Half-metallic zigzag carbon nanotube dots

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A comprehensive first-principles theoretical study of the electronic properties and half-metallic nature of finite zigzag carbon nanotubes is presented. Unlike previous reports, we find that all nanotubes studied present a spin-polarized ground state, where opposite spins are localized at the two zigzag edges in a long-range antiferromagnetic configuration. Relative stability analysis of the different spin states indicate that, for the shorter segments, spin-ordering should be present even at room temperature. The energy gap between the highest occupied and the lowest unoccupied molecular orbitals of the finite systems is found to be inversely proportional to the nanotubes segments length, suggesting a route to control their electronic properties. Similar to the case of zigzag graphene nanoribbons, half-metallic behavior is obtained under the influence of an external axial electric field.

I. INTRODUCTION

Magnetism in carbon based materials has attracted considerable scientific interest in recent years both from an experimental\cite{1-17} and a theoretical\cite{18-53} viewpoint. While the origin of magnetic ordering in such systems is yet to be fully understood, it has been suggested that spin polarization may arise from local structural defects,\cite{33,36,41,53} sterically protected carbon radicals\cite{34} and chemical impurities.\cite{30,40,43} A unique mechanism for spin ordering in graphene based systems is related to the appearance of edge states.\cite{18-29,42,45-52} When cutting a graphene sheet along its zigzag axis to form a narrow and elongated graphene nanoribbon (GNR), distinct electronic states appear, which are localized around the exposed edges.\cite{54-59} These states are predicted to carry spin polarization, resulting in a well defined magnetic ordering.\cite{19-26,28,29,42,45-52} Due to the bipartite hexagonal structure of graphene, the electronic ground state of such zigzag graphene nanoribbons (ZZ-GNRs) is characterized by an antiferromagnetic (AFM) spin ordering, where the edge states located at the two zigzag edges of the ribbon have opposite spins. Under the influence of an external electric field, these systems have been predicted to become half-metallic with one spin channel being semiconducting and the other metallic,\cite{45,47} thus acting as perfect spin filters with important implications to the field of spintronics. Furthermore, this behavior has been shown to be preserved for finite graphene nanoribbons, where the zigzag edge may be as short as a few repeating units.\cite{48-52}

Similar to graphene nanoribbons, is has recently been suggested that spin ordering may occur on the zigzag edges of hydrogen terminated finite sized carbon nanotubes (CNTs)\cite{32,37} Based on density functional theory (DFT) calculations within the local spin density approximation (LSDA), it was predicted that the ground electronic state of these systems strongly depends on their circumferential dimension ranging from AFM to ferromagnetic (FM) ordering, where both edges of the nanotube bear spins of the same flavor. This conclusion is in striking difference from the case of ZZ-GNRs, where the ground electronic state was found to have an AFM spin ordering regardless of the dimensions of the ribbon.\cite{19-26,28,29,42,45-52}

Interestingly, contradicting results have been reported in the literature,\cite{33} indicating that the ground state of unpassivated zigzag CNTs has a low-spin AFM ordering even for nanotubes that have earlier been considered to present a high-spin ferromagnetically ordered ground state.\cite{32}

In light of the considerable progress that has been made in the synthesis and fabrication of ultra-short\cite{60-64} and open ended\cite{65} CNTs and ultra-narrow GNRs,\cite{66-69} it is desirable to obtain a full understanding of their electronic properties. Such understanding may prove important in future applications of these molecules in nanoelectronic and nanospintronic devices.
the application of an external axial electric field results in half-metallic behavior.

II. METHOD

We have studied a set of sixteen finite segments of the (7,0), (8,0), (9,0), and (10,0) zigzag CNTs (see Fig. 1). For each CNT four segments of 0.93, 1.56, 2.20, and 2.84 nm in length are considered. All nanotubes considered are hydrogen terminated, i.e., each carbon edge atom is passivated with a single hydrogen atom. We label the CNTs by \((N,M,L)\), where \((N,M)\) is the infinite CNT from which the relevant finite segment is derived and \(L\) is the number of zigzag carbon rings stacked together to form the finite CNT (see Fig. 1). This set of nanotubes includes all those previously predicted to present a ferromagnetically ordered ground state.32

All the calculations presented in this work were carried out using the development version of the Gaussian suite of programs.70 Spin polarized ground state calculations were performed using the screened exchange hybrid density functional of Heyd, Scuseria and Ernzerhof (HSE06),71–74 which has been tested on a wide variety of materials and has been shown to accurately reproduce experimental bandgaps75–77 and first and second optical excitation energies in metallic and semiconducting single walled CNTs.78,79 The inclusion of short-range exact-exchange in the HSE06 functional makes it suitable to treat electronic localization effects,80–84 which are known to be important in this type of materials.18–29,42,45–48,52,56–59 This is further supported by the good agreement, which was recently obtained, between predicted bandgaps85 of narrow graphene nanoribbons and measured values.66–68 To obtain a reliable ordering of the different magnetization states, we find it important to relax the geometry of the finite CNTs for each spin polarization. Therefore, unless otherwise stated, all reported electronic properties are given for fully optimized structures using the double-zeta polarized 6-31G** Gaussian basis set.86 It should be noted that since our calculations are performed within a single determinant framework, we can determine only the total spin vector projection along a given axis, \(m_s\), and not the total spin. This is standard in unrestricted Kohn-Sham theory.

