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First-principles calculations of spin-polarized electron transport in a molecular wire: Molecular spin valve

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Using first-principles density functional theory and the Landauer-Büttiker formalism, we have studied the spin-polarized transport of electrons in a benzene-1-4-dithiolate (BDT) molecule sandwiched between two Ni cluster layers, followed by nonmagnetic gold contacts. Our calculation reveals that the current for a parallel (ON) alignment of the spins at opposite ends of the molecular wire is significantly higher than for the antiparallel (OFF) alignment. We also find that the ground state of such a system has an antiparallel alignment suggesting that experiments could be performed in which an external magnetic field would be needed only for ferromagnetic alignment to switch the system from the OFF to the ON state.

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The controlled transport of electrons/holes through a single molecule attached to electrodes forms the basis of molecular electronics. Though the concept of molecular electronics was proposed by Aviram and Ratner a quarter century ago,[1] the utilization of simple organic molecular structures to build electronic devices[2] and their integration into electronic circuits is still far from realization. However, recent advancements in experimental techniques and successes in measuring electron transport through a single, or at best a few, molecules[2–4] have kindled the hope that the realization of these devices is not far away. Though the idea of utilizing electron spins, in addition to charge, to control the electrical conduction in electronic circuits, leading to a field of electronics called spintronics[5–7] was discovered long ago, almost all experiments and theory on molecular wires[2–4,8–12] have thus far only considered the charge of conduction electrons. The spin orientation of conduction electrons survives for a relatively long period of time ($\sim$ ns),[7] which makes spintronic devices attractive for many applications ranging from memory storage and magnetic sensors to quantum computing devices. Depending upon the relative orientation of magnetization in the magnetic layers, the device resistance changes from minimal for parallel magnetization to maximal for antiparallel magnetization, i.e. an order of magnitude change in resistance between the two configurations. This giant magnetoresistance[13] (GMR) effect or spin-valve effect has already been demonstrated experimentally in bulk magnetic/semiconductor heterostructures. However, in a molecular wire comprised of magnetic-(nonmagnetic) molecule-magnetic junctions, this effect has not been observed. Very recently, using a tight-binding model, Emberly *et al.*[14] proposed that this spin-valve effect might be readily observable in Ni-BDT-Ni junctions. Since the dimension of the molecule between the two magnetic layers is in the nanoscale regime, the magnetic property is expected to be different than that of the bulk and new phenomena arising from the dominance of quantum mechanical effects is expected to play an important role. Thus, it is necessary to address this problem from a first-principles theory in which spin-polarization effects are included to the fullest possible extent.

No first-principles theoretical study has yet been carried out to understand this effect and gain insight into the role of spin on electronic transport in a molecular wire. In this letter, we have used a state-of-the-art first-principles density functional (DFT) method to study the effect of spin alignment on the transport property in a molecular wire. The effects of spin polarization are explicitly incorporated in our calculations. The Landauer-Büttiker approach[15] is used to study the conduction in a model molecular device. Our quantum transport calculation shows that for a parallel alignment of the spins at opposite ends of the molecular wire, the current is significantly higher than for the antiparallel alignment. We term the more conductive parallel spin configuration state as the ON state and the antiparallel configuration as the OFF state. We also find, that the ground state of such a system has an antiparallel spin alignment suggesting that an experiment could be performed in which an external magnetic field would be needed only for the ferromagnetic alignment to switch from the OFF state to the ON state.

For our calculations, we created a model molecular wire comprised of benzene-1-4-dithiolate molecule sandwiched between a pair of Ni layers followed by nonmagnetic Au contacts. The magnetic layers are modeled by a 5-atom Ni cluster on each end. The electronic structures are obtained for both parallel and antiparallel spin alignments using a self-consistent spin-polarized local density functional (LSDA) method.[16] The spin states are simultaneously optimized to obtain the ground state spin configuration. The antiparallel spin configuration is obtained using a broken symmetry formalism.[17] For geometry optimization in parallel and antiparallel configuration, the threshold for forces at each atomic site were set at 10^{-3} a.u./Bohr. The convergence threshold for energy and electron density were set at 10^{-5} a.u. and 10^{-6}, respectively. We have used double numerical atomic basis sets (DNP) augmented by polarization functions[16] and the computations were performed using a DFT code (DMol^3).[18]

