Energy Gaps in Graphene Nanoribbons

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Based on a first-principles approach, we present scaling rules for the band gaps of graphene nanoribbons (GNRs) as a function of their widths. The GNRs considered have either armchair or zigzag shaped edges on both sides with hydrogen passivation. Both varieties of ribbons are shown to have band gaps. This differs from the results of simple tight-binding calculations or solutions of the Dirac’s equation based on them. Our ab initio calculations show that the origin of energy gaps for GNRs with armchair shaped edges arises from both quantum confinement and the crucial effect of the edges. For GNRs with zigzag shaped edges, gaps appear because of a staggered sublattice potential on the hexagonal lattice due to edge magnetization. The rich gap structure for ribbons with armchair shaped edges is further obtained analytically including edge effects. These results reproduce our ab initio calculation results very well.

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The electronic structure of nanoscale carbon materials such as fullerenes and carbon nanotubes has been the subject of intensive research during the past two decades 1 due to fundamental scientific interest in nanomaterials and because of their versatile electronic properties that are expected to be important for future nanoelectronics 2, 3. Among the carbon nanostructures, a simple variation of graphene, ribbons with nanometer sized widths, has been studied extensively 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15. Because of recent progress in preparing single graphite layers on conventional device setups, the graphene nanoribbons (GNRs) with varying widths can be realized either by cutting 16 mechanically exfoliated graphenes 17, 18 or by patterning epitaxially grown graphenes 19, 20.

Since GNRs are just geometrically terminated single graphite layers, their electronic structures have been modeled by imposing appropriate boundary conditions on Schrödinger’s equation with simple tight-binding (TB) approximations based on π-states of carbon 4, 5, 6, 7 or on a 2-dimensional free massless particle Dirac’s equation with an effective speed of light (≈10^6 m/s) 8, 9, 10. Within these models, it is predicted that GNRs with armchair shaped edges can be either metallic or semiconducting depending on their widths 4, 5, 6, 7, 8, 9, 10, and that GNRs with zigzag shaped edges are metallic with peculiar edge states on both sides of the ribbon regardless of its widths 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.

Although the aforementioned models are known to describe the low energy properties of graphene very well 17, 18, 19, 20, 21, 22, a careful consideration of edge effects in nanometer sized ribbons are required to determine their bandgaps because, unlike the situation in graphene, the bonding characteristics between atoms change abruptly at the edges 2, 13. Moreover, the spin degree of freedom is also important because the GNRs with zigzag shaped edges have narrow-band edge states at the Fermi energy (E_F) implying possible magnetization at the edges 4, 11, 12, 13. Motivated by the recent experimental progress in this area, we have carried out first-principles calculation and theoretical analysis to explore the relation between the bandgap and the geometries of GNRs.

In this Letter, we show that GNRs with hydrogen passivated armchair or zigzag shaped edges both always have nonzero and direct bandgaps. The origins of the bandgaps for the different types of homogenous edges vary. The bandgaps of GNRs with armchair shaped edges originate from quantum confinement, and edge effects play a crucial role. For GNRs with zigzag shaped edges, the bandgaps arise from a staggered sublattice potential due to spin ordered states at the edges 4, 11, 12, 13. Although the ribbon widths and energy bandgaps of the GNRs are related to each other primarily in inverse proportion, there is a rich structure in the ratio of the proportionality as in the behavior of carbon nanotubes 1.

For GNRs with armchair edges, analytic scaling rules for the size of the bandgaps are obtained as a function of width including the effect of the edges and give a good agreement with our first-principles calculations.

Our electronic structure calculation employs the first-principles self-consistent pseudopotential method 23 using the local (spin) density approximation (L(S)DA) 23, 24. An energy cutoff (for a real space mesh size) of 400 Rydbergs is employed and a double-ζ plus polarization basis set 24 is used for the localized basis orbitals to deal with the many atoms in a unit cell of the GNRs of various widths. We obtained the electron density by integrating the density matrix with a Fermi-Dirac distribution 23, 25. The geometry for each GNR studied is fully relaxed until the force on each of the atoms is less than 16pN. A k-point sampling of 32 (96) k-points that are uniformly positioned along the 1D Brillouin zone is employed for GNRs with armchair (zigzag) shaped edges.
We have tested the change of gap size by increasing the vacuum between edges from 20 to 40 Å and between planes from 16 to 25 Å and found no changes.

Following previous convention \[ \text{[12, 13, 14, 15]} \], the GNRs with armchair shaped edges on both sides are classified by the number of dimer lines \( N_a \) across the ribbon width as shown in Fig. 1(a). Likewise, ribbons with zigzag shaped edges on both sides are classified by the number of zigzag chains \( N_z \) across the ribbon width [Fig. 1(b)]. We refer to a GNR with \( N_a \) dimer lines as a \( N_a \)-AGNR and a GNR with \( N_z \) zigzag chains as a \( N_z \)-ZGNR.

