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Oscillatory spin-polarized conductance in carbon atom wires

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Zero temperature spin-polarized transport in atomic wires consisting of magnetic (Co) and nonmagnetic (C) atoms sandwiched between gold electrodes is investigated using gradient-corrected density functional theory and Landauer's formalism. Our calculation shows a spin valve behavior with the parallel magnetization state between the two Co atoms giving higher conductance than the respective antiparallel magnetization state and a nonmonotonic variation of magnetoconductance with wire length. We term the more conductive parallel magnetization state the on state and the antiparallel magnetization state the off state. The ground state of wires containing up to five carbon atoms has antiparallel (off) spin configurations between the Co. The additional stability of the antiferromagnetic state in wires containing an even number of carbon atoms is ascribed to an enhanced superexchange mechanism facilitated by σ-π-conjugation present in the systems.

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Current trends in the miniaturization of electronic devices have prompted considerable interest in studying transport in nanoscale systems. Electron transport in atomic wires represents the ultimate miniaturization of electronic devices and has attracted much attention recently.[1,2] It is now possible to fabricate wires containing only a few atoms and measure their electrical properties. Carbon nanowires containing up to twenty atoms, also known as cumelenes, have been synthesized[3] and are considered ideal one-dimensional (1D) wires. Lang and Avouris[4] have recently studied the quantum transport properties of these carbon nanowires at $T=0$ using the density functional method. They described the metal electrodes using a semi-infinite uniform background (Jellium) model and reported that the conductance of carbon wires varies in a semiperiodic manner; chains with odd number of carbon atoms having lower resistance than the even numbered ones. Subsequently, Larade *et al.*[5] have studied the conductance behavior of carbon atom wires sandwiched between atomic electrodes using density functional theory and nonequilibrium Green's function method. They explicitly included the crystalline structure of the electrodes by considering aluminum contacts in their calculation and found that the atomic wires exhibited negative differential resistance (NDR) behavior at high applied bias. These interesting results[4,5] show that transport in an atomic wire, where the transport process is dominated by the quantum nature of the current carrying state, can exhibit very different behavior than the bulk, where the diffusion of electrons dominates the transport process. In addition, detailed electronic structure of the contact also influences transport in the nanoscale regime. When the contact is a magnetic material, the problem becomes even more interesting as the spin configuration of the contacts plays a crucial role in the transport. The role of electron spins, in addition to charge, to control the device characteristics, referred to as spintronics,[6-8] was discovered a long time ago. However, almost all experiments and theory on atomic or molecular wires[1,2,4,5,9-13] have thus far considered only the charge of conduction electrons to understand the transport mechanism. Interestingly, the spin orientation of conduction electrons survives for a relatively long period of time ($\sim$ns)[8] compared to the electron momentum decay time ($\sim$fs), making spintronic devices attractive for many applications ranging from memory storage and magnetic sensors to quantum computing devices. Very recently, using a tight-binding model, Emberly *et al.*[14] have proposed that the spin-valve effect can be readily observed in a benzene dithiolate molecule sandwiched between two Ni contacts.

No first-principles theoretical study has yet been carried out to understand the role of spin on electronic conduction in a molecular system. As mentioned before, atomic carbon wires represent an ideal case to investigate the transport process in finite systems. In addition to studying the spin-valve behavior in an atomic wire, there are many interesting questions one needs to address in these finite systems. For example, what is the magnetic ground state of such a system, i.e., what is the nature of coupling between the two magnetic contacts? Does this coupling depend on the size of the atomic wire? How does spin transport vary as a function of length of the molecular wire—is it Ohmic, ballistic, or some nonperiodic variation as seen in the case of electron transport in carbon wires with non-magnetic contacts? In order to answer these subtle questions and further gain insight into spin-dependent transport, one has to resort to first-principles theory, where spin polarization can be explicitly taken into account.

In the present paper, we have used the *ab initio* gradient-corrected density functional approach[15] to address the problem of carbon atom wires sandwiched between magnetic Co atoms, attached to gold contacts. Our quantum conductance calculation in the C-atom wire shows a spin valve effect with the parallel magnetization state between the two Co atoms giving higher conductance than the respective antiparallel magnetization state. We term the more conductive parallel magnetization state between the Co atoms as the on state and the antiparallel magnetization state as the off state. We also found a non-monotonic variation of the magnetoconductance with wire length. The ground states of carbon atom wires sandwiched between atomic Co contacts are found to have

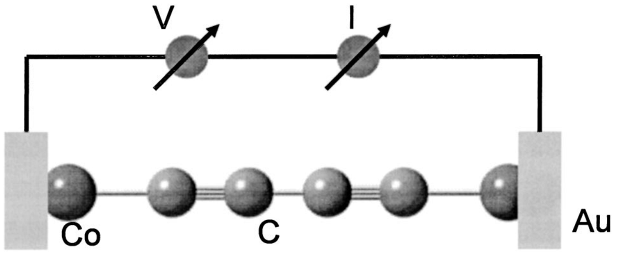

FIG. 1. A schematic of the atomic wire device.

antiferromagnetic alignments. This is an exciting result since the ground state is found to be the off state and by applying an uniform external magnetic field one can switch the off state to the on state. In contrast, if the ground state is ferromagnetic (parallel spin configuration) one has to apply a staggered magnetic field to obtain the antiferromagnetic state, which is extremely difficult to obtain in practice (changing the spin orientation from parallel to antiparallel by applying magnetic field between two magnetic contacts separated only by a few Å). Thus our calculation here suggests that one does not need to apply a complex magnetic field configuration in the experiment for such system to attain the off state.

For our calculation, we created a model wire structure from C atoms and sandwiched them between two Co atoms, and then inserted the Co-C-Co chains between two gold electrodes as shown in Fig. 1. Electronic structures are obtained for both parallel and antiparallel spin alignments (of the Co atoms) using a self-consistent spin-polarized gradient-corrected density functional method.[15] The structure of the wire assembly is optimized using a gradient-corrected functional (PW91)[15] and the DMOL3 code.[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] We have used double numerical polarized basis sets for the calculation. By varying the number of carbon atoms from one to five between the two Co atoms, we calculated the conductance for both the parallel and antiparallel spin configurations between the Co atoms using the Landauer formalism[18] as described below. It is essential to point out that taking up to five carbon atoms in the wire assembly was inspired by the work of Lang and Avouris,[4] who considered only up to six carbon atoms in the wires and found oscillatory behavior in conductance as a function of the wire length. Our goal here is to explore the spin-polarized transport using magnetic atom contacts in such short atomic wires and to see how the relative magnetic orientation of the two Co atoms affects the charge transport.

Energetics. First we discuss our results for the structure and energetics of the atomic wires. We find that the ground state for all the atomic wires correspond to antiparallel (antiferromagnetic) spin orientation of the two Co atoms at the ends. The energy difference between the antiferromagnetic and ferromagnetic states $[\Delta E = E(\text{ferro})\text{-}E(\text{antiferro})]$ as a function of the carbon atoms (shown in Fig. 2) exhibits oscillatory variation with the number of carbon atoms in the atomic wire; ΔE is larger in chains having an even number of carbon atoms than in wires containing an odd number of carbon atoms. The additional stability of the antiferromagnetic state in the carbon chains having even number of carbon atoms can be ascribed to an enhanced superexchange mechanism in these wires due to σ-π conjugation. Consider, for example, atomic wires composed of 3 and 4 carbon atoms. In the case of the three-atom carbon wire, none of the carbon atoms can exhibit triple C-C bonds; only a C-C double bond is possible between them and the carbon atoms at either end will have double bonds with the Co atoms in order to satisfy the valence of carbon. As a result the wire has continuous π conjugation from one Co end to the other. In contrast, in a four-atom wire it can be seen clearly that the carbon atoms can exhibit C-C triple bonds and Co-C single bonds. Figure 3 illustrates these phenomena. A similar variation of Co-C and C-C bond distance as a function of the number of carbon atoms in the wire further confirms this picture, i.e., shorter Co-C bond distance means continuous π conjugation in atomic wires with odd numbers of carbon atoms. The various computed properties such as Mulliken charges and spin density associated with the Co atoms in the wire [shown in Figs. 4(a) and 4(b)] also shows odd-even