Energetics. The total magnetic moment for the parallel alignment in the ground state configuration is found to be $8\mu_B$ ($4\mu_B$ at each end of the magnetic contact). In the case of antiparallel alignment, the magnetic moments are found to be $4\mu_B$ and $-4\mu_B$ at the two opposite ends. The antiparallel magnetic state is found to be the lower energy state. The energy difference between the two configurations is found to be ~ 0.34 mRy. This value is comparable to a energy difference (of the order 0.3 mRy) obtained in a bulk multilayer[19,20] where the antiferromagnetic state is also found to be lower in energy in agreement with experiment. For a short molecular wire (~ 10 Å), one may wonder whether the spin-valve effect could be due to the direct spin-spin interaction between the two contacts. Using a simple classical model, we estimated the change in energy due to magnetic dipolar interaction and found it to be an order of magnitude lower than the one we obtained from DFT. This suggests that the lower energy for the antiparallel spin configuration is due to the strong super-exchange interaction through the molecule. It is worthwhile to point out here that the use of a magnetic field to obtain an antiparallel spin alignment between a pair of magnetic contacts separated by the subnanometer length of the molecular species has been problematic and has been a bottleneck in experiments. Our result here, with a cluster contact, suggests that there is no need to apply external magnetic fields in such a system since the natural ground state of this structure has an antiparallel spin configuration. The parallel configuration, on the other hand, could be obtained by applying an external magnetic field.

I-V calculations. In order to obtain the current in both parallel and antiparallel configurations, we have used the Green's function-based Landauer-Büttiker formalism. This method has been used extensively to study spin-unpolarized transport[8–12] in molecular wires. Assuming the scattering to be coherent and neglecting the spin-flip scattering, the current in magnetic systems can be obtained as $I=I^{\uparrow}+I^{\downarrow}$ where $I^{\uparrow}$ is the contribution to the current from spin-up electrons and $I^{\downarrow}$ is the contribution from the spin-down electrons. From the Landauer-Büttiker approach:[15]

$$I^{\uparrow}=e/h\int_{\mu_1}^{\mu_2}T^{\uparrow}(E,V)[f(E,\mu_1)-f(E,\mu_2)]dE, \qquad (1)$$

where $\mu_{1,2}$ are the electrochemical potentials of the two contacts. Since the potential drop is expected to be equally distributed between the left and right for a strongly coupled short molecular wire, the electrochemical potentials can be evaluated as: $\mu_{1,2}=E_f\mp eV/2$. E_f is the Fermi energy (-5.53 eV) of the nonmagnetic gold contact. E is the injection energy of the tunneling electron, f is the Fermi distribution function, and V is the applied potential. $T^{\uparrow}(E,V)$ is the transmission function for the spin-up electrons calculated using the Green's function approach[15] discussed in details in Ref. 21. It is important to point out that single Au atom on either end was included to calculate explicitly the coupling matrix for evaluation of self energy functions.[21] The spin-polarized molecular Hamiltonian and overlap matrix were obtained using a spin-unrestricted gradient corrected DFT (B3LYP—Becke's three parameter hybrid functional with Lee-Yang-Parr correction functional) (Ref. 16) and LANL2DZ (Los Alamos effective core potential with double zeta) basis set.[22] Because of the computational expense, a single point gradient corrected DFT(B3LYP) (Ref. 16) calculation was carried out at the LSDA optimized geometry to extract the Hamiltonian and overlap matrix. The contributions to the current due to spin-down electrons are evaluated similarly. It is important to point out that under the application of an external bias, one would expect some modification in the molecular energy levels. In order to see the effect of external field (in the low bias regime) on the molecular energy spectra, we have applied an electric field of 0.001 a.u. (~ 0.909 V) in parallel and antiparallel configurations, and in both cases we optimized the spin as well as electronic configurations within the LSDA in a self consistent manner. Our calculations indicate no significant shift in energy levels as well as no change in magnetic moment in both the cases. Most importantly, we found that after application of the field the antiparallel spin configuration state is still found to be the ground state. These results are consistent with a recent theoretical (DFT) calculation in nonmagnetic system[10] under fixed electric field, which showed that no significant differences are noted in the transmission under small bias. Thus we have used the zero field molecular spectra for our calculation, as used by Heurich *et al.*[10] Though we have presented our results for higher voltage, the results for higher voltages should be used with caution as incoherent effects are important in this range.

