Ligand-based transport resonances of single-molecule magnet spin filters: Suppression of the Coulomb blockade and determination of the orientation of the magnetic easy axis

Fatemeh Rostamzadeh Renani and George Kirczenow

Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

(Dated: November 23, 2011)

We investigate single molecule magnet transistors (SMMTs) with ligands that support transport resonances. We find the lowest unoccupied molecular orbitals of Mn$_{12}$-benzoate SMMs (with and without thiol or methyl-sulfide termination) to be on ligands, the highest occupied molecular orbitals being on the Mn$_{12}$ magnetic core. We predict that SMM transistors identified in this way we predict the molecular easy axis to be approximately parallel to the direction of current flow. Thus the present theory provides a practical way to use standard non-spin-resolved current measurements to determine the orientation of the SMM magnetic easy axis, over which there was no control in SMM transistor experiments to date. Moreover, we predict these magnetically oriented SMM transistors to be effective spin filters at low and moderate source-drain voltages.

The results that we present are based on the semi-empirical extended Hückel tight-binding model of quantum chemistry that we generalize in this paper to include spin polarization and spin-orbit coupling. For Mn$_{12}$ SMMs (both neutral molecules and negatively charged ions) the present model yields results consistent with experiment for the total spin of the SMM, for the spins of the individual Mn ions, for the direction of the magnetic easy axis, for the size of the magnetic anisotropy barrier (MAB), for the size of the molecular HOMO-LUMO gap and for the spins of the HOMO and LUMO states. This overall degree of agreement with experiment obtained with the present model is comparable to or better than that achieved with DFT calculations corrected by inclusion of the adjustable Hubbard $U$ parameter. However, calculations based on the present model are much less compute intensive than those based on DFT. Thus, we are able to study transport in larger molecules than are readily accessible to DFT computations and therefore, unlike in previous theoretical studies, to include complete sets of ligands none of which have been shortened or replaced by hydrogen atoms.

Our SMM Hamiltonian is $H_{\text{SMM}} = H_{\text{EH}} + H_{\text{spin}} + H_{\text{SO}}$. Here $H_{\text{EH}}$ is the extended Hückel Hamiltonian. 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 $|\psi_{\alpha\alpha}\rangle$; $|\psi_{\alpha\alpha}\rangle$ is the $i^{\text{th}}$ orbital of the $\alpha^{\text{th}}$ atom. The diagonal elements of $H_{\text{EH}}$ are the experimentally determined negative valence orbital ionization energies $\varepsilon_{\alpha}$, $(\psi_{\alpha\alpha}|H_{\text{EH}}|\psi_{\alpha\alpha}) = H_{\text{EH}}^{\alpha\alpha} = \varepsilon_{\alpha}$.
The non-diagonal matrix elements are assumed to be proportional to the orbital overlaps $D_{iα, j′α′} = \langle Ψ_{iα} | Ψ_{j′α′} \rangle$, i.e.,

$$H^{EH}_{iα, j′α′} = D_{iα, j′α′} K^{αα′ + j′j}$$

where $K$ is chosen empirically for consistency with experimental molecular electronic structure data. In our calculations, $K = 1.75 + 0.75A_{iα, j′α′} - 0.75D_{iα, j′α′}$ where $A_{iα, j′α′} = \frac{ε_{iα} - ε_{j′α′}}{ε_{iα} + ε_{j′α′}}$.

For non-magnetic systems, transport calculations based on extended Hückel theory have yielded elastic and inelastic conductances in agreement with experiments for molecules thiol-bonded to gold electrodes and have also explained transport phenomena observed in scanning tunneling microscopy (STM) experiments on molecular arrays on silicon as well as electroluminescence data from current-voltage characteristics and STM images of molecules on complex substrates.

