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Tuning electronic and magnetic properties of zigzag graphene nanoribbons by large-scale bending

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Using density-functional theory calculations, we show that the electronic and magnetic properties of zigzag graphene nanoribbons (ZGNRs) are highly sensitive to large scale curvature. As the curvature increases, the system experiences a transformation from the antiferromagnetic state to a nonmagnetic state and then back to the antiferromagnetic state. The energy gap first remains almost invariant and then decreases monotonically. The results demonstrate a facile strategy to tune the electronic and magