster sizes and geometries. Therefore, the spin-valve effect that we predict here does not depend critically on the gold nanocluster size. The nonmagnetic leads are modeled as a small number of semi-infinite one-dimensional ideal channels that represent macroscopic electron reservoirs (as in previous studies of electron and spin transport through single molecules with gold contacts) to simulate moderately weak coupling between the nanodevice and electrodes.

The geometries of our nanodevices are shown in Figs. 1(a) and 1(b). The Mn-containing magnetic cores of the Mn12-Ph molecules are surrounded by organic ligands that are terminated by thiol-methyl (SCH3) groups, the methyl (CH3) being absent where a sulfur atom forms a chemical bond with the gold nanocluster. SMMs can bond to a gold nanocluster in various configurations, two of which we consider here: In
SMMs are misaligned so that their easy axes are not collinear. The SMM's easy axes are (a) aligned and parallel to the $z$ axis, (b) misaligned by 36°. The red circles indicate the gold atoms coupled to leads. Atoms are color labeled: gold (orange), manganese (red), carbon (gray), sulfur (yellow), oxygen (blue), and hydrogen (white). (c) In the thermally activated process (red arrows) to the magnets (c), (d). The SMM's easy axes are (a) aligned and parallel (a), (b) and the dynamics of the magnetization in single molecule magnets. These measurements reveal that the SMM. These measurements reveal that the SMM's easy axes are (a) aligned and parallel (a), (b) and the dynamics of the magnetization in single molecule magnets. Therefore, for simplicity, in what follows we will refer to this as the “parallel configuration” (PC) whether the easy axes of the two SMMs are strictly collinear as in Fig. 1(a) or misaligned as in Fig. 1(b). The system will remain in the PC until the external magnetic field switches direction; then at some point one of the SMMs will flip its spin direction and the system will go into the antiparallel configuration (APC). Because of the energy barriers that hinder reversal of the magnetic moments of the SMMs, these parallel and antiparallel spin configurations can be maintained for some time after the magnetic field is set to zero at sufficiently low temperatures. Therefore, for simplicity, in what follows we will consider transport through the structures shown in Figs. 1(a) and 1(b) in the parallel and antiparallel spin configurations at zero externally applied magnetic field.

Our SMM Hamiltonian is $H^{\text{SMM}} = H^{\text{EH}} + H^{\text{Spin}} + H^{\text{SO}}$, as introduced in Refs. 9 and 10. Here $H^{\text{EH}}$ is the extended Hückel Hamiltonian.27 The spin Hamiltonian $H^{\text{Spin}}$ gives rise to the magnetic polarization of the molecule. Spin-orbit coupling is described by $H^{\text{SO}}$. In extended Hückel theory the basis is a small set of Slater-type atomic valence orbitals $|\Psi_i\rangle$; $|\Psi_{ij}\rangle$ is the $i$th orbital of the $j$th atom. In this basis the extended Hückel Hamiltonian elements are $H_{ij} = \langle \Psi_i | \hat{H}_{ij} | \Psi_j \rangle$, where $\hat{H}_{ij} = D_{ij} \epsilon_{ij} - \frac{\epsilon_{ij}}{2}$, where $D_{ij}$ are orbital overlaps, $\epsilon_{ij}$ is the experimentally determined negative ionization energy of the $i$th valence orbital of the $j$th atom, and $K$ is chosen empirically for consistency with experimental molecular electronic structure data. In our calculations $K = 1.75 + \Delta_{ij}^{valence} - 0.75\Delta_{ij}^{exchange} - \Delta_{ij}^{spin}$, where $\Delta_{ij}^{valence} = \epsilon_{ij}^{valence} - \epsilon_{ij}^{orbital}$, $\epsilon_{ij}^{valence}$ is the orbital energy of the $i$th orbital of the $j$th atom, and $\epsilon_{ij}^{orbital}$ is the orbital energy of the $i$th orbital of the $j$th atom, as was proposed in Ref. 28. The spin Hamiltonian matrix elements between valence orbitals $i$ and $i'$ of atoms $\alpha$ and $\alpha'$ with spin $s$ and $s'$ are defined by

$$\langle i \alpha | \hat{H}^{\text{Spin}} | i' s' \alpha' \rangle = D_{i \alpha i' \alpha'} (A_{i \alpha} + A_{i' \alpha'})(s) |\hat{n} - \hat{S}^z| s'| / \hbar,$$