The extended Hückel Hamiltonian $H^{EH}$ does not describe spin polarization whereas the Mn$_{12}$ SMMs the four inner and eight outer Mn ions are spin polarized with antiparallel spins. In our model, $H^{SO}$ addresses this issue. We define its matrix elements $⟨iσα|H^{spin}|i′σα′⟩ = H^{spin}_{iσα, i′σα′}$ between valence orbitals $i$ and $i'$ of atoms $α$ and $α'$ with spin $s$ and $s'$ by

$$H^{spin}_{iσα, i′σα′} = D_{iα, i′α′}(A_{iα, i′α′})|s\hat{n} \cdot S(s')|/2\hbar$$

$$A_{iα} = \begin{cases} A_{inner} & \text{for inner Mn $d$-valence orbitals} \\ A_{outer} & \text{for outer Mn $d$-valence orbitals} \\ 0 & \text{otherwise} \end{cases}$$ (1)

Here $\hat{n}$ is a unit vector aligned with the magnetic moment of the SMM, and $S$ is the one-electron spin operator. $A_{inner}$ and $A_{outer}$ are parameters chosen so that in the Mn$_{12}$ ground state the spin of each inner (outer) Mn is $S_{inner(outer)} \equiv -\frac{\tilde{S}}{2} (+2)$.

Spin-orbit coupling is also not included in extended Hückel theory. However, it is responsible for the magnetic anisotropy of SMMs. We therefore generalize extended Hückel theory to include spin-orbit coupling by evaluating approximately the matrix elements of the spin-orbit coupling Hamiltonian $H^{SO}$ starting from the standard expression

$$H^{SO} = \sum_{i,j}(1/\hbar)\not{s}\times \not{p} \phi_i \phi_j$$

where $\phi_i$ and $\phi_j$ are the eigenstates of $H^{EH}$ and the sum is over all occupied states. Since $H^{SO}$ represents electron-electron interactions at a mean field level, the second summation on the right hand side is required to avoid double counting the corresponding interaction energy.

Experimental estimates of the spin-orbit coupling constant for Mn $d$-orbitals have been in the range 0.023–0.051 eV, while theoretical estimates have been in the range 0.038–0.055 eV. In this paper for Mn atoms we use the value 0.036 eV, which is consistent with the experimental and theoretical values. We find that the spin-orbit coupling constants of the other atoms do not affect the SMMs’ properties significantly and that the intra- and inter-atomic terms in Eq. (2) make contributions of the same order of magnitude to the magnetic anisotropy barriers of Mn$_{12}$ SMMs. In this work the values of $H^{EH}_{iα, j′α′}$ and $D_{iα, j′α′}$ that enter the extended Hückel model, Eqs. (1) and (2), were adopted without change from Refs. 14 and 15. The molecular geometries that we studied were based on the experimentally measured geometry of Mn$_{12}$-Ph modified as necessary by adding thiol or methyl sulfide groups to the ligands. Thus the only free parameters in the present theory are the $A_{iα}$ of Eq. (1) that control the spin polarizations of the Mn atoms; we chose $A_{iα} = 3.0$ eV and $A_{outer} = -3.5$ eV. For these parameter values in the Mn$_{12}$-Ph ground state we find the inner and outer Mn ions to have spins $-1.6$ and $1.99$, the SMM to have a total spin of $10$, and the calculated MAB to be $2.50$ meV, all consistent with experiment.

The calculated densities of states projected on the inner and outer Mn atoms, and carbon atoms of Mn$_{12}$-Ph are shown in Fig. 1. The HOMO and nearby levels are on the outer Mn and are filled with spin-up electrons (parallel to the total spin), consistent with $S_{outer} = +2$. The occupied inner Mn states are filled with spin-down electrons consistent with $S_{inner} = -\frac{5}{2}$. The carbon atoms are weakly spin polarized. The calculated HOMO-LUMO energy gap is $\sim 0.7$ eV. (Note that experimental and theoretical estimates for the Mn$_{12}$ family range from a few tenths of an electron Volt to more than 1 eV). As is seen in Fig. 1, our calculation predicts the LUMO of Mn$_{12}$-Ph to be mainly on the carbon atoms of the ligands. There is at this time no direct experimental evidence as to whether the LUMO of Mn$_{12}$-Ph is located on the ligands as in Fig. 1 or on the Mn$_{12}$ core of the molecule. However, experimental data...
measurements of the MAB carried out on the neutral \(^{27}\) and negatively charged \(^{29}\) \(\text{Mn}_{12}\)-Ph species yielded values of 3.3 and 2.41 meV, respectively, a difference of only 27\%. Since the main source of the MAB of \(\text{Mn}_{12}\) is the Jahn–Teller distortion of the \(\text{Mn}_{12}\) core of the molecule\(^5\) this insensitivity of the MAB to the oxidation state of the molecule is consistent with the added electron of the negatively charged species residing mainly on the ligands rather than on the \(\text{Mn}_{12}\) core, as one might expect if the LUMO of the neutral molecule is on the ligands as in Fig. 1. Our calculations also predict only a small change in the MAB when an electron is added to the neutral \(\text{Mn}_{12}\)-Ph molecule, since in our model the added electron locates primarily on the ligands rather than on the magnetic molecular core. Our prediction that the LUMO is on the ligands (i.e., the benzoate groups, including both their carbon and oxygen atoms) and not on the \(\text{Mn}_{12}\) core is also consistent with the large 3.3–3.6 eV electron affinity of the benzoate species\(^{30,31}\).

The ligands of SMMs that are studied in transport experiments with gold electrodes are normally thiolated and we shall therefore focus our attention on \(\text{Mn}_{12}\)-Ph-Th, i.e., \(\text{Mn}_{12}\)-Ph terminated with methyl sulfide (SCH\(_3\)) groups, the methyl being displaced by gold when the molecule bonds to the contacts. The calculated densities of states of \(\text{Mn}_{12}\)-Ph-Th (and of \(\text{Mn}_{12}\)-Ph with thiol end groups) projected on the Mn and C atoms are similar to those shown in Fig. 1 for \(\text{Mn}_{12}\)-Ph. The locations and spins of the HOMO and LUMO and of orbitals close to these in energy are also similar for \(\text{Mn}_{12}\)-Ph with and without thiol or methyl sulfide end groups. The calculated HOMO, LUMO and another representative molecular orbital close in energy to the LUMO are shown in Fig. 2 for \(\text{Mn}_{12}\)-Ph-Th. The HOMO is located on the magnetic core of the molecule. However, the LUMO and molecular orbitals close in energy to the LUMO are located on ligands, and specifically on those ligands that are oriented approximately parallel to the magnetic easy axis of the molecule which points in the \(z\)-direction in Fig. 2. This finding has important implications for electron and spin transport in \(\text{Mn}_{12}\)-Ph-Th-based SMM transistors: The HOMO and molecular orbitals close in energy to the HOMO have very little overlap with any of the ligands. Therefore all of the ligands that couple the molecule to the contacts act as strong tunnel barriers for transport mediated by the HOMO and molecular orbitals nearby in energy. For this reason transport via the HOMO and molecular orbitals close in energy to the HOMO is predicted to display the classic signature of Coulomb blockade. By contrast if any gold contact bonds to a ligand on which certain molecular orbitals close in energy to the LUMO (for example, that in Fig. 2(c)) have a strong presence, those molecular orbitals will hybridize strongly with the gold contact and therefore transport via that molecular orbital (or orbitals) will not be subject to Coulomb blockade. Furthermore, because these orbitals occupy ligands that are oriented approximately parallel to the molecular easy axis as in Fig. 2, if such transport that is not subject to Coulomb blockade is observed experimentally, then the molecule must be oriented relative to the gold contacts in such a way that the magnetic easy axis is approximately parallel to the direction of current flow through the molecule. We note that although there have been theoretical suggestions previously of possible ways to determine the orientation of the easy axis in a SMM transistor\(^{31,32}\) these suggestions have been difficult to implement in practice and no experimental control over the orientation of the easy axis in SMM transistors has been achieved experimentally to date. The present theory is much more promising in this regard since the experimental observation of the presence or absence of Coulomb

![Figure 1](image1.png)

**Figure 1.** Projected densities of states for majority (spin-up) and minority (spin-down) electrons on Mn and carbon atoms for the isolated \(\text{Mn}_{12}\)-Ph molecule without thiol or methylsulfide end groups.