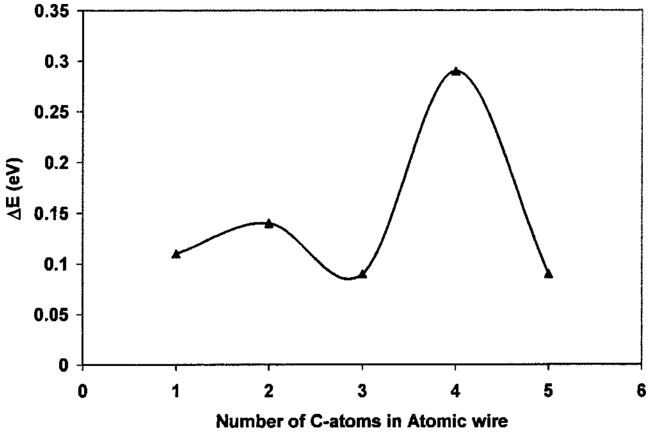

FIG. 2. The energy difference $[\Delta E = E(\uparrow\uparrow) - E(\uparrow\downarrow)]$ between the parallel and anti-parallel spin configurations in carbon atom wires as a function of the number of carbon atoms in the wire.

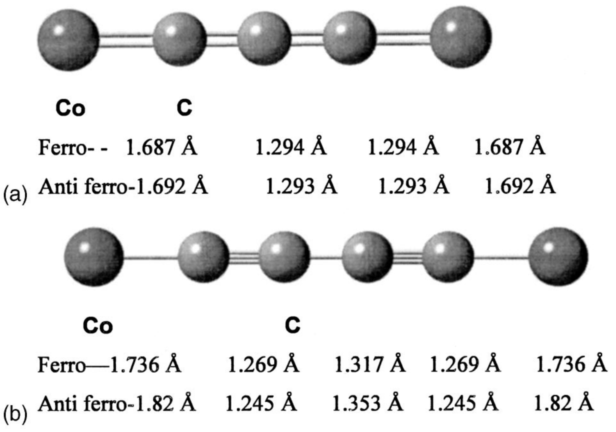

FIG. 3. A schematic showing the bonding pattern in a carbon wire having (a) 3 and (b) 4 carbon atoms. All the optimized bond distances are noted for both the ferromagnetic and antiferromagnetic states of the C-atom wire.

