

Energy gaps in zero-dimensional graphene nanoribbons

Philip Shemella,^{a)} Yiming Zhang, and Mitch Mailman

Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180

Pulickel M. Ajayan

Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180

Saroj K. Nayak

Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180

(Received 29 May 2007; accepted 28 June 2007; published online 25 July 2007)

The finite size effects on the electronic structure of graphene ribbons are studied using first principles density functional techniques. The energy gap [difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)] dependence for finite width and length is computed for both armchair and zigzag ribbons and compared to their one-dimensional (infinite length) cases. The results suggest, in addition to quantum confinement along the width of the ribbon, an additional finite size effect emerges along the length of ribbons *only* for metallic armchair ribbons. The origin of additional quantum confinement in these structures is analyzed based on the energy states near the Fermi energy: both HOMO and LUMO energy levels for metallic armchair ribbons are delocalized entirely on the ribbons while for nonmetallic ribbons, these states are localized at the edges only. The results are discussed in light of effect of passivation on the electronic properties of graphenes and their impact on nanoelectronic devices based on graphenes. © 2007 American Institute of Physics. [DOI: 10.1063/1.2761531]

The two-dimensional graphite crystal structure, or graphene, has become of great interest to the scientific community recently as a result of experimental techniques to make single layered graphene sheets, a two-dimensional crystal structure.¹⁻³ Graphene nanoribbons (GNRs), for which the width of the sheet is confined to be a finite size while the length is considered infinitely long, have attracted much attention for their unique electronic properties that includes either metallic or semiconducting behavior as a function of ribbon width.⁴⁻⁶ GNRs show distinct electronic properties when compared to two-dimensional graphene, and can be classified as either armchair graphene nanoribbons (AGNRs) or zigzag graphene nanoribbons (ZGNRs). AGNRs are either semiconducting or metallic depending on their width, and ZGNRs are found to be metallic for all widths. In addition, recent reports have found that ZGNRs are magnetic due to spin polarization along the width of the ribbon.⁵

One-dimensional (1D) AGNRs are characterized by their width; the nanoribbon is metallic if the number of rows of carbon is $3M-1$, where M is an integer.⁷⁻⁹ In confining the structure along the length, and hence going from one to zero dimensions, one induces edge states by terminating the length dimension with zigzag shaped edges. In this letter, we show that the electronic structure of zero-dimensional (0D) armchair graphene nanoribbons has length dependence for certain widths, which varies greatly from the one-dimensional results, as calculated with density functional theory. In addition, AGNRs are magnetic due to the zigzag terminated length-confined edges. Experiments are now being carried out with graphene ribbons of tens of nanometers in length^{4,10-13} and hence the finite length effect on the mag-

netic properties of such systems is important to understand. Indeed, since 1D GNRs do not physically exist it is important to study these 0D graphenes for both fundamental understanding as well as for applications.

We have used density functional theory (DFT) for both cluster calculations (0D GNRs) as well as periodic calculations (1D GNRs). We have used the generalized gradient approximation (GGA), and, in particular, the Perdew-Burke-Ernzerhof exchange-correlation functional.¹⁴ Both periodic and cluster calculations are implemented with GAUSSIAN code.¹⁵ Results calculated with GGA were compared independently to the local spin density approximation, which has been previously used,⁵ with good agreement. We have used the 3-21G* basis set, which was confirmed adequate in size by comparing electronic and geometric minimizations with the 6-31G** basis set.¹⁶ Dangling bonds are passivated with hydrogen atoms. We have compared our results with those obtained using the pseudopotential and plane wave based method and obtained the same conclusions. For example, the band gap for the 0D ribbon (length of 2.6 nm) with $N=8$ is found to be 0.60 eV from the pseudopotential method compared to 0.62 eV obtained from Gaussian based method.

