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First-principles investigation of spin-polarized conductance in atomic carbon wires

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We analyze spin-dependent energetics and conductance for one-dimensional (1D) atomic carbon wires consisting of terminal magnetic (Co) and interior nonmagnetic (C) atoms sandwiched between gold electrodes, obtained by employing first-principles gradient-corrected density functional theory and Landauer's formalism for conductance. Wires containing an even number of carbon atoms are found to be acetylenic with σ-π bonding patterns, while cumulene structures are seen in wires containing an odd number of carbon atoms as a result of strong π conjugation. In the case of even C-atom wires, the antiparallel Co spin state remains the ground state up to 12 carbon atoms. For odd C-wire systems, the antiparallel spin configuration between the two terminal Co atoms remains the ground state irrespective of the number of C atoms in the wire. The 14-carbon atom wire is seen to have a parallel Co spin configuration in the ground state. The stability of the antiferromagnetic state in the wires is ascribed to the superexchange effect. For the cumulenic wires, this effect is constant for all wire lengths. For the acetylenic wires, the superexchange effect diminishes as the wire length increases, with the exception of the wire containing two carbon atoms. The superexchange characteristic length in acetylenic C wires is found to be ~20 Å. Conductance calculations at the zero-bias limit show spin-valve behavior, the parallel Co spin-configuration state giving higher conductance than the corresponding antiparallel state, and a nonmonotonic variation of conductance with the length of the wires for both spin configurations.

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I. INTRODUCTION

Miniaturization from submicron conventional solid state devices to extreme small scale single organic molecule-based devices has been the focus of intensive research in recent years, motivated by the emerging field of molecular-scale electronics and quantum information technology. Controlled transport of electrons in molecular wires containing only a few atoms forms the basis of molecular-scale electronics. Significant recent advances in experimental techniques have made it possible to fabricate nanowires containing only a few atoms and to measure their electrical properties.[1] Specifically, atomic carbon wires containing up to 20 atoms have been synthesized.[2] These carbon wires serve as ideal models to develop an understanding of the mechanism for electron transport in finite one-dimensional (1D) systems. Previous theoretical and experimental studies[3–8] on atomic and molecular wires have been primarily limited to charge transport, with some recent exceptions.[9–14] Recent experimental measurements have shown that electron-spin polarization can persist considerably longer than charge polarization.[15] It is consequently highly desirable to learn how to control the electron transport in molecular systems offered by spin degrees of freedom, adding another dimension to the emerging field of molecular-scale electronics and revealing important information for potential applications in spin-based molecular electronics (spintronics).

Pure carbon clusters have a long history.[16,17] Small carbon clusters are known to have low-energy linear structures characterized by cumulenic bonding (C═C═C═C) with near-equal bond lengths. These structures are stabilized by strong π conjugation between the double bonds, which are alternately directed in the x and y planes perpendicular to the bonds.[16] Some of these clusters also possess cyclic forms, which also become the stable form for larger sizes.[17] Lang and Avouris calculated the conductance of such a cumulenic carbon atom wire, i.e., with all C-C bond lengths constrained to be equal, connected on both ends directly to metal electrodes.[5] They found an oscillatory behavior, with wires composed of odd numbers of carbon atoms having a higher conductance than even-numbered wires. This was contrary to expectations based on a simple molecular-orbital theory of the cumulene structure, and was attributed to electron donation from the metal contacts into additional π bonds formed between the terminal carbon atoms and the electrodes.

The presence of terminal magnetic atoms has recently been shown[14] to modify both the structures and the conductance properties of these wires. Pati *et al.* have reported first-principles calculations[14] of spin-dependent electronic structures and energetics, as well as spin-polarized conductance of small carbon wires containing up to five carbon atoms that are terminated by magnetic atoms that are in turn attached to gold electrodes. The magnetic atoms can act as spin polarizers or filters, resulting in a strong spin-valve effect. These results have shown that when terminated by magnetic atoms, the π-conjugated structure is not necessarily the lowest energy structure. In particular, for the short even-numbered carbon wires, the acetylenic structure with alternating σ and multiple π bonds becomes more stable. The calculations have also shown that the ground states of these magnetically terminated carbon wires have antiparallel terminal-atom spin configurations, which could be rationalized by a contribution from super-exchange effects. The conductance of the wires is found to be nonmonotonous with wire length, as in the pure C wires,[5] and is shown to depend strongly on the magnetic configuration of the terminal atoms, with the result that the wires could be made to act as a molecular spin valve.

This study of spin-dependent properties of short carbon wires[14] raised a number of fundamental questions. In particular, how are the relative energetics of the wire structures for different spin configurations affected by increasing the length of the carbon wire spacer between the terminal magnetic atoms? How does the ground-state spin configuration between the terminal magnetic atoms depend upon the size of the spacer? How does the effective exchange coupling between the magnetic species change with the number of carbon atoms in the wire? What is the critical length of the connecting wire up to which the superexchange effects identified for the short wires survive?

In order to address these subtle questions and to thereby improve our understanding of spin-dependent electron transfer in 1D molecular system, we extend here the work in Ref. 14 up to wires containing 15 carbon atoms. Our-first principles calculations, which explicitly include spin-polarization effects, reveal that for even C-atom wires the antiparallel Co spin state remains the ground state for wires with up to 12 carbon atoms. For odd C-wire systems, the antiparallel spin configuration between the two terminal Co atoms remains the ground state irrespective of the number of C atoms in the wire. Wires containing an odd number of C atoms are found to have cumulenic structures, while acetylenic structures are evident in even C-wire systems. The 14-carbon atom wire is seen to have a parallel Co spin configuration in the ground state. Interestingly, we find that for wires containing an odd number of carbon atoms, the energy difference (ΔE) between the antiferromagnetic and ferromagnetic state (antiferromagnetic being the ground state) remains constant as a function of wire length. In contrast, in the acetylenic carbon chains, this energy difference decreases exponentially as a function of the number of atoms with the exception of the 2-carbon atom wire. Analysis of this change in ground-state spin configuration (14-carbon atom wire) in terms of the superexchange contribution allows us to estimate the characteristic length for superexchange in acetylenic carbon wires as ~20 Å. We also find that the π-conjugated cumulenic wires exhibit higher conductance than the acetylenic wires. Finally, the calculated magnetoconductance for different wire lengths shows a large difference between the two magnetization states, particularly for C wires containing 13 and 14 C atoms, suggesting its potential applications in molecular magnetoelectronics.

The remainder of the paper is organized as follows. Our computational approach is described in Sec. II. The results and discussions are presented in Sec. III. Section IV summarizes our results.

II. COMPUTATIONAL DETAILS

As in the previous study of short atomic wires,[14] we utilize an architecture consisting of linear chains of nonmagnetic C atoms connecting two magnetic Co atoms. The Co-$(\mathrm{C})_n$-Co wire structures, with $n=6$–15, are subsequently inserted between two metal gold electrodes for calculation of spin-polarized conductance. In a magnetic system like this, the total conductance can be evaluated as

$$g_t = g_{Spin\ Conserved} + g_{Spin\ Flip}, \tag{1}$$

where $g_{Spin\ Conserved}$ is the conductance from the spin-conserved part and $g_{Spin\ Flip}$ is the conductance due to spin-flip scattering. The latter contribution plays a significant role only when the spin-orbit coupling plays a significant role. Since the spin-orbit coupling effect in highly ordered, strongly conjugated C-wire structures is expected to be small, leading to a large spin-flip scattering length, we have assumed the scattering to be coherent and have not included relativistic spin-orbit coupling effects in the present paper. The spin-conserved part of the conductance is calculated as

$$g_{Spin\ Conserved} = g^{\alpha} + g^{\beta}, \tag{2}$$

where g^{α} and g^{β} are the contribution to conductance from up (α) and down (β) spin states, respectively. Since at low bias the conduction primarily occurs in the close proximity of the Fermi energy of the metal contact, we can use Landauer's approach[18] to calculate g^{α} and g^{β} at the Fermi energy. In the zero-bias limit, we have