Our calculations show that the \( N_a \)-AGNRs are semiconductors with energy gaps which decrease as a function of increasing ribbon widths \( w_a \). The variations in energy gap however exhibit three distinct family behaviors [Fig. 2]. Moreover, the energy gaps obtained in energy gap however exhibit three distinct family behaviors [Fig. 2]. Moreover, the energy gaps obtained in previous calculations [4, 5, 6, 7, 8, 9, 10] are quite larger values compared to those (0 \( \text{meV} \)) across the middle of the AGNRs. The bonding distances between carbon atoms at the edges are also expected to change accordingly. Such effects have been observed in large aromatic molecules, e.g., ovalene \( (C_{32}H_{14}) \) [26]. In Fig. 3(a), we show that the bond lengths parallel to dimer lines at edges \( (a_1 \text{ and } a_{N_a} \text{ for } N_a\text{-AGNR in Fig. 1(a)}) \) are shortened by 3.3–3.5% for the 12-, 13-, and 14-AGNR as compared to those in the middle of the AGNRs. The \( \text{H} \) bonding in the middle of the ribbon. From the analytic expressions for \( \text{H} \) matrix elements between carbon atoms in Ref. 27, a 3.5% decrease in interatomic distance from 1.422Å would induce a 12% increase in the hopping integral between \( \pi \)-orbitals.

To see the consequence of such effects more clearly, we introduce a lattice model [Fig. 3(b)] which is equivalent to the AGNRs within the \( \text{H} \) approximation \[ | \begin{array}{l} 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \end{array} \]\]. The set of eigenvalues of a brick type lattice shown in Fig 3(b) at \( k d_a = 0 \) is further equivalent to that of a two-leg ladder system with \( N_a \) rungs \[ | \begin{array}{l} 1 \ 2 \ 3 \ 4 \ 5 \end{array} \]\]. The Hamiltonian of this simpler model can be written as \( \text{H} = \sum_{n=1}^{N_a} \frac{1}{2} \sum_{\mu} \sum_{n} E_{\mu,n} a_{\mu,n}^\dagger a_{\mu,n} + \sum_{n=1}^{N_a} t_n^\parallel (a_{1,n}^\dagger a_{2,n} + h.c.) - \sum_{n=1}^{N_a-1} \sum_{\mu} t_n^{\perp} (a_{\mu,n}^\dagger a_{\mu,n+1} + h.c.) \text{, where } \{ n, \mu \} \text{ denote a site, } E_{\mu,n} \text{ site energies, } t_n^\parallel \text{ and } t_n^{\perp} \text{ the nearest neighbor hopping integrals within each leg and between the legs respectively, and } a_{\mu,n} \text{ the annihilation operator of } \pi \text{-electrons on the } n\text{-th site of the } \mu\text{-th leg. As}
FIG. 3: (a) The ratio of the calculated change in the carbon-carbon distance \( \delta_n \) (see Fig. 1(a)) to the carbon-carbon distance in the middle of the \( \text{N}_a\)-AGNRs, i.e., \( \delta_{a} = 100 \times \frac{\delta_n}{\delta_0} \) where \( \delta_0 = 0.12 \), \( \delta_c = 0.13 \), \( \delta_t = 0.14 \) Å for \( \text{N}_a = 12 \), \( \delta_0 = 1.422 \) Å for \( \text{N}_a = 13 \), and \( \delta_0 = 1.423 \) Å for \( \text{N}_a = 14 \), respectively. (b) Topologically equivalent structure to the \( \text{N}_a\)-AGNR shown in Fig. 1(a). For the special case of \( k = 0 \), a lattice with periodic ladders (left) can be folded into a two-leg ladder with \( \text{N}_a \) rungs (right).

discussed above and shown in Fig. 3(a), \( t_n \) and \( \epsilon_{\mu,n} \) at the edges would differ from those in the middle of GNRs. Hence, considering the simplest but essential variation from the exact solvable model to approximate the realistic situations, we assume that \( t_n^t = t_{N_a} \equiv (1 + \delta) t \) and \( t_n^l \equiv t \) for \( n = 2, \ldots, N_a - 1 \), and \( t_{n,n+1}^l \equiv t \) for all \( n \)'s. The site energies are set at \( \epsilon_{\mu,n} \equiv \epsilon_0 \) for \( n = 1 \) and \( N_a \) and 0 otherwise regardless of \( \mu \). This model Hamiltonian is solved perturbatively and the resulting energy gaps to the first order in \( \delta \) and \( \epsilon_0 \) are as follows,

\[
\Delta_{3p} \simeq \Delta_0^{3p} - \frac{8\delta t}{3p + 1} \sin^2 \frac{p\pi}{3p + 1}, \\
\Delta_{3p+1} \simeq \Delta_0^{3p+1} + \frac{8\delta t}{3p + 2} \sin^2 \frac{(p + 1)\pi}{3p + 2}, \\
\Delta_{3p+2} \simeq \Delta_0^{3p+2} + \frac{2\delta t}{p + 1},
\]