Narrow GNRs are described by the number of carbon atoms across their width, namely, N [see Fig. 1(a)]. Predicted from tight binding and analytical methods,^{8,9,17,18} infinitely long AGNRs are metallic if the number of rows of C atoms in the width of the ribbon is $N=3M-1$, where M is an integer. We have considered ribbons with widths ranging from $N=4$ to 11, so we expect the 5-, 8-, and 11-AGNRs to have metallic behavior. Note that as shown by Son *et al.*,⁵ and consistent with our calculations, DFT predicts finite gaps for metallic AGNRs ($N=3M-1$) with small widths ($N<2.5$ nm) while tight binding calculations predict the energy gap in these systems to be zero. The DFT gap arises due

^{a)}Electronic mail: shemep@rpi.edu

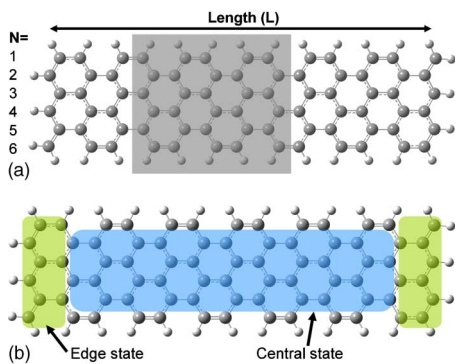


FIG. 1. (Color online) (a) Zero-dimensional (0D) armchair graphene nanoribbon of width $N=6$ and length $L=2.6$ nm. Highlighted with a gray box is a periodic cell for the one-dimensional ribbon; this 1D ribbon has infinite length (L) but finite width (N). (b) Central and edge states projected onto the 0D AGNR. Central states are consistent with the 1D ribbon. Edge states are created when the length dimension is confined and zigzag terminated.

to correct representation of end carbon atoms which are saturated with foreign atoms such as hydrogen. With tight binding approximations, the bond difference between carbon atoms in the ribbons is, in general, absent.

It will be interesting to study the effect of length on the energy gap of nanoribbons particularly for AGNRs since the edge states may have an immense impact on the resulting electronic structure. For 0D AGNR, the length is confined (therefore creating a zero-dimensional structure) with a zigzag orientation. For experimental graphene ribbons, the edge states are always present and such study could provide insight into transport measurements. Figure 1(b) shows a schematic for the 0D ribbon highlighting central and edge states. It has been pointed out that unlike in two-dimensional graphenes, edge states in ribbons provide large density of states near the Fermi energy. The magnetic moments in these cases are located on the zigzag edge state. Of course, our finite size AGNRs have zigzag states which are absent in the 1D case. Indeed, our spin density functional calculations find that the 0D AGNR ribbons have magnetic ground states, unlike their 1D counterpart.^{19,20} Our magnetic calculations for 0D ribbons find that the antiferromagnetic and ferromagnetic states are nearly degenerate in energy and the nonmagnetic state is typically about 0.8 eV higher in energy.

We have shown the variation of energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for a 2.6 nm length as a function of width of the ribbon in Fig. 2 and as a comparison, we have also shown energy gap for 1D ribbons. The 1D result agrees well with earlier studies and follows that ribbons that satisfy the $N=3M-1$ rule, where M is an integer, exhibit metallic behavior.²¹ In contrast, the finite size ribbons do not follow this rule. In particular, one sees in Fig. 2 that the ribbons with $N=5, 8,$ and 11 that are predicted to be metallic for the 1D case have a noticeable HOMO-LUMO gap for finite sized ribbons. In fact, the energy gaps for these metallic 0D ribbons ($N=3M-1$) are found to be higher compared to their bulk band gap, which is a signature of quantum confinement. In contrast, the HOMO-LUMO gaps for finite, nonmetallic ribbons ($N \neq 3M-1$) are not only different from their 1D counterparts, but are found to be much lower compared to their absolute value of the 1D ribbons. We have analyzed the orbital character of HOMO and LUMO energy levels as a function of width of the rib-

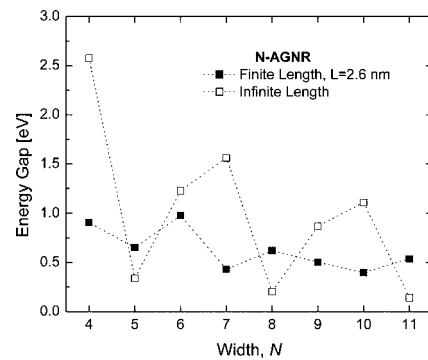


FIG. 2. Plot of HOMO-LUMO energy gaps as a function of width for zero-dimensional graphene (filled squares) and for one-dimensional graphene with no edge states (empty squares). The $3M-1$ rule for conducting AGNR appears to not hold when the ribbon is confined from 1D to 0D.

bons from $N=4$ to 11 . For nonmetallic ribbons (4-, 6-, 7-, 9-, 10-AGNRs) both HOMO and LUMO energy levels are localized at the length-confined zigzag edges while for metallic ribbons (5-, 8-, 11-AGNRs) the HOMO and LUMO are instead delocalized over the length of the AGNR (central states), matching the 1D result. Figure 3 shows, as an example, the plot of HOMO and LUMO energy levels for a nonmetallic ($N=7$) as well as for a metallic case ($N=8$).