$$g^{\alpha(\beta)}(E_f) = \frac{e^2}{h} T^{\alpha(\beta)}(E_f), \tag{3}$$

where $T^{\alpha\beta}$ is the transmission function for the spin-up (α) or spin-down (β) electrons. This is evaluated using the Green's function derived from the Kohn-Sham matrix obtained from self-consistent spin unrestricted density functional calculations.[19] We have employed a gradient-corrected Perdew-Wang 91 exchange and correlation functional[19] and double numerical polarized basis set[20] for the calculation of energetics and magnetic structures. Both the spin configurations and geometry for parallel and antiparallel magnetic states between the Co atoms are simultaneously optimized using the self-consistent density functional theory (DFT) approach. Antiparallel magnetic configurations between the Co atoms are obtained by making use of the broken symmetry formalism.[13,14] Particularly for the conductance calculation, we incorporated a single gold atom on both ends of the wire Co-$(\mathrm{C})_n$-Co to form an extended molecular system to explicitly calculate the coupling matrices for the evaluation of the self-energy functions. Details of this procedure can be found in Refs. 13 and 14. From the calculated spin-polarized conductance, we estimate the magnetconductance (MC) according to

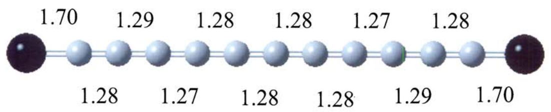
$$\mathrm{MC} = \frac{g_t(\uparrow\uparrow) - g_t(\uparrow\downarrow)}{g_t(\uparrow\uparrow)}, \tag{4}$$

where $g_t(\uparrow\uparrow)$ and $g_t(\uparrow\downarrow)$ are given by the total conductance, Eq. (1) in the parallel and antiparallel configurations, respectively.

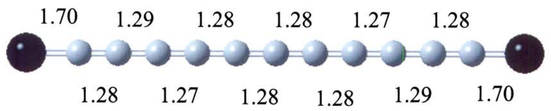
III. RESULTS AND DISCUSSION

A. Structures, magnetic properties, and energetics

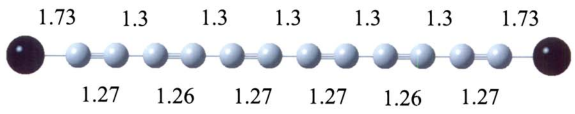
Using the procedures summarized in the previous section, we have optimized both the spin state and geometry for the Co-$(\mathrm{C})_{n=6\text{-}15}$-Co wire structures in parallel and antiparallel magnetic configurations between the Co atoms. Similar to the earlier report for short atomic wires containing up to five carbon atoms,[14] we find a clear π-π and σ-π bonding pattern for the C atoms in the wire. This is illustrated in Fig. 1 for



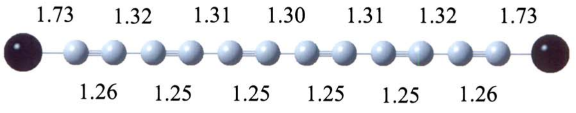
Ferro Co_2C_{11}



Antiferro Co_2C_{11}



Ferro Co_2C_{12}



Antiferro Co_2C_{12}

FIG. 1. (Color online) Schematic of the bonding pattern in a carbon wire containing (a) 11 and (b) 12 carbon atoms. Terminal black spheres are cobalt atoms and gray spheres are carbons. All the optimized bond distances are indicated for both parallel (ferromagnetic) and antiparallel (antiferromagnetic) spin configurations of the atomic carbon wire.