where $\hbar$ is a unit vector aligned with the magnetic moment of the SMM. The S is the one-electron spin operator, $A_{i \alpha}$ and $A_{i' \alpha'}$ are parameters chosen so that the Hamiltonian gives rise to the correct spin for transition-metal ions in the SMM ground state. Spin-orbit coupling is responsible for the magnetic anisotropy of SMMs. We evaluate the matrix elements of the spin-orbit coupling Hamiltonian $H^{\text{SO}}$ approximately from the
standard expression\(^{29}\) \(H^{SO} = \sigma \cdot \mathbf{V}(\mathbf{r}) \times \mathbf{p} h/(2mc)^2\), where \(\mathbf{p}\) is the momentum operator, \(\mathbf{V}(\mathbf{r})\) is the electron Coulomb potential energy, \(\sigma = (\sigma_1, \sigma_2, \sigma_3)\), and \(\sigma_1\), \(\sigma_2\), \(\sigma_3\) are the Pauli spin matrices. Evaluating the matrix elements of \(H^{SO}\) between valence orbitals \(i\) and \(i'\) of atoms \(\sigma\) and \(\sigma'\) with spin \(s\) and \(s'\) we find

\[
\langle \sigma \sigma' \| H^{SO} \| \sigma' \sigma \rangle \approx E_{\sigma \sigma', \sigma' \sigma} \delta_{\sigma \sigma'} + (1 - \delta_{\sigma \sigma'}) \sum_j (D_{\sigma \sigma' j \alpha} E_{\sigma \sigma', j \alpha} + [D_{\sigma' \sigma j \alpha} E_{\sigma', j \sigma}]^*).
\]

The first term on the right-hand side is the intra-atomic contribution, the remaining terms are the inter-atomic contribution, and

\[
E_{\sigma \sigma', \sigma' \sigma} = \langle \sigma_\alpha, l_\alpha, d_\alpha, s| \mathbf{L}_\alpha| \sigma_\alpha, l_\alpha, d_\alpha, s'\rangle \times \langle R_\alpha, d_\alpha| \frac{1}{2m\epsilon^2} \frac{1}{\mid \mathbf{r} - \mathbf{r}_\alpha \mid} \frac{dV((\mathbf{r} - \mathbf{r}_\alpha))}{d(\mid \mathbf{r} - \mathbf{r}_\alpha \mid)} | R_\alpha, d_\alpha \rangle \delta_{l_\alpha l_\alpha'},
\]

where the atomic orbital wave function \(\Psi_{\sigma_\alpha}\) has been expressed as the product of a radial wave function \(R_{\alpha, l}\) and directed atomic orbital \(| \sigma_\alpha, l_\alpha, d_\alpha, s\rangle\). Here \(l_\alpha\) is the angular momentum quantum number and \(d_\alpha\) may be \(s, p_x, p_y, p_z, d_{x^2}, d_{xz}, \ldots\) depending on the value of \(l_\alpha\), while the radial integrals are the spin-orbit coupling constants.

This model describes the fundamental properties of single Mn\(_{12}\) SMMs quite well, yielding calculated values of the SMM total spin, the magnetic moments of the inner and outer Mn atoms, the magnetic anisotropy barrier, and the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap that are consistent with experiment.\(^{5,10}\)

Our transport calculations are based on Landauer theory and the Lippmann-Schwinger equation. According to the Landauer formula, \(G = \frac{e^2}{h} T(E_F)\), the conductance is proportional to the total transmission electron probability through the device at the Fermi energy \(E_F\) given by \(T(E, V) = \sum_{i,j} |t_{ij}|^2 \langle t_{ij}\rangle^2\). Here \(E\) is the incident electron’s energy, and \(t_{ij}\) is the transmission amplitude from \(i\)th electronic channel of left lead with spin \(s\) and velocity \(v_{ij}\) to the \(j\)th electronic channel of the right lead with spin \(s'\) and velocity \(v_{ij'}\). We find the transmission amplitudes \(t\) by solving the Lippmann-Schwinger equation.

Figure 2(a) shows the calculated total electron transmission probability through the device in Fig. 1(a) as a function of the electron energy for the two SMMs with collinear easy axes and their magnetic moments in the parallel and antiparallel configurations. The PC and APC transmission probabilities are very similar for energies below \(0.46\) eV. More importantly, the PC and APC transmission probabilities differ significantly at energies around \(0.5\) eV, where the LUMOs of the two SMMs and molecular orbitals (MOs) close in energy to the LUMOs are located. [Note that the broad peak at energies near \(0.38\) eV is due to MOs located mainly on the gold nanocluster as it is present also in the transmission probability of the gold nanocluster in the absence of the SMMs, the blue curve in Fig. 2(a). For this reason the PC and APC transmission probabilities around this energy are very similar.]