Based on the observation that for all nonmetallic cases both the HOMO and LUMO are localized at the edge states while central states do not contribute the HOMO-LUMO energy levels, one would argue that the energy gap may not depend on the length for nonmetallic ribbons. To show that metallic ribbons exhibit length dependence while for nonmetallic ribbons the energy gap should be length independent, we have studied the nonmetallic 7-AGNR and the metallic 8-AGNR with widths $L \sim 2.6, 4.7,$ and 8.1 nm. Figure 4 shows the HOMO-LUMO energy gaps for different lengths. For comparison we have plotted band gaps for 1D cases for these ribbons, shown with dotted lines. One notices that for nonmetallic ribbons such as $N=7$ the energy gap does not change with length and confirms our above conjecture. This is due to the fact that for nonmetallic cases ($N \neq 3M-1$) both HOMO and LUMO states are localized at the edges and central atoms do not contribute to these states. However, for metallic states ($N=3M-1$) the energy gap varies as a function of length and approaches that of 1D band gap with increase in length. This is consistent with the delocalized nature of both HOMO and LUMO states for metallic cases, as shown in Fig. 3. Our results are in agreement with experimental observations such as through measurement of density of states of graphene ribbons of different lengths using scan-

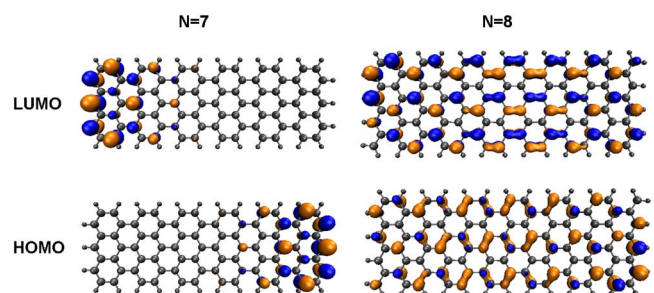


FIG. 3. (Color online) Spatial projections of molecular orbitals for nonmetallic ($N=7$) and metallic ($N=8$) AGNR. The HOMO and LUMO energy levels for nonmetallic ribbons are located on the length-confined zigzag edge, in contrast with the metallic ribbons.

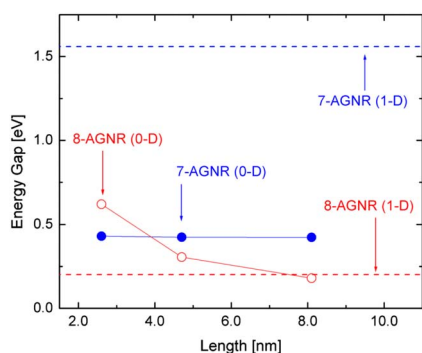


FIG. 4. (Color online) Length dependence for nonmetallic ($N=7$) and metallic ($N=8$) ribbons. The energy gap for the nonmetallic case (filled circles) shows no length dependence, while the energy gap for the metallic case (empty circles) shows length dependence converging to the 1D limit.

ning tunneling spectroscopy. In related contexts, finite length dependence studies on carbon nanotubes have been carried out using both theoretical²² and experimental approaches.²³ Experimental results have shown that semiconducting nanotubes do not show any band gap change with length while noticeable finite length dependence are observed for metallic nanotubes. Similar experimental measurements could be of great interest for graphene-based systems. These interesting differences between metallic and nonmetallic nanoribbons could be exploited for various applications. For example, it may be possible to control the band gaps of graphene ribbons using different functionalized groups. Based on our findings, one would expect that passivations will have an immense impact in the controlling the band gaps in nonmetallic ribbons since the HOMO and LUMO are localized at the edges: these edge states could be controlled through different functionalizations.

