Inverse Magnetoresistance of Molecular Junctions

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We present calculations of spin-dependent electron transport through single organic molecules bridging pairs of iron nanocontacts. We predict the magnetoresistance of these systems to switch from positive to negative with increasing applied bias for both conducting and insulating molecules. This inverse magnetoresistance phenomenon does not depend on the presence of impurities and is unique to nanoscale magnetic junctions. Its physical origin is identified and its relevance to experiment and to potential technological applications is discussed.

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I. INTRODUCTION

Electronic devices composed of ferromagnetic electrodes separated by a connecting junction whose resistance can be altered with magnetic fields offer enormous potential for technological applications such as magnetic random access-memory (MRAM). Spin-dependent transport in ferromagnetic nanosystems is currently receiving increased attention owing to the expectation that nanoscale size constraints may maximize the potentially useful magnetoresistance effects. In particular, theories have predicted that molecules bridging ferromagnetic electrodes may present pathways for building ultra-small spintronic devices that take advantage of weak molecular spin-orbit interaction to maximize the magnetoresistance. Recently, experiments have been reported in which electrons transmitted through insulating octanethiol molecular self-assembled monolayers (SAMs) between nickel contacts, and through 100nm organic molecular films with magnetic electrodes, retained their spin polarization leading to observed magnetoresistance, proving that individual or groups of organic molecules may potentially be used as building blocks for the ultimate miniaturization of spintronic devices. However, bias dependence and inversion of the magnetoresistance were also reported and were attributed to the presence of impurities within the molecular junction. Bias dependence of the magnetoresistance has since been predicted in insulating molecular junctions, indicating that bias-dependent magnetoresistance may be intrinsic to molecular spintronic devices. However, most technological device applications based on magnetoresistance require a relatively bias-independent magnetoresistance for stable device operation. In this article, we report predictions of magnetoresistance in ideal molecular spintronic junctions where single molecules bridge iron electrodes, systems that until now have received little experimental or theoretical attention. We predict strong bias dependence in the positive magnetoresistance regime, but we also predict the magnetoresistance to become negative with increasing applied bias and we show that the magnetoresistance is potentially larger and stable under applied bias in this negative magnetoresistance regime. Our calculations reveal negative magnetoresistance to be an intrinsic property of some molecular junctions (i.e., unlike the effect reported in Ni/octanethiol/Ni junctions, not dependent on the presence of impurities) and thus offer a path to stable operation of devices (such as molecular MRAM) based on molecular spintronics but operating in the negative magnetoresistance regime. Therefore, understanding the origins of negative magnetoresistance is paramount to fundamental studies of spin-dependent transport in molecular junctions and potentially applicable to technological endeavors.

We explore theoretically two very different molecular junctions: a conducting (conjugated) benzene-dithiolate (BDT) molecule and an insulating octane-dithiolate (ODT) molecule bridging ferromagnetic Fe nanocontacts. The phenomena that we predict appear in both.