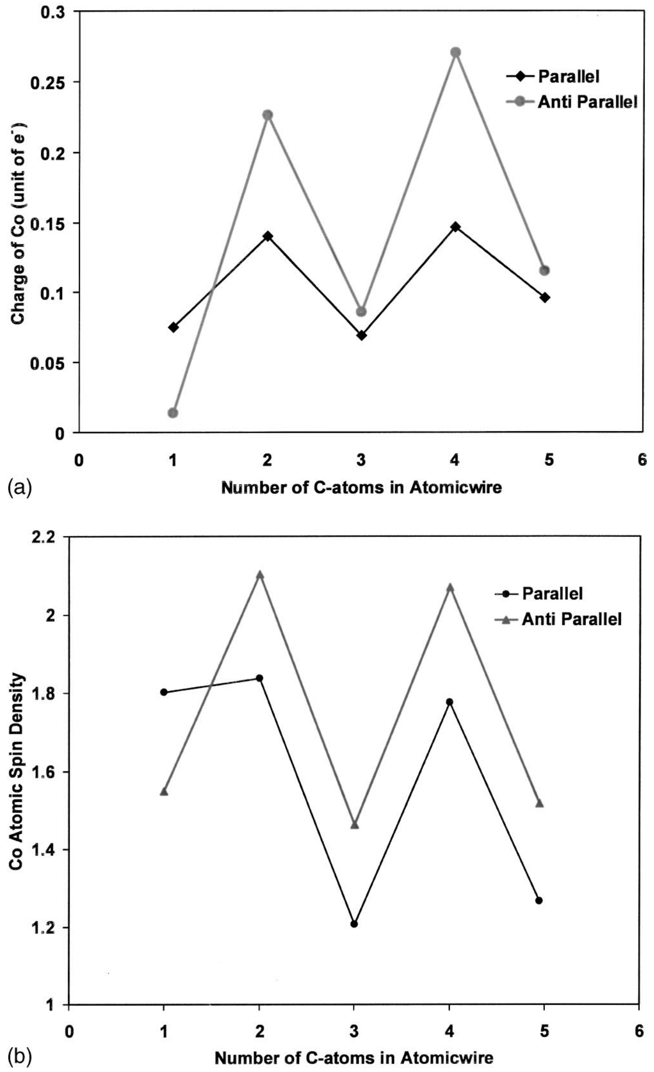

FIG. 4. (a) Mulliken charge at the Co and (b) atomic spin density at Co for both the parallel and antiparallel spin configurations between the two Co atoms in C wires as a function of the number of C atoms in the wire.

variation as a function of size. The variation of the bonding pattern (odd-even) in these atomic wires has a profound effect on the conductance of the wires as discussed below.

Conductance calculation. Assuming the scattering to be coherent[18] for these short atomic wires and ignoring the spin-flip scattering (important only when spin-orbit coupling is significant), one can calculate the conductance in a magnetic system as $G=G^{\alpha}+G^{\beta}$, where G^{α} and G^{β} are the contributions to the conductance from the α and β spin states, respectively. Since the transport occurs around the Fermi energy, we have evaluated the conductance using Landauer's formula[18] in the zero bias limit, i.e., at the Fermi energy. From Landauer's theory

$$G^{\alpha,\beta}(E_f)=\frac{e^2}{h}T^{\alpha,\beta}(E_f), \tag{1}$$

where the transmission function, $T^{\alpha,\beta}$ is defined as[18]

$$T^{\alpha,\beta}=Tr[\Gamma_1^{\alpha,\beta}g^{\alpha,\beta}\Gamma_2^{\alpha,\beta}g^{\alpha+,\beta+}]. \tag{2}$$

The $\Gamma_{1,2}^{\alpha,\beta}$ are broadening functions and can be evaluated from self-energy terms, $\Sigma_{1,2}^{\alpha,\beta}$.[11,18] The self-energy terms take into account the interaction of the wire with the two leads. Unlike Jellium model, we have used a single gold atom at either end of the wire to explicitly calculate the coupling matrices for the evaluation of the self-energy terms using the scheme developed by Datta.[18] The semi-infinite nature of the contact is incorporated through these self-energy terms. The Green's function of the gold contact is approximated as a diagonal matrix with each element proportional to the local density of states of the *s* band of gold (0.035 per electron spin) which dominates near the Fermi energy. Since the contact structure is crucial, we have kept the distance (2.4 Å: optimized Au-Co dimer distance) between gold and Co atoms fixed for all the calculations. In principle, one could incorporate more gold atoms for a better representation of the self-energy functions to obtain a better estimate of the conductance. But this procedure would be computationally cumbersome. Since we have used the same contact geometry for all the wires and for both parallel and antiparallel magnetization states, we do not anticipate any significant change in the relative conductance of wires of various lengths as well as the spin valve effect. $g^{\alpha,\beta}$ In Eq. (2) represent the Green's functions of the combined metal-wire system for α (spin up) or β (spin down) orbitals and are defined as

$$g^{\alpha,\beta}=(ES-H^{\alpha,\beta}-\Sigma_1^{\alpha,\beta}-\Sigma_2^{\alpha,\beta})^{-1}, \tag{3}$$