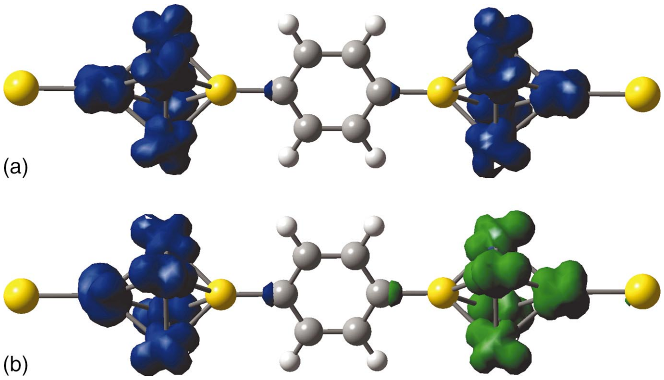

FIG. 1. (Color) Electron spin density plot for the (a) parallel (‖), and (b) antiparallel (anti)alignment of spins in the magnetic layers in the two opposite sides of the BDT molecule. Blue represents the positive (up) spin density and green represents the negative (down) spin density.

Results and Discussion. The spin density plots obtained from self-consistent calculations, for both parallel and antiparallel configurations, are shown in Fig. 1. The corresponding current-voltage (*I-V*) characteristics are given in Fig. 2. Several interesting features are apparent from Figure 2. First, zero current is observed near zero applied voltage, suggesting a Coulomb gap arising from the energy mismatch between the Fermi-energy of the nonmagnetic (Au) contact and the lowest unoccupied molecular orbital (LUMO) levels of the molecular system (Ni-BDT-Ni). Secondly, a staircase-like effect in the *I-V* curve is observed. This effect, inherent to the molecular wire, is attributed to the discrete energy levels of the molecular system. Most importantly, the remarkable feature observed in Fig. 2 is the order of magnitude difference in the current between parallel and antiparallel magnetization in the magnetic layers, suggesting a strong

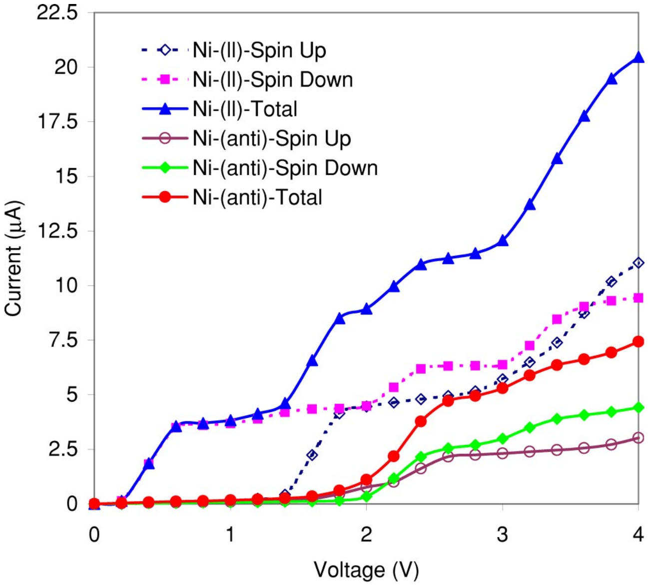

FIG. 2. (Color online) Calculated current-voltage characteristics of the model molecular device for both parallel (∥) and antiparallel (anti) alignment of spins in the magnetic (Ni) layers at the two opposite sides of the BDT molecule.

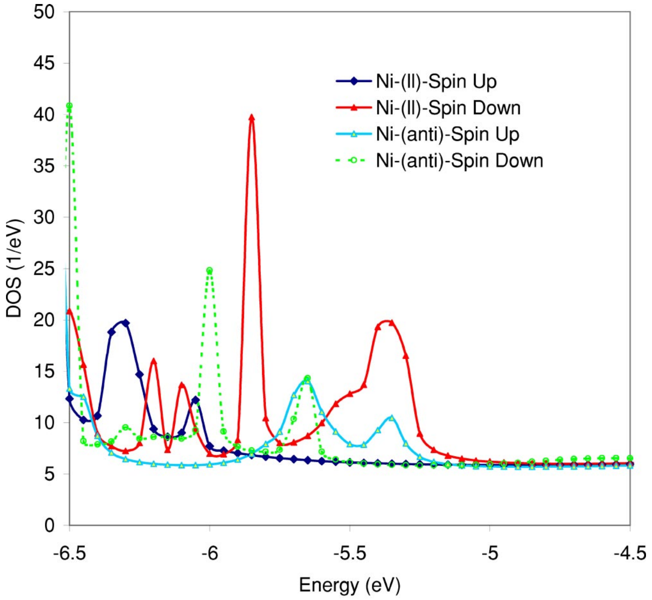

FIG. 3. (Color online) Spin-up and spin-down density of states (DOS) for the parallel (∥) and antiparallel (anti) magnetization in the magnetic (Ni) layers at the opposite sides of the BDT molecule.

spin-valve effect in the molecular wire. It is worth mentioning that the spin-valve effect observed here, though qualitatively in agreement with the tight-binding calculation of Emberly *et al.*,[14] has some significant quantitative differences. The current is an order of magnitude larger in our calculations than what has been reported,[14] and the computed difference in current between the two magnetic states is much larger than the tight-binding result.[14] The quantitative differences between our results and the tight-binding model calculation could be due to the nature of the contact and exact details of the models considered in both calculations. In our calculations, both parallel and antiparallel spin configurations are obtained by optimizing the entire molecular system using a first-principles self-consistent DFT approach. By doing this we have explicitly incorporated the spin polarization effect on the molecular spectra. In contrast, in the tight-binding model,[14] the spin polarization effects were incorporated[14] by using spin-up and spin-down parameters obtained from bulk. By not incorporating the relaxation in different spin configurations in the tight-binding model, the perturbation due to spin polarization has not been taken into account properly in the molecular (BDT) spectra. This could lead to the differences between first principles and tight-binding results.

GMR Result. The resistances for the parallel (R_p) and antiparallel (R_{ap}) magnetization states are estimated by fitting the linear portions of the *I-V* curves in Fig. 2 to straight lines, giving $R_p \sim 58.6\,\mathrm{k}\Omega$ and $R_{ap} \sim 3122.3\,\mathrm{k}\Omega$, respectively. The change in resistance $((R_{ap}\text{-}R_p)/R_{ap})$ between the two configurations is about 98%. The change reported in the original paper by Baibich *et al.*[13] showing the GMR effect in magnetic heterostructures of Fe and Cr was about 100%. The GMR ratio defined as, $(R_{ap}\text{-}R_p)/R_p$, is found from our calculation to be about 52.82.

In order to obtain insight into the order of magnitude increase in current for the parallel magnetization case, we have calculated the density of states (DOS) for spin-up and spin-down electrons separately for both parallel and antiparallel alignment as shown in Fig. 3. One notices from Fig. 3, that near the Fermi energy (-5.53 eV) of the Au contact, the calculated DOS is significantly higher for the spin-down electrons in the case of parallel alignment. This suggests that electrons from spin-down states contribute significantly more to the current and thus are the majority carriers for conduction. In contrast, for the antiparallel alignment, the transport of spin-down electrons from one end to the other involves spin flipping which requires higher energy. The resistance in this alignment is, therefore, considerably higher than that in the parallel configuration.

Mn Result. The use of different magnetic materials as contacts could potentially have large impact in realistic spin transport systems, as revealed in our study. To study the effect of different magnetic contacts on transport, we replaced the Ni clusters with Mn clusters of similar size to model Au-Mn-BDT-Mn-Au junctions. From the geometry optimization, we found a total magnetic moment of $46\mu_B$ ($23\mu_B$ on each end) for the parallel configuration which is consistent with earlier study (more than $4\mu_B$ at each Mn) on Mn based clusters.[17] For the antiparallel alignment, the magnetic moments are found to be $23\mu_B$ and $-23\mu_B$. The antiparallel state is found to be the lower energy state (3 mRy lower), about 10 times lower than that obtained in the Ni system. The stronger stability of the antiparallel state in Mn could be due to the enhanced super-exchange interaction in this system. The *I-V* characteristics of this system are summarized in Fig. 4. One notices that the total current in this system is significantly higher (between 0 to 2 V) in the antiparallel alignment than that of the Ni system (almost zero current). The higher DOS for the Mn system (not shown here) near