![Figure 2](image2.png)

**Figure 2.** Wave functions for \(\text{Mn}_{12}\)-Ph-Th (a) spin-up HOMO (b) spin-down LUMO (c) spin-up orbital near LUMO in energy. The magnetic easy axis and total molecular spin are parallel to the \(z\)-axis. Although the LUMO and near LUMO orbitals are mainly on the ligands they are spin polarized due to their small but non-zero overlaps with the magnetic core of the molecule that are visible in (b) and (c).

![Figure 3](image3.png)

**Figure 3.** Calculated spin resolved current parallel (\(\parallel\)) and perpendicular (\(\perp\)) to the easy axis for (a) positive and (b) negative gate voltage vs. bias voltage at zero temperature. The gate potential at the molecule = +0.2 and –0.2V in (a) and (b), respectively.
blockade in single–molecule transistors is currently carried out routinely, and we predict that if Coulomb blockade is observed at negative gate voltages (transport via the HOMO and nearby states) but not at positive gate voltages (transport via the LUMO or nearby states) then the easy axis is approximately parallel to the direction of current flow.

Our transport calculations based on Landauer theory and the Lippmann-Schwinger equation predict Mn$_{12}$–Ph–Th-based SMM transistors with gold contacts to be effective spin filters at low source-drain bias for both positive and negative gate voltages. Representative results for a Mn$_{12}$–Ph–Th molecule bonded to gold contacts via ligands on which near-LUMO orbitals have a strong presence (and therefore the current through the SMM is roughly parallel to the magnetic easy axis) are shown in Fig. 3. Here mainly spin-up electrons are transmitted through the SMM at low bias for both positive (Fig. 3(a)) and negative (Fig. 3(b)) gate voltages. The gradual rise of the current with bias voltage (from ~0.2 to ~0.67V) in Fig. 3(a) is a direct manifestation of the large broadening of the near-LUMO molecular orbitals responsible for transport that is due to the strong hybridization of those orbitals with the gold contacts that also suppresses Coulomb blockade for positive gate bias. By contrast, the abrupt step-like rise to much lower values of the current for negative gate voltages (Fig. 3(b)) is due to the near-HOMO molecular orbitals being very weakly coupled to the gold contacts and therefore being only very weakly broadened, they are subject to Coulomb blockade. For molecules bonded to gold electrodes via ligands that are roughly perpendicular to the easy axis, neither near-LUMO nor near-HOMO orbitals have significant presence on the ligands, see Fig. 2. Thus, for geometries with a current through the SMM that is roughly perpendicular to the magnetic easy axis, the ligands act as strong tunnel barriers for both positive and negative gate voltages (Fig. 3). Coulomb blockade is therefore predicted for both signs of the gate voltage.

In conclusion, previous studies of transport in single molecule magnets have considered the situation where the HOMO and LUMO both reside on the magnetic core of the molecule. Here we have proposed that this need not always be the case, Mn$_{12}$ benzoate with and without terminating methyl–sulfide or thiol groups being a possible example. We have predicted that for these systems the LUMO and molecular orbitals close in energy to the LUMO reside on the organic ligands that are oriented approximately parallel to the magnetic easy axis of the molecule and that when the molecule bonds via these ligands to gold electrodes in a single–molecule transistor, transport via some of the near-LUMO orbitals should not be in the Coulomb blockade regime. For other orientations of the molecule transport via the LUMO and near-LUMO orbitals is predicted be in the Coulomb blockade regime, as is transport via the HOMO and near-HOMO orbitals for all molecular orientations. This effect should make it possible to study experimentally the transport in single molecule magnet transistors that behave as spin filters and in which the orientation of the magnetic easy axis relative to the electrodes is known. In single–molecule magnet transistor experiments to date the orientation of the magnetic easy axis has not been determined although it controls the spin polarization of the current in such devices.