Figure 2(b) presents the calculated PC and APC transmission probabilities of the same device as for Fig. 2(a) but with a positive gate voltage applied to the SMMs; the gold nanocluster is not gated. Here the gating has shifted the SMM LUMOs and MOs close in energy to the LUMOs to the vicinity of the Fermi energy of gold, indicated by the dotted vertical line in Fig. 2. Because the PC and APC transmission probabilities at the Fermi energy now differ significantly, the system exhibits a substantial magnetoresistance ratio \(MR = (G_{PC} - G_{APC})/G_{APC}\). Since \(G_{APC} = \frac{e^2}{h} T_{APC}(E_F)\), therefore \(MR = [T_{PC}(E_F) - T_{APC}(E_F)]/T_{APC}(E_F)\).

Note that although the transmission resonances around the Fermi energy in Fig. 2(b) resemble those around \(0.5\) eV in Fig. 2(a) qualitatively, the gating has modified the detailed structure of the transmission peaks and dips, as should be expected for a mesoscopic quantum interference effect. We find similar magnetoresistance ratios (MRs) for SMMs with noncollinear easy axes as is seen in Fig. 2(c), where we present
energy range seen in Fig. 4(a), and the consequent spin-valve functionality transmission probability functions for the two configurations are different. This results in the differing total electron antiparallel configurations of the SMM magnetic moments. The spin resolved densities of states for the parallel and DOS and resonant peaks in transmission probability plots.

Figures 4(b) and 4(c) show the densities of states (DOS) to the SMMs in the parallel and antiparallel configurations. These results show that gating is able to transform such SMMs' magnetic moments. Gate voltage, \( V_g \approx 0.5 \) eV, is applied to the SMMs. Arrows in (b) and (c) indicate spin up and spin down. The axis of spin quantization is the \( z \) axis shown in Fig. 1(a). (d)–(g) Isosurface plots of molecular orbitals of this spin-valve system. The letters d, e, f, and g in (b) and (c) mark the corresponding MOs that are depicted below. Red (blue) represents the spin up (spin down) isosurface.

In Fig. 4(a) the spin-valve effect is most pronounced in the energy range \(-0.02\) to \(0.03\) eV, where the transmission probabilities for the device shown in Fig. 1(b) gated so as to bring the SMM LUMOs and nearby MOs close to the gold Fermi level. Similar MRs are expected regardless of the SMMs’ misalignment angle.

In summary, spin-valve functionality is a much sought property of molecular nanostructures. We have proposed a molecular spintronic prototype, based on transition-metal \( \text{Mn}_{12} \)-Ph SMMs coupled to a gold quantum dot, and predict it to exhibit a large magnetoresistance spin-valve effect due to resonant transport. The transport resonances are mediated by electronic states that extend over the entire system due to hybridization between the gold cluster and spin-polarized SMM molecular orbitals with a strong presence on the SMM’s magnetic cores to the gold nanocluster. This direct connection favors a hybridization between SMMs and gold nanocluster. In cases where this hybridization occurs, resonant and off-resonant transport is expected. On the other hand, these ligands bridge between the individual SMMs’ magnetic cores and the gold nanocluster, causing a strong interaction between the SMMs’ magnetic cores which leads to the spin-valve effect predicted by these calculations. By contrast, the transport resonances due to the MOs that are well separated [Figs. 4(f) and 4(g)] from the gold nanocluster are narrow and the calculated spin-valve effect due to these resonances is confined to very narrow energy ranges.

In Fig. 4(a) the DOS are projected onto carbon atoms of the system for (b) parallel and (c) antiparallel configurations of the two SMMs’ magnetic moments. Gate voltage, \( V_g \approx 0.5 \) eV, is applied to the SMMs. Arrows in (b) and (c) indicate spin up and spin down. The axis of spin quantization is the \( z \) axis shown in Fig. 1(a). (d)–(g) Isosurface plots of molecular orbitals of this spin-valve system. The letters d, e, f, and g in (b) and (c) mark the corresponding MOs that are depicted below. Red (blue) represents the spin up (spin down) isosurface.