where \( \Delta_0^{3p}, \Delta_0^{3p+1} \) and \( \Delta_0^{3p+2} \) are the gaps of the ideally terminated ribbon when \( \delta = \epsilon_0 = 0 \). They are given by \( t \left[ 4 \cos \frac{\beta t}{3p + 1} - 2 \right] t \left[ 2 - 4 \cos \frac{(p + 1)\pi}{3p + 1} \right] \) and 0 respectively. The zeroth-order gaps are identical to the values obtained from numerical calculations in Fig. 2(a). With \( t = 2.7 \) (eV) \(^{22} \) and \( \delta = 0.12 \), the calculated gaps obtained using Eq. (1) are in good agreement with our LDA results [Fig. 2(b)]. This implies that the 12\% increase of the hopping integrals between carbon atoms at the edges opens the gaps of the (3p + 2)-AGNRs and decreases (increases) the gaps of 3p-AGNRs ((3p + 1)-AGNRs). This analysis provide the physical explanation of the changes in the gap hierarchy discussed before. We note that there is no contribution from the variation in the site energies \( (\epsilon_0) \) at the edges to first order.

Next, we find that nanoribbons with zigzag shaped edges also have direct bandgaps which decrease with increasing width \( (w_z) \). The eigenstates of the ZGNRs near \( E_F \), without considering spins, have a peculiar edge-state structure. As noted earlier within the tight-binding picture \(^4 \), there are two edge states decaying into the center of the ZGNR with a decay profile depending on their momentum as \( \sim e^{-\alpha_k x} \) where \( \alpha_k = -\frac{2}{\sqrt{3}a_z} \ln \left| 2 \cos \frac{k d_z}{2} \right| \) \( (\frac{2\pi}{3} \leq k d_z \leq \pi, \ d_z = \text{unit cell length shown in Fig. 1(b)} \). Our first-principles calculation also predicts a set of doubly degenerate flat edge-state bands at \( E_F \) when not considering spins (not shown here). Since the edge-states around \( E_F \) form flat bands, they give rise to a very large density of states at \( E_F \). Thus infintesimally small onsite repulsions could make the ZGNRs magnetic \(^4 \), unlike the case with two dimensional graphene which has a zero density of states at \( E_F \).

As pointed out in a TB study earlier \(^{14} \) and later confirmed by first-principles studies \(^{11,12,13} \), our LDA calculation also shows that the ground state of ZGNRs with hydrogen passivated zigzag edges indeed have finite magnetic moments on each edge with negligible change in atomic structure \(^{11,12,13,14} \).

Upon inclusion of the spin degrees of freedom within LSDA, the ZGNR are predicted to have a magnetic insulating ground state with ferromagnetic ordering at each zigzag edge and antiparallel spin orientation between the two edges. The spatial spin distributions of the ground state in the case of 12-ZGNR is displayed in Fig. 4(a). The small spin-orbit coupling \(^{28} \) in carbon atoms is neglected in the present study, and we label one spin orientation as \( \alpha \)-spin (red) and the opposite as \( \beta \)-spin (blue) in Fig. 4 (a). The total energy difference per edge atom between nonspin-polarized and spin-polarized edge states increases from 20 meV \( (N_z = 8) \) to 24 meV \( (N_z = 16) \). These energy differences are further stabilized by an antiferromagnetic coupling between the two edges. The total energy difference between ferromagnetic- and antiferromagnetic couplings between edges, however, decreases as \( N_z \) increases and eventually becomes negligible if the width is significantly larger than the decay length of the spin polarized edge states \(^{12} \).
32-ZGNR, respectively. Our LSDA results agree with previous studies [4,11,12] and consistent with a theorem based on the Hubbard Hamiltonian on a bipartite lattice [29]. Though infinite range spontaneous magnetic ordering in a one dimensional Heisenberg model is ruled out [30], spin orderings in nanoscale system are realizable in practice [31,32,33,34] at finite temperature assisted by the enhanced anisotropy on substrates [33,34].

The energy gaps in ZGNRs originate from the staggered sublattice potentials resulting from the magnetic ordering, which introduce bandgaps for electrons on a honeycomb hexagonal lattice [32]. This is realized because the opposite spin states on opposite edges occupy different sublattices respectively (black rectangles on the left side and grey ones on the right belong to different sublattices respectively (black rectangles on the left side and grey ones on the right belong to different sublattices respectively in Fig. 1(b)). So, the ZGNRs can be considered as the magnetic analog of a single BN sheet located in Fig. 1(b)) converges to 0.53 eV (32-ZGNR) from 0.51 eV (8-ZGNR).

In summary, we have shown that graphene nanoribbons with homogeneous armchair or zigzag shaped edges all have energy gaps which decrease as the widths of the system increase [32]. The role of the edges are crucial for determining the values and scaling rule for the bandgaps.

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