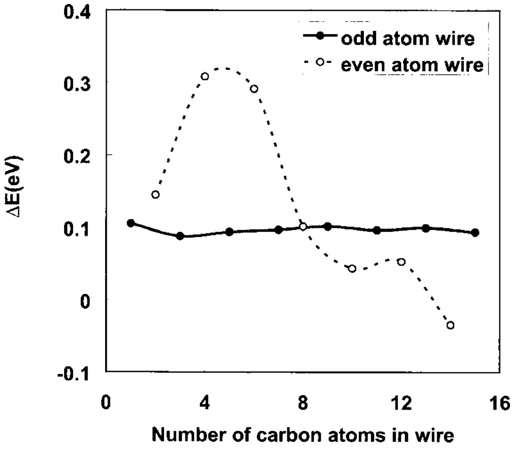


FIG. 2. The energy difference $[\Delta E = E(\uparrow\uparrow) - E(\uparrow\downarrow)]$ between parallel and antiparallel spin configurations in carbon atom wires, as a function of the number of carbon atoms in the wire, n. Even n chains are connected with a dashed line and odd n chains are connected with a solid line. Values for $n=1$–5 carbon atoms are taken from Ref. 14.

$n=11$ and 12 carbon atom wires, which shows the ground-state structures of both magnetic configurations. The bond distances in the even carbon wires show a clear alternation, both for ferromagnetic and antiferromagnetic, consistent with σ-π bonding. In contrast, the odd wires show no evidence of bond alternation, consistent with a pure π-conjugated structure. Comparing the energy for parallel (ferromagnetic) and antiparallel (antiferromagnetic) spin configurations in the wires, we find that the antiferromagnetic state is lower in energy for all even wires studied here, except $n=14$, which shows a ferromagnetic ground state. The calculated energy difference between ferromagnetic and antiferromagnetic configurations, $\Delta E = E(\uparrow\uparrow) - E(\uparrow\downarrow)$, as a function of number of C atoms in the atomic wire, is shown in Fig. 2. For comparison purposes we have also shown here the results for short atomic wires obtained in Ref. 14. The energy difference between the two magnetization states is found to be larger than k_BT at room temperature, suggesting that these antiferromagnetic states are stable in normal operating conditions. The lower energy for the antiferromagnetic spin configuration between the terminal Co atoms can be attributed to the superexchange interaction that is facilitated by a strong overlap of the magnetic Co and the nonmagnetic C atoms. A careful analysis of ΔE as a function of wire length suggests that for the strongly π-conjugated wires, i.e., for cumulenic structures (odd number of C atoms), the energy difference is approximately independent of the number of C atoms in the wire. For σ-π conjugated C wires (even number of C atoms), ΔE exhibits a nonmonotonic behavior with the wire length. In particular, the antiferromagnetic state for C wires containing two, four, and six carbon atoms are more stable than those for the π-conjugated C wires. For acetylenic wire, ΔE decreases in an exponential manner (with the exception of the two-carbon atom wire) and is found to be negative for the wire containing 14 C atoms. This suggests that the superexchange, which stabilizes the antiferromagnetic phase in a σ-π conjugated system, attenuates exponentially and becomes negligible for a wire containing 14 C atoms. This allows us to estimate the superexchange characteristic length for a σ-π conjugated system to be ~20 Å.

The additional stability for the wires containing two, four, and six C atoms compared to one, three, and five C atom wires could be explained as follows. In wires containing one, three, and five C atoms, the exchange interaction is facilitated between the two terminal Co atoms through delocalized spins shared by both the Co atoms, stabilizing further the ferromagnetic coupling compared to that in short even atom wire, as shown in Fig. 3. This type of so-called double-exchange effect, which stabilizes the ferromagnetic ordering has been seen in the Fe^{3+}-Fe^{2+} compound.[21] This extra stability of ferromagnetic ordering in the short odd atom wire leads to a smaller ΔE as compared to wires containing two, four, and six C atoms. In odd C wires, double-exchange and superexchange effects remain constant due to continuous π conjugation. However, the superexchange effect exceeds the double-exchange effect resulting in antiferromagnetic con-

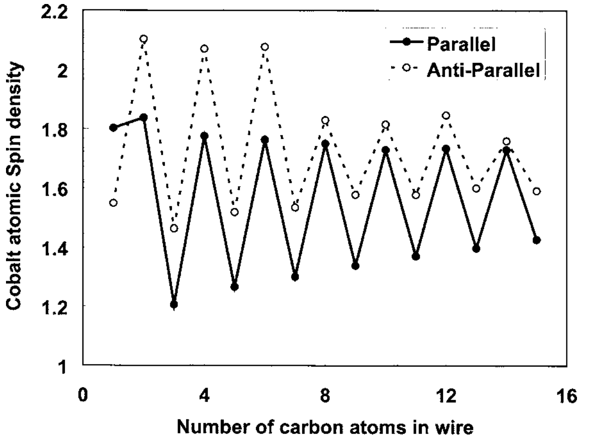


FIG. 3. Atomic spin density of the terminal Co atoms for both parallel and antiparallel Co spin configurations, shown as a function of the number of carbon atoms in the wire, n.