where S is the overlap Hamiltonian and $H^{\alpha,\beta}$ is the Hamiltonian matrix for the $\alpha(\beta)$ orbitals. For our calculation, we have carried out a self-consistent spin unrestricted density functional calculation for both the parallel and antiparallel spin configurations between the two Co atoms. Two sets of Kohn-Sham equations[15] are solved self-consistently to obtain the Hamiltonian matrices for the α and β orbitals. We have used a gradient corrected approach and PW91 exchange and correlation functionals in our calculation. The GAUSSIAN 98 electronic structure code with LANL2DZ Gaussian basis sets[19] was utilized for this calculation.

Discussion. Using the above procedure, we have computed the conductance of the atomic wires and the results are summarized in Fig. 5. Several interesting features are noticeable in this figure. Both for parallel and antiparallel spin configurations of the Co atoms, we have an oscillatory variation in conductance with the length of the atomic wire; the conductance in an odd atom carbon wire is larger than the neighboring even atom carbon wires. This is clearly due to stronger, π-conjugation between C atoms in the chain for which the conductance is expected to be higher. A similar oscillation in conductance was obtained by Lang and Avouris[4] and later by Larade *et al.*[5] in carbon atom wires with nonmagnetic contacts. Incorporating a magnetic atom, which acts as a spin polarizer/filter, increases the conductance, but the oscillation of the pure C-atomic wire persists. This suggests that the oscillation in conductance is governed by the intrinsic electronic structure of the C-atom wires (e.g., the fully or partially occupied nature of the highest occupied molecular orbital).[4] The conductance observed in our calcu-

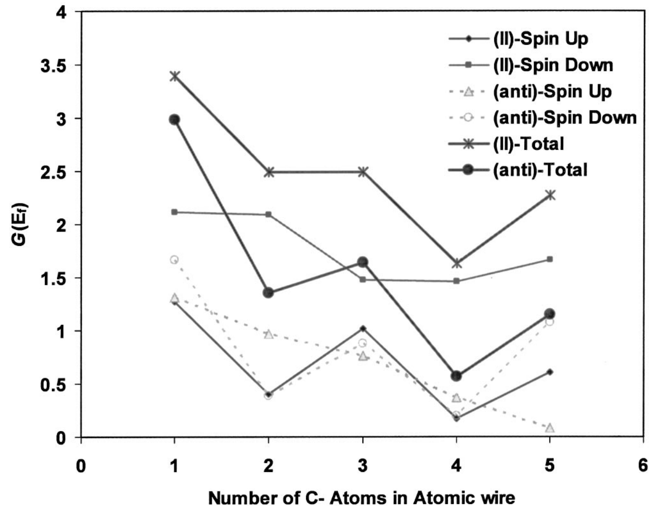

FIG. 5. Conductance (in units of e^2/h) evaluated at the Fermi energy for both parallel (ll) and antiparallel (anti) spin configurations in the C wires as a function of the number of C atoms in the wires.

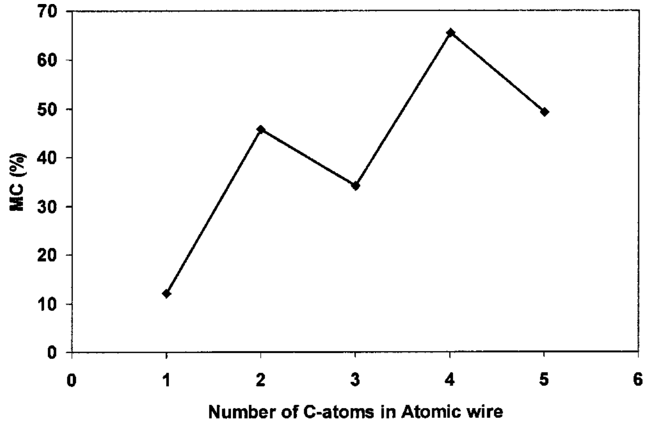

FIG. 6. Magneto conductance $\mathrm{MC}=[G(\uparrow\uparrow)-G(\uparrow\downarrow)]/G(\uparrow\uparrow)$, as a function of the number of C atoms in the atomic wire.