II. THEORY

In our calculations the system is partitioned into semi-infinite ideal ferromagnetic source and drain leads and an extended molecular junction consisting of the molecule and clusters of nearby Fe atoms for BDT this “extended molecule” is shown in the inset of Fig. 1(a). The Fe-thiol bonding geometries are estimated with ab initio relaxations. The electronic structure of the Fe clusters is described by a tight-binding Hamiltonian and non-orthogonal s, p, d basis. The tight-binding parameters are based on fits to ab initio band structures of Fe crystals and have previously been employed successfully to study magnetic multilayers and non-magnetic nanocontacts, and ferromagnetic Ni molecular junctions. For Fe structures with surfaces this model yields spin-resolved surface densities of states and enhanced surface magnetic moments similar to those of ab initio surface calculations. Thus our model incorporates both the bulk and surface magnetic properties of Fe which together influence the spin-dependent transport through a nanoscale junction of bulk Fe leads bridged with molecules. Spin flip processes are not considered, consistent with weak spin-orbit interaction in molecules and the high degree of spin polarization retained in spin-dependent observations of molecular junctions. The molecular electronic parameters
are described by a tight-binding formalism based on extended-Hückel (EH) theory. This approach has been used successfully to explain the experimental current-voltage characteristics of molecular nanowires connecting non-magnetic metal electrodes. The EH parameters are based on atomic ionization energies while the electronic parameters from Ref. describing the Fe clusters are defined up to an arbitrary additive constant. We adjust this constant to align the Fermi energy of the contacts relative to the highest occupied molecular orbital (HOMO) of the BDT molecule, according to the difference in ionization energies of the isolated structures estimated with \textit{ab initio} total energy calculations. For Fe electrodes and the molecules considered here, this agrees well with the difference between the work function of Fe and the HOMO energy of the isolated molecule obtained from density functional theory, a method that has been used successfully to align the Fermi energy of gold with the HOMO of BDT. The potential profile of the nanointerface arising from the bias voltage applied between the two electrodes is difficult to calculate from first principles since it is a non-equilibrium many-body property. However, appropriate heuristic models for the profile can yield accurate results for the current. We adopt this approach here, assuming the majority of the applied bias to drop over the metal-molecule interface. Nearly identical current-voltage characteristics emerge if the details of the model potential profile are varied. Thus these details are not crucial to our predictions. Our transport calculations are based on Landauer theory and Lippmann-Schwinger and Green’s function techniques. We define the junction magnetoresistance as $JMR = \frac{(I_{\text{par}} - I_{\text{anti}})}{(I_{\text{par}} + I_{\text{anti}})}$. $I_{\text{par}}$ ($I_{\text{anti}}$) is the current through the junction for parallel (anti-parallel) magnetizations on the Fe electrodes.

### III. RESULTS

Fig. (a) shows the calculated transmission probabilities at zero bias for the BDT molecular junction. The spin $up \rightarrow up$ (uu) and $down \rightarrow down$ (dd) transmission is for parallel magnetization of the two contacts; $up \rightarrow down$ (ud) is for anti-parallel magnetization. Quite similar results for the transmissions and currents are obtained if the 5x5 outer Fe layer is deleted from each of the clusters indicating that the clusters and ideal leads in our model adequately represent real (macroscopic) Fe leads. The molecular HOMO and HOMO-1 give rise to the strong transmission 1.5-2eV below the Fermi energy $E_F = 0eV$; the peaks 3-4eV above the Fermi energy are due to the molecular LUMO and LUMO+1. The sharp resonance at 3.1eV results from extremely weak hybridization between the Fe leads and the isolated molecule’s LUMO which has very little sulfur content. The transmission resonance is present and transmits for all spin configurations. More important, however, for potential device applications are resonant states arising from strong hybridization between the molecular sulfur and the Fe $d$-electron orbitals. In Fig. (a) these states give rise to the broad transmission features between the Fermi energy and the HOMO resonances mentioned above. They allow electrons to transmit efficiently through the metal-molecule interface and so give rise to moderately strong transmission dominating the current in the experimentally accessible moderate bias regime. Together with the energetically localized and highly spin-split Fe $d$ bands, these hybrid states give rise to strongly spin-dependent transport characteristics.

At zero applied bias for parallel magnetization of the contacts, the spin $up$ Fe $d$ orbitals hybridize very strongly with sulfur states on both sides of the molecule as shown for a typical state in Fig. (a). This results in the dominant uu transmission near below the Fermi energy in Fig. (a). The spin $down$ d orbitals, occurring higher in energy, hybridize only weakly with molecular sulfur states. For anti-parallel magnetizations [i.e., $up(down) \rightarrow down(up)$ transmission], only the source (drain) contact hybridizes strongly with the molecular end group (Fig. (b)), resulting in much weaker ud transmission (anti-parallel magnetization) than the uu transmission in Fig. (a). As the hybrid states are not located exactly at the Fermi energy they contribute to the current at very low bias through their off-resonant tails.