While this work has focused on Mn$_{12}$ benzoate and its derivatives, we expect other single molecule magnets with LUMO and/or HOMO states located on the ligands to exist as well due to the small HOMO-LUMO gaps exhibited by a variety of organic molecules that may be chosen as ligands. For example it is well established that polyacetylene and polythiophene have HOMO-LUMO gaps of 1.4 eV$^{37}$ and 0.85 eV$^{38}$ respectively. Both of these are smaller than the experimentally measured energy gap (~1.8 eV)$^{39}$ between the highest occupied and lowest unoccupied orbitals localized on the cores of the Mn$_{12}$ molecules. It is reasonable to expect oligomers (consisting of several monomers) derived from these polymers to have similarly small HOMO-LUMO gaps. If such oligomers are used as ligands for Mn$_{12}$ SMMs contacted with gold electrodes, the gold Fermi level is expected to lie within the oligomer HOMO-LUMO gap and also within the HOMO-LUMO gap of the Mn$_{12}$ core. Therefore either the HOMO or the LUMO (or both) of the Mn$_{12}$ SMM with such ligands is expected to lie on the ligands.

This research was supported by CIFAR, NSERC, Westgrid and Compute Canada. We thank B. Gates and B. L. Johnson for helpful comments and discussions.

1 For a recent review see G. Kirczenow, in The Oxford Handbook of Nanoscience and Technology, Volume I: Basic Aspects, edited by A. V. Narlikar and Y. Y. Fu, (Oxford University Press, Oxford, U.K. 2010), Chap. 4.
2 D. Gatteschi, R. Sessoli, and J. Villain, Molecular Nanomagnets (Oxford University Press, New York, 2006).
3 L. Bogani and W. Wrnsmorfer, Nature Mater. 7, 179 (2008)
4 H. B. Heersche et al., Phys. Rev. Lett. 96 206801 (2006).
5 M.-H. Jo et al., Nano Lett. 6, 2014 (2006).
6 A. S. Zyazin et al., Nano Lett. 10, 3307 (2010).
7 G.-H. Kim and T.-S. Kim, Phys. Rev. Lett. 92, 137203 (2004); C. Romenke, M. R. Wegewijs, H. Schoeller, Phys. Rev. Lett. 96, 196805 (2006); C. Timm, and F. Elste, Phys. Rev. B 73, 235304 (2006); M. Mi- siorny, L. Weymann, J. Barnas, Phys. Rev. B 79, 224420 (2009); H.-Z. Lu, B. Zhou, and S.-Q. Shen, Phys. Rev. B 79, 174419 (2009); F. Elste, C. Timm, Phys. Rev. B 81, 024421 (2010).
8 C. Timm, Phys. Rev. B 76, 014421 (2007).
9 S. Barraza-Lopez, K. Park, V. García-Suárez and J. Ferrer, J. Appl. Phys. 105, 07E309 (2009); Phys. Rev. Lett. 102, 246801 (2009).
10 C. D. Pemmaraju, I. Runger, S. Sanvito, Phys. Rev. B 80, 104422 (2009).
11 L. Michalak, C. M. Canali, M. R. Pederson, M. Paulsson, and V. G. Benza, Phys. Rev. Lett. 104, 017202 (2010).
12 K. Park, S. Barraza-Lopez, V. M. García-Suárez, and J. Ferrer, Phys. Rev. B 81, 125447 (2010).
13 The results of our systematic studies for members of the Mn$_{12}$ SMM family other than Mn$_{12}$–Ph–Th will be presented elsewhere.
14 J. H. Ammeter et al., J. Am. Chem. Soc. 100, 3686 (1978).