III. RESULTS AND DISCUSSION

We start by performing ground state calculations on the full set of sixteen finite CNTs studied. In Fig. 2 spin-density maps of the ground state of four representative CNT segments are presented. In contradiction with previously reported LSDA results32,37 which predict the (8,0) CNT derivatives to have an AFM ground state and the (7,0) and (10,0) nanotube segments to have a ferromagnetically ordered ground state, our HSE06 calculations indicate that all CNTs studied have an antiferromagnetically ordered ground state, with a total spin vector projection of \(m_s = 0\) and a spatially resolved spin density. Similar to the case of finite GNRs,48,52 one zigzag edge of the CNTs segments has a high density of spin \(\alpha\) electrons (blue color in Fig. 2) while the other edge is rich with spin \(\beta\) electrons (red color in the figure).

To understand the origin of this discrepancy between the predictions obtained using the semi-local and the screened-hybrid functionals, we have repeated the calculations using the LSDA functional and the same atomic basis set. Interestingly, we encountered considerable convergence problems when performing the calculations at this level of theory. For many of the systems we have found it necessary to start the SCF with a pre-designed initial guess in order to achieve convergence to the appropriate spin state. Once convergence was achieved we have found that for the (7,0,7) and (7,0,10) systems the LSDA functional does predict a ferromagnetically ordered ground state. Nevertheless, this state is only 5 meV below the antiferromagnetically ordered state. For the rest of the systems considered, whenever convergence was achieved, an AFM ground state has been found.

We attribute this behavior to the self-interaction error appearing in the LSDA functional, which tends to considerably over estimate electron delocalization.87,88 Since some of the most important physical characteristics of the systems under consideration relate to pronounced localized edge states, care should be taken when using the LSDA functional to capture the correct energetic ordering of the different spin polarized states. As mentioned above, the inclusion of Hartree-Fock exchange within hybrid functionals considerably reduces the delocalization error and thus makes them more appropriate to treat
scenarios where electron localization plays an important rule in determining the electronic structure of the system.\textsuperscript{80–84}

To quantify our findings, we study the stability of the antiferromagnetically ordered ground state with respect to the above lying ferromagnetically ordered spin state. In Fig. 3 the energy differences between the antiferromagnetic ground state and the above lying higher spin multiplicity ferromagnetic state for the four sets of CNTs segments studied, as calculated by the HSE06 functional. $k_B T$ at room temperature is indicated by the dashed magenta line. Inset: Energy difference between the antiferromagnetic ground state and the above lying higher spin multiplicity ferromagnetic state for the four sets of CNTs segments studied, as calculated by the HSE06 functional.

FIG. 3: Energy differences between the antiferromagnetic ground state and the above lying higher spin multiplicity ferromagnetic state for the four sets of CNTs segments studied, as calculated by the HSE06 functional. $k_B T$ at room temperature is indicated by the dashed magenta line. Inset: Energy difference between the antiferromagnetic ground state and the above lying higher spin multiplicity ferromagnetic state for the four sets of CNTs segments studied, as calculated by the HSE06 functional.

Before discussing the effect of an electric field on the electronic properties of finite CNTs, it is essential to study their ground state characteristics in the absence of external perturbations. The length dependence of the HOMO-LUMO (highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively) gap would be the most important parameter to address. In Fig. 4 the energy gap as a function of the length of the CNTs segments are presented, for the four subsets of nanotubes considered. All studied finite zigzag CNT segments have sizable HOMO-LUMO gaps, including the (9,0,L) and (8,0,L) series, which in the limit of $L \rightarrow \infty$ is expected to become metallic. The HOMO-LUMO gap is inversely proportional to the length of the CNTs segments for all nanotubes studied and its value strongly depends on the length, changing by more than 0.8 eV for lengths in the range of 0.9 and 2.8 nm. This suggest that careful tailoring of the nanotube length can be used as a sensitive control parameter over its electronic properties.\textsuperscript{89}