figurations as the ground states. In even C wires containing two, four, and six C atoms, the double-exchange effect is smaller compared to one, three, and five C wires, respectively. This is due to the lack of delocalization in even wires (shown in Fig. 3), which in effect destabilizes ferromagnetic ordering, leading to a large energy difference between the two magnetic configurations (ΔE in Fig. 2). In summary, both double exchange and super exchange play an important role in stabilizing the magnetic ordering in these systems.

It is worthwhile to note that thus far we have only considered a linear C-wire structure for our calculation. However, in real experimental set up, the contact and the molecule are always under stress, which may lead to a nonlinear wire structure. To understand the stress effects on the wires, we considered wire containing only five C atoms and artificially induced a strain by pulling the middle C atom in the chain to form a V-shaped wire, with the angle at the Co with respect to the ground-state linear structure being 20° deg. The results from energetics calculations indicated a 7% reduction in ΔE (with antiferromagnetic configurations being the lower energy state) compared to our reported ΔE for the ground-state structures, suggesting the importance of string tension on the magnetic interaction energy.

B. Spin-polarized conductance

Using Landauer's approach as outlined in Sec. II, we have calculated the spin-polarized conductance in the zero-bias limit. The results are summarized in Fig. 4. Several interesting features are apparent here. First, the conductance in the C wire is found to be higher for parallel than for the antiparallel spin configuration between the terminal Co atoms. This is a prerequisite for the spin-valve effect, which is primarily due to spin-dependent scattering and has been observed in magnetic/nonmagnetic heterobulk structures.[22,23] Second, both parallel and antiparallel spin configurations show oscillations in conductance as a function of the wire length. For the parallel spin configurations, the conductance oscillation is damped after $n=8$ C atoms and remains almost constant at $\sim 1g_0$ ($g_0=2e^2/h$) for the wire with $n=12$, 13, 14, and 15 C atoms. In contrast, in the antiparallel case, the conductance decreases with the increase of wire length and finally vanishes for 12 and 14 C atom wires. The faster decrease of conductance with the wire length for even C wires in the antiparallel case is due to the presence of σ bonds in these systems, which can act as tunnel barriers for electron conduction. In fact, recent calculations on σ-bonded structures have shown that the tunnel barrier increases with the increase of wire length,[24] leading to an exponential decay in the electronic conduction. In contrast, in odd-C atom wires, the π orbitals are highly delocalized, providing pathways for electron transfer and consequently leading to higher conductance, as seen in Fig. 4.

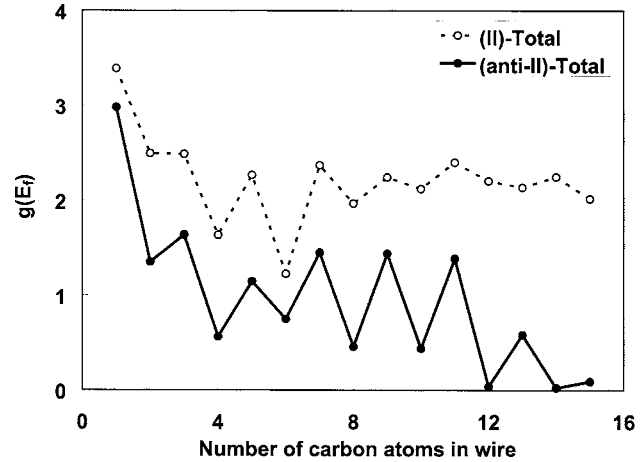


FIG. 4. Conductance (in units of e^2/h) evaluated at the Fermi energy for both parallel (ferromagnetic) and antiparallel (antiferromagnetic) spin configurations in the carbon wires, as a function of the number of carbon atoms in the wires, n.

In order to understand the oscillatory pattern in conductance, we have also calculated the Mulliken charges and spin densities at individual atoms for different wire lengths. The spin densities at the Co atoms, i.e., the difference between the number of spin-up and spin-down electrons, are shown in Fig. 3. We see that for both parallel and antiparallel magnetization states, the spin density at the Co atoms oscillates with the number of C atoms in the wire. Also, the σ-π conjugated wires show a higher atomic spin density at Co than the π-conjugated wires. This is not surprising since, as noted above, the π-conjugated systems have a stronger delocalization of spin compared to the σ-π conjugated wires. We have also calculated the magnetoconductance (MC) according to Eq. (4). Figure 5 summarizes the MC values as a function of the number of C atoms in the wires, with MC displayed as a percentage. We find an oscillatory behavior in the magnetoconductance, with a maximum value of 100% change in resistance between the parallel and antiparallel magnetization states for wires containing 12 and 14 C atoms. This large change in resistance between the two magnetization states suggests potential applications of these nanoscale materials in molecular magnetoelectronics.

IV. SUMMARY

We have investigated the chain-length-dependent magnetic structures and energetics associated with highly conju-

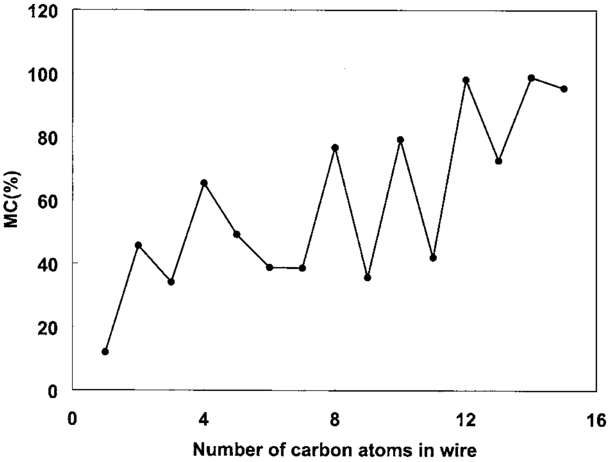


FIG. 5. Dependence of magnetoconductance (MC), Eq. (4), on the number of carbon atoms in the atomic wire, *n*.

gated, 1D carbon wires sandwiched between magnetic Co atoms using the gradient-corrected density functional approach. The Co-terminated wires show an alternation of structure between cumulenic for odd numbers of C atoms and acetylenic for even numbers of C atoms. The spin-polarized conductance was calculated as a function of the number of C atoms in the wire in the zero-bias limits using Landauer's formalism. These length-dependent calculations reveal an oscillatory pattern in conductance, with a significantly higher conductance arising in the parallel magnetization state compared to that in the antiparallel magnetization state. For odd C wire systems, the antiparallel spin configuration between the two terminal Co atoms remains the ground state irrespective of the number of C atoms in the wire. The even-C wire structures containing up to 12 carbon atoms are found to have an antiferromagnetic spin configuration between the terminal Co atoms. For the wire with 14 carbon atoms, a parallel Co spin configuration is found to be the ground state. The energy difference between the parallel and antiparallel magnetization states is found to be larger than k_BT at room temperature, suggesting that these two magnetization states are not interchangeable at normal operational temperatures. The stability of the antiferromagnetic spin configuration between the terminal Co atoms is due to the superexchange interaction, which is facilitated by strong orbital overlap of the terminal magnetic Co atoms and the nonmagnetic C atoms of the wire. The superexchange effect diminishes exponentially for even C atom wires and becomes negligible for the C wire containing 14 C atoms. This allows us to estimate the characteristic length for the superexchange interaction in these σ-π conjugated carbon wires as ~20 Å. For carbon wires containing 12 and 14 C atoms, we found almost no conductance in the antiparallel spin configuration states, resulting in a maximum value of 100% change in resistance for carbon wires with 12 and 14 carbon atoms.

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