An applied bias breaks the symmetry between the source and drain electrodes in the parallel magnetization configuration. Thus the symmetric zero bias molecular orbitals (as in Fig. (a)) are supplanted by states associated mainly with either the source or drain electrode as shown in in Figure (c,d) for the uu transmission. The orbital in Figure (c) is shifted upwards in energy and is associated with the source electrode, while that in Fig-
At low bias, the current grows stronger the case of anti-parallel magnetizations is weaker. No mixing of their off-resonant tails and the current in transmission processes are mutually incoherent, there is no resonant enhancement. Since the uu transmission dominates, the parallel magnetization current is larger, resulting in a positive magnetoresistance of about 10 percent. At larger applied bias, the applied electrostatic potential breaks the symmetry between the contacts further and the uu transmission decreases as the hybridized Fe $d$ states associated with the source and drain move apart. However, at high bias in the case of anti-parallel magnetizations, hybridized states associated with down $d$ electron orbitals on the drain are shifted into resonance with up $d$ electron states on the source and hybridized transmitting states connecting both sides of the molecule with the electrodes form in the case of up $\rightarrow$ down transmission as shown in Fig. 2(f), enhancing the transmission. No such resonant effect occurs for du transmission which decreases with increasing bias and so the overall effect of the applied bias on the net transmission for anti-parallel magnetization is small. No resonant enhancement occurs at increased bias for parallel magnetizations where hybridized states are shifted apart (Fig. 2(e)) and transmission is reduced. Therefore, because it selectively depresses transmission for parallel magnetization of the contacts, the bias-induced symmetry breaking results in a crossover with increasing bias from positive to negative values of the JMR in Fig. 1(b).

![Image](image.png)

Fig. 2: (Color online) Representative hybridized energy eigenstates of the entire extended molecule near the Fermi energy are depicted on the BDT molecule and the 2x2 Fe planes on either side. (a) At 0V the uu source and drain electrode $d$ states hybridize with sulfur orbitals on both sides of the molecule forming transmitting states. (b) Only the source strongly hybridizes with the sulfur states in the ud configuration. At 0.1V, uu states in (a) split into a state mainly on the source that shifts upwards in energy and a state mainly on the drain (d) that shifts downwards. (e) At 1.0V uu hybridized states on the source and drain have shifted well apart. (f) Source up hybridized states are shifted into resonance with drain down states in the ud configuration creating states that transmit strongly through the molecule.

The wave functions of the hybridized states responsible for transport at moderate bias are located primarily on the Fe electrodes. Therefore their energy levels are pinned to the electrodes and shift rigidly with applied bias explaining why our moderate bias results are insensitive to the assumed potential profile. If one partitions the entire system into halves associated with either the source or with the drain so that the hybridized states on the source (drain) side of the system are grouped with the source (drain) to form a "composite" source (drain) electrode, the negative magnetoresistance argument can be rephrased in the language of conventional solid-state magnetic tunnel junctions: At the bias required to bring hybridized down states on the drain into resonance with hybridized up states on the source, the spin polarization of the composite drain is negative (the current is dominated by down electrons) while that of the composite source remains positive. Therefore, the Julliere theory of tunneling would predict negative magnetoresistance.

Because its mechanism relies on the simultaneous suppression of transmission for parallel magnetizations on the contacts and enhancement of the transmission in the anti-parallel ud transmission channel, this intrinsic negative magnetoresistance requires strongly spin-split energy bands providing a large magnetic moment. No such negative magnetoresistance has been reported for calculations on molecules bridging ferromagnetic nickel junctions and our calculations on similar systems suggest that this different behavior may be related to the smaller spin-splitting in Ni: At sufficient bias to induce resonant transmission in the ud channel (the required bias is relatively small for Ni) much symmetry and overlap remain in the uu transmission channel where energy...
levels are not adequately shifted apart. Therefore the mechanism should be less effective in nanosystems based on nickel.\textsuperscript{28,29}