In order to compare the length effect found for metallic AGNRs, we have tested the length dependence on the energy gap for the ZGNRs of width $N=8$ and lengths $L=1.9$, 2.9 , and 4.7 nm, which are terminated with armchair geometry on their length-confined edge. Recall that there is no integer width dependence on the energy gap for ZGNRs such as for AGNRs.⁸ As expected, we find that the HOMO/LUMO energy levels are localized to the zigzag edges that run along the length of the ribbon. Specifically, the energy gaps were 0.56, 0.56 and 0.59 eV with increased length suggesting no length dependence on the energy gap for 0D ZGNRs.

In summary, we have studied the finite size effect on the electronic structure of zero-dimensional graphitic structures using density functional theory. Our results suggest that, in addition to quantum confinement arising due to ribbon width, finite size effects emerge along the length of the ribbons and drastically modify electronic states, particularly for armchair graphene nanoribbons with zigzag terminated (length-confined) edges. The origin of confinement in armchair structures is due to the dominant behavior of edge states near the HOMO-LUMO gap for nonmetallic widths ($N \neq 3M - 1$) and is unique to the zero-dimensional system because of the confinement of the length. For ribbons with $N \neq 3M - 1$, the HOMO and LUMO energy levels are located on the edge states, and the energy gap shows no length dependence. The finite size zigzag graphene ribbons, however, do not show any length dependence since the states near the Fermi energy are mostly derived from states located along the widths of

ribbons. Such properties will be essential in designing future electronic devices. For example, for interconnect applications, where one needs metallic ribbons, zigzag ribbons will be of great interest. In contrast, for transistor applications, one would consider armchair ribbons with controlled band gaps. One possibility is to control the band gaps in finite size armchair ribbons is through functionalization. Further theoretical and experimental works are necessary in order to understand the role of passivation in graphene ribbons.

This work is supported by the NSF (Grant Nos. 0333314 and CTS03-04055-NIRT), the ONR (No. N0014-06-0481), and at RPI by NSEC, IFC, and SCOREC.

- ¹K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. U.S.A. **102**, 10451 (2005).
- ²J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth, Nature (London) **446**, 60 (2007).
- ³A. K. Geim and K. S. Novoselov, Nat. Mater. **6**, 183 (2007).
- ⁴D. A. Areshkin, D. Gunlycke, and C. T. White, Nano Lett. **7**, 204 (2007).
- ⁵Y. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **97**, 216803 (2006).
- ⁶Y. Son, M. L. Cohen, and S. G. Louie, Nature (London) **444**, 347 (2006).
- ⁷H. Hosoya, H. Kumazaki, K. Chida, M. Ohuchi, and Y. D. Gao, Pure Appl. Chem. **62**, 445 (1990).
- ⁸K. Nakada, F. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).
- ⁹K. Wakabayashi, M. Fujita, H. Ajiki, and M. Sigrist, Phys. Rev. B **59**, 8271 (1999).
- ¹⁰C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).
- ¹¹J. S. Bunch, Y. Yaish, M. Brink, K. Bolotin, and P. L. McEuen, Nano Lett. **5**, 287 (2006).
- ¹²M. Y. Han, B. Oezylmaz, Y. Zhang, and P. Kim, Phys. Rev. Lett. **98**, 206805 (2007).
- ¹³D. Gunlycke, H. M. Lawler, and C. T. White, Phys. Rev. B **75**, 085418 (2007).
- ¹⁴J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ¹⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. 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, V. Bakken, 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 03, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.
- ¹⁶O. Hod, V. Barone, J. E. Peralta, and G. E. Scuseria, arXiv:cond-mat/07042043.
- ¹⁷K. Wakabayashi and M. Sigrist, Phys. Rev. Lett. **84**, 3390 (2000).
- ¹⁸K. Wakabayashi, Phys. Rev. B **64**, 125428 (2001).
- ¹⁹K. Kobayashi, Phys. Rev. B **68**, 075308 (2003).
- ²⁰Y. Kobayashi, K. Fukui, T. Enoki, and K. Kusakabe, Phys. Rev. B **73**, 125415 (2006).
- ²¹V. Barone, O. Hod, and G. E. Scuseria, Nano Lett. **6**, 2748 (2006).
- ²²A. Rochefort, D. R. Salahub, and P. H. Avouris, J. Phys. Chem. B **103**, 641 (1999).
- ²³T. W. Odom, J. L. Huang, P. Kim, and C. M. Lieber, J. Phys. Chem. B **104**, 2794 (2000).