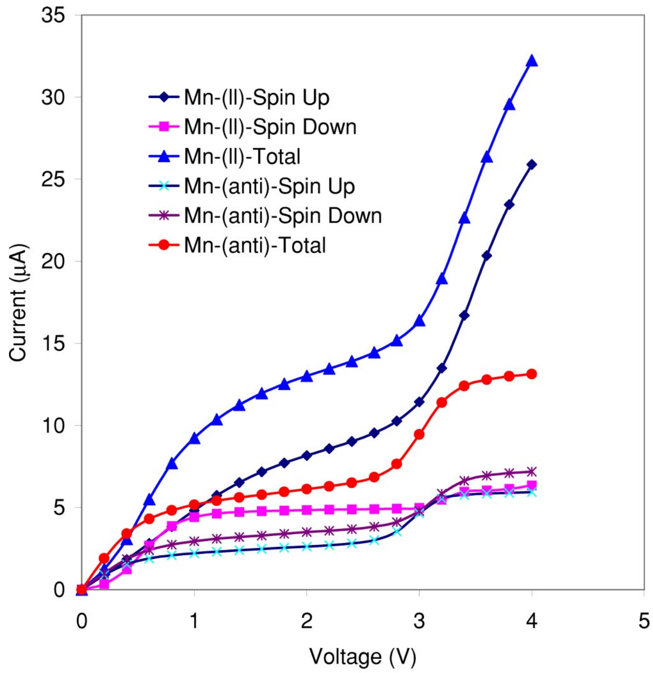

FIG. 4. (Color online) Calculated current-voltage characteristics of the model molecular device for both parallel (∥) and antiparallel (anti) alignment of spins in the magnetic (Mn) layers in the two opposite sides of the BDT molecule.

the Fermi energy explains the observed increase in current for the antiparallel case. We found the HOMO-LUMO gap in case of Mn system (~0.3 eV) to be substantially smaller than Ni system (~1.9 eV). The DOS analysis also shows that there are quantum channels available close to the Fermi level resulting in no gap around the zero voltage regime in contrast to the Ni system. In the parallel alignment case for Mn, we found the current to be more smeared and the step-like effect (as seen in Ni) is not seen. This is due to closely spaced energy levels near the Fermi energy as found from the DOS analysis for Mn. The GMR ratio value obtained (after a threshold voltage of ~0.5 V) is about 3.4, substantially lower than that obtained in the Ni system. In the case of Mn, we find that the spin-up electrons are the majority carriers in conduction in contrast to the Ni system where the spin-down electrons are the majority carriers. The modulation (ON/OFF ratio) in current in Ni is about an order of magnitude larger than that in Mn.

In summary, our first-principles density functional calculations suggest that the ground state of benzene-1-4-dithiolate molecule sandwiched between nickel clusters has an antiparallel spin configuration (OFF state) suggesting that a structure with magnetic cluster as a contact would eliminate the need for applying a local magnetic field to obtain an OFF state. The resistance of such system is predicted to be an order of magnitude larger than in the ferromagnetic alignment (ON state), which can be obtained by applying an external magnetic field. Using Mn as the magnetic contact, we find the total current (for voltage between 0 to 2 V) in the antiparallel case is much larger than that with Ni contacts. The majority carriers for conduction in the Mn system are spin-up electrons in contrast to the spin-down electrons in the Ni system. The GMR value is found to be an order of magnitude smaller in the case of Mn than in Ni. This suggests that spin transport behavior in molecular circuit depends critically on various properties; e.g., coupling between molecule and contact, total magnetization in magnetic layers, location of electronic energy levels.

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[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).

[2] For recent reviews, see C. Joachim *et al.*, Nature (London) **408**, 541 (2000).

[3] M. A. Reed *et al.*, Science **278**, 252 (1997).

[4] J. Reichert *et al.*, Phys. Rev. Lett. **88**, 176804 (2002).

[5] G. A. Prinz, Science **282**, 1660 (1998).

[6] M. Johnson and R. H. Silsbee, Phys. Rev. Lett. **55**, 1790 (1985).

[7] S. A. Wolf *et al.*, Science **294**, 1488 (2001).

[8] V. Mujica *et al.*, J. Chem. Phys. **104**, 7296 (1996).

[9] W. Tian *et al.*, J. Chem. Phys. **109**, 2874 (1998).

[10] J. Heurich *et al.*, Phys. Rev. Lett. **88**, 256803 (2002).

[11] M. Di Ventra *et al.*, Phys. Rev. Lett. **84**, 979 (2000).

[12] A. W. Ghosh *et al.*, Chem. Phys. **281**, 225 (2002).

[13] M. N. Baibich *et al.*, Phys. Rev. Lett. **61**, 2472 (1988).

[14] E. Emberly and G. Kirczenow, Chem. Phys. **281**, 311 (2002).

[15] S. Datta, *Electron Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1997).

[16] Robert G. Parr and Weitao Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford Science Publications, 1994).

[17] S. K. Nayak and P. Jena, Phys. Rev. Lett. **81**, 2970 (1998).

[18] Computer code DMOL: Biosym Technologies Inc., San Diego, CA, 1995.

[19] M. Schilfgaarde and F. Herman, Phys. Rev. Lett. **71**, 1923 (1993).

[20] P. Lang *et al.*, Phys. Rev. Lett. **71**, 1927 (1993).

[21] R. Pati *et al.*, Phys. Rev. B **68**, 014412 (2003).

[22] M. J. Frisch *et al.*, computer program G98, Gaussian Inc., Pittsburgh, PA, 1998.