For BDT bridging Fe nanocontacts, the crossover to negative magnetoresistance occurs at relatively low bias, near 0.7V, well within the range of current experimental techniques and therefore the predicted negative magnetoresistance should be accessible to experiment. With magnitude reaching a value of more than 30 percent, the negative magnetoresistance may be more easily observed in this system than positive values. Clearly the mechanism is expected to be unique to systems that can both sustain a significant potential drop and allow for resonant transmission of d-electrons through the junction, i.e., nanosystems. Negative magnetoresistance emerging as a result of applied bias has already been observed experimentally in systems where ferromagnetic electrodes are separated by thin film tunnel junctions of only a few nanometers in width where the junction couples strongly to the electrode d states.\textsuperscript{31,32} Since d-electrons are not expected to contribute to transport in conventional thin film magnetic tunnel junctions,\textsuperscript{32,33,34,35} negative magnetoresistance when observed in those devices is attributed to impurities.\textsuperscript{36} However, we predict intrinsic negative magnetoresistance in ideal systems demonstrating that bias-dependent and negative magnetoresistance are not necessarily signatures of impurities in molecular nanosystems.

Interestingly, the region exhibiting the greatest bias independence in our magnetoresistance calculations emerges in the negative magnetoresistance regime (around 1.7V in Figure 1(b)). Since magnetoresistance devices can in principle exploit magnetoresistance of either sign but require a relatively bias independent magnetoresistance for stable device operation, molecular-Fe systems may be attractive candidates for technological applications in devices based on molecular spintronics (molecular MRAM) but operated in the negative magnetoresistance regime.

For comparison, we have also studied an Fe/BDT/Fe molecular junction having a different geometry where single Fe tip atoms have been added to each of the clusters and the molecular sulfur atoms bind directly over them at the same heights considered previously. This geometry results in stronger and sharper resonances associated with the hybridized states and therefore the mechanism responsible for negative JMR is even more prominent. Here we find the cross-over to negative magnetoresistance to occur at a lower bias voltage of 0.25V.

Next we consider ferromagnetic Fe contacts bridged with an octane-dithiolate (ODT) molecule, shown in Fig. 3(a) with the zero bias transmission probabilities. As ODT is an insulator, the strongest transmission features near the Fermi energy are weak resonant features associated with the HOMO, about 1.8eV below the Fermi energy. Other weakly transmitting states appear closer to the Fermi energy (about 0.5 eV below) due to hybridization of Fe d and molecular sulfur orbitals. These states are similar to those predicted in the case of BDT: the up $\rightarrow$ up transmission is largest as hybridization occurs at both ends of the molecule allowing for efficient transmission into and out of the metal-molecule interface, decreasing the width of the tunnel gap. The calculated current-voltage characteristics are shown in Figure 3(b). At moderate bias, the symmetry between the source and drain electrodes in the parallel magnetization configuration leads to positive magnetoresistance. At higher applied bias, by the same mechanism described for BDT, the magnetoresistance becomes negative, but here the crossover doesn’t occur until nearly 1.2V. Again a large region of relative bias stability emerges in the negative bias regime (around 1.5V in Figure 3(b)) with possible implications for future molecular spintronic technology.

**IV. CONCLUSION**

In conclusion: We have predicted an inverse magnetoresistance phenomenon intrinsic to systems where ferromagnetic Fe electrodes are bridged by two very different molecules (conducting and insulating), and for different bonding geometries. We also predict qualitatively similar behavior in Fe junctions bridged by a pair of Fe atoms.\textsuperscript{37} Thus negative magnetoresistance should be available in a variety of molecular junctions under appropriate conditions. The value of the bias required to induce negative magnetoresistance depends on the chemistry of the junction: 0.25-0.7V for Fe/benzene-dithiolate/Fe (depending on the bonding geometry), 1.2V for Fe/octane-dithiolate/Fe and higher still\textsuperscript{37} for Fe contacts bridged by a Fe dimer. These changes in the chemistry make it possible to vary the onset of negative magnetoresistance, the magnitudes of both positive and negative magnetoresistances and the regions of bias indepen-
dence important for device applications.

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