lation is more than $1.5G_0$ for a single C atom, and more than G_0 for the rest, where $G_0=2e^2/h$. In a simple C wire (with no magnetic filter), Lang and Avouris obtained[4] a conductance of about $2G_0$. The increase in conductance (more than G_0) in our calculation is due to the strong coupling between Co and gold, which leads to metal induced gap (MIG) states near the Fermi energy. These MIG states open up quantum channels for conduction, especially for a single C atom in the wire. In addition, we also note that the overall conductance decreases with increasing number of carbon atoms showing a nonballistic behavior. Similar behavior was observed by Larade *et al.*[5] when they optimized the structure with nonmagnetic contact.

We notice that the parallel spin configurations between the Co atoms give rise to higher conductance than the antiparallel spin configurations. The spin valve effect, also seen in bulk multilayers,[20] is due to the spin-dependent electron scattering. In the antiferromagnetic case, the resistance is high since an electron (say, spin up) at one end of the magnetic contact will not be able to go through the Co (spin down) at the other end due to the suppressed α density of states. Since the spin valve effect or the magnetoresistive effect of the device relies primarily on the change in resistances between parallel and antiparallel magnetization states in the magnetic layers, we have estimated the magnetoconductance (MC) (the reciprocal of the magnetoresistance), defined as

$$\mathrm{MC}=\frac{G(\uparrow\uparrow)-G(\uparrow\downarrow)}{G(\uparrow\uparrow)}, \tag{4}$$

where $G(\uparrow\uparrow)$ and $G(\uparrow\downarrow)$ refers to the conductance in the parallel and antiparallel configurations, respectively. The result for MC (in %) for different lengths of the wire is shown in Fig. 6 where the oscillatory behavior in MC is evident. This suggests that by controlling the length of an atomic wire (the number of C atoms between the two magnetic atomic contacts), one can tune the MC *or magnetoresistance* to a higher or lower value. For example, for a wire structure with four carbon atoms, we found about 65% change in resistance between parallel and antiparallel spin configurations. A similar effect on length dependence was noted in bulk Fe/Cu multilayers.[21] It is important to point out that even though our results are strictly valid for zero temperature, we do not expect a change in the spin valve effect at experimentally realizable temperature. From Fig. 2, one can notice that the difference in energy between the two magnetization states (on and off state) is significantly higher than k_BT (~ 0.026 eV corresponding to room temperature) suggesting by increasing the temperature to ~ 300 K one would not switch between these two magnetization states.

In summary, we have studied spin-assisted transport in atomic carbon wires using a first-principles gradient corrected density functional method and the Landauer approach. The calculated quantum conductance shows a spin valve effect. Our results suggest that the ground states of carbon atom wires sandwiched between atomic Co contacts have antiferromagnetic alignments (an off state). This is an exciting result since from an experimental point of view it is a difficult task to obtain an antiferromagnetic coupling between two magnetic contacts separated only by several Ås. Our calculations show that one can obtain the antiferromagnetic state of carbon wires up to five atoms naturally and that the ferromagnetic state (on) between the two Co atoms can be obtained with the application of an uniform external magnetic field. In addition, we also find that the even numbered (carbon atom) wires exhibit enhanced stability of the antiferromagnetic (AF) state due to a super exchange mechanism facilitated by the σ-π conjugation present in the systems. It will be useful in the future to study longer chains of carbon atoms in order to investigate the energy difference between the magnetic states and how long carbon chains can sustain an AF ground state. We find that the magnetoconductance in carbon atom wires shows an oscillatory behavior and this behavior arises due to the intrinsic electronic structure of carbon chains. The nonperiodic conductance behavior of carbon wires shows a very different behavior than nanotubes made of the same carbon material where one finds a ballistic transport.

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