15 The YAEHMOP code implementation of the extended Hückel theory (Ref. 14) by G. A. Landrum and W. V. Glasssey (Source-Forge, Fremont, California, 2001) was used. YAEHMOP does not include spin-orbit coupling.
16 S. Datta et al., Phys. Rev. Lett. 79, 2530 (1997); E. G. Emberly, G. Kirczenow, Phys. Rev. Lett. 87, 269701 (2001); Phys. Rev. B 64, 235412
(2001); J.G. Kushmerick et al., Phys. Rev. Lett. 89, 086802 (2002).
17 D. M. Cardamone and G. Kirczenow, Phys. Rev. B 77, 165403 (2008).
18 F. Demir and G. Kirczenow, J. Chem. Phys. 134, 121103 (2011).
19 G. Kirczenow et al., Phys. Rev. B 72, 245306 (2005); Phys. Rev. B 80, 035309(2009); P. G. Piva et al., Phys. Rev. Lett. 101, 106801 (2008).
20 J. Buker and G. Kirczenow, Phys. Rev. B 78, 125107 (2008).
21 J. Buker and G. Kirczenow, Phys. Rev. B 72, 205338 (2005).
22 See C. Kittel, Quantum Theory of Solids (Wiley, New York, 1963), p. 181.
23 S. Konschuh, M. Gmitra, J. Fabian, Phys. Rev. B 82, 245412 (2010).
24 CRC Handbook of Chemistry and Physics, 68th ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 1987–1988); J. Bendix, M. Brorson, and C. E. Schaffer, Inorg. Chem. 32, 2838-2849 (1993); M. Gerloch, Orbitals, Terms and States (Wiley, Chichester, 1986).
25 F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963); E. Francisco and L. Pueyo, Phys. Rev. B 37, 5278(1988); M. Vijayakumar, M. S. Gopinathan, J. Mol. Struct.: THEOCHEM 361, 15 (1996); E. Francisco and L. Pueyo, Phys. Rev. A 36, 1978 (1987); A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon Press, Oxford, U.K., 1970).
26 S. M. J. Aubin et al., Inorg. Chem. 40, 2127 (2001).
27 K. Takeda, K. Awaga, and T. Inabe, Phys. Rev. B 57, R11062 (1998).
28 J. M. North et al., Phys. Rev. B 67, 174407 (2003); D. W. Boulkhalov et al., Phys. Rev. B 75, 014419 (2007).
29 K. Takeda, K. Awaga, Phys. Rev. B 56, 14560 (1997).
30 H.-K. Woo, X.-B Wang, B. Kiran, L.-S Wang, J. Phys. Chem. A 109, 11395 (2005).
31 Since the LUMO is located on the whole benzoate group, the appropriate electron affinity to consider is that of the benzoate group rather than that of the benzene molecule.
32 The methodology used has been described in Refs. 17, 19, 33–35.
33 G. Kirczenow, Phys. Rev. B 75, 045428 (2007).
34 H. Dalgleish and G. Kirczenow, Nano Lett. 6 1274 (2006).
35 H. Dalgleish and G. Kirczenow, Phys. Rev. B 72, 155429 (2005).
36 The calculation in Fig.3(b), in common with those based on DFT,10,12 does not include Coulomb blockade, but still provides information regarding the energy level broadening due to hybridization between the molecular orbitals and gold leads that controls whether Coulomb blockade occurs.
37 C. R. Fincher, et al., Phys. Rev. B 20, 1589 (1979).
38 K. Lee, G. K. Sotzing, Macromolecules 34, 5746 (2001).
39 S. Voss, M. Fonin, U. Rudiger, M. Burgert, U. Groth, Appl. Phys. Lett. 90, 133104 (2007)