We now turn to check whether the similarity between finite zigzag CNTs and finite GNRs extends also to the case of half-metallic behavior under the influence of an external electric field.\textsuperscript{45,52} In Fig. 5 we present the spin-polarized HOMO-LUMO gap dependence on an external electric field applied parallel to the main axis of the nanotubes (perpendicular to the zigzag edges) for four repre-
The main differences observed are splitting (clearly seen on the upper left panel of Fig. 5). Reducing the total spin polarization and the energy gap final field results in spin transfer between both edges thus creating a half-metallic state or a perfect spin filter. At this point, due to the increased mobility of the metallic electrons, further increase in the external field results in spin transfer between both edges thus reducing the total spin polarization and the energy gap splitting. This gap splitting continues up to a point, where one spin channel presents a vanishing gap, thus creating a half-metallic state or a perfect spin filter. At this point, due to the increased mobility of the metallic electrons, further increase in the external field results in spin transfer between both edges thus reducing the total spin polarization and the energy gap splitting.

FIG. 5: Spin-polarized HOMO-LUMO gap dependence on the strength of an external axial electric field for the (7,0,7) (upper left panel), (8,0,7) (upper right panel), (9,0,7) (lower left panel), and (10,0,7) (lower right panel) finite zigzag CNTs as calculated by the HSE06 functional. Fixed geometries of the relaxed structures in the absence of the external field were used. Full and open marks stand for the α and β spin gaps, respectively.

To summarize, intrigued by reports of contradicting results regarding the ground state properties of finite zigzag carbon nanotubes, we performed a comprehensive study of the electronic character of a representative set of sixteen CNT segments. Unlike previously reported results, we found that all finite zigzag CNTs possess a spin-polarized ground state with antiferromagnetic spin ordering. This state is characterized by high spin-density of opposite spins located at the two zigzag edges of the molecule. Our HSE06 results predict the antiferromagnetic ordering to be considerably stable with respect to higher spin multiplicity states and the non-magnetic closed shell state, suggesting that their spin polarization is detectable at room temperature. The HOMO-LUMO gap was found to be inversely proportional to the length of the zigzag CNT segment. The high sensitivity of the gap to changes in the length of the CNT segment suggests a way to control the electronic properties of such systems. Similar to the case of zigzag GNRs, the half-metallic nature of finite zigzag CNTs under an external in-plane electric field was verified. Due to the recent success of the HSE06 functional in predicting the electronic properties of GNRs and CNTs of different nature and dimensions, we are confident about the reliability of the predictions presented here.

V. ACKNOWLEDGMENTS

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Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *GAUSSIAN Development Version, Revision F.02*, Gaussian, Inc., Wallingford, CT, 2004.

71 J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, 8207 (2003).

72 J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 124, 219906 (2006).

73 A. F. Izmaylov, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. 125, 104103 (2006).

74 The screened hybrid approximation is obtained using the HSE1PBE keyword in the development version of Gaussian.

75 J. Heyd and G. E. Scuseria, J. Chem. Phys. 121, 1187 (2004).

76 J. Heyd, J. E. Peralta, and G. E. Scuseria, J. Chem. Phys. 123, 174101 (2005).

77 E. N. Brothers, A. F. Izmaylov, J. O. Normand, V. Barone, and G. E. Scuseria, J. Chem. Phys., in press (2008).

78 V. Barone, J. E. Peralta, M. Wert, J. Heyd, and G. E. Scuseria, Nano Lett. 5, 1621 (2005).

79 V. Barone, J. E. Peralta, and G. E. Scuseria, Nano Lett. 5, 1830 (2005).

80 K. N. Kudin, G. E. Scuseria, and R. L. Martin, Phys. Rev. Lett. 89, 266402 (2002).

81 I. D. Prodan, J. A. Sordo, K. N. Kudin, G. E. Scuseria, and R. L. Martin, J. Chem. Phys. 123, 014703 (2005).

82 I. D. Prodan, G. E. Scuseria, and R. L. Martin, Phys. Rev. B 73, 045104 (2006).

83 P. J. Hay, R. L. Martin, J. Uddin, and G. E. Scuseria, J. Chem. Phys. 125, 034712 (2006).

84 D. Kasinathan, J. Kunes, K. Koepenik, C. V. Diaconu, R. L. Martin, I. D. Prodan, G. E. Scuseria, N. Spaldin, L. Petit, T. C. Schultess, and W. E. Pickett, Phys. Rev. B 74, 195110 (2006).

85 V. Barone, O. Hod, and G. E. Scuseria, Nano Lett. 6, 2748 (2006).

86 P. C. Hariharan and J. A. Pople, Theoret. Chimica Acta 28, 213 (1973).

87 A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, J. Chem. Phys. 125, 194112 (2006).

88 P. Mori-Sánchez, A. J. Cohen, and W. Yang, J. Chem. Phys. 125, 201102 (2006).

89 A. Rochefort, D. R. Salahub, and P. Avouris, J. Phys. Chem. B 103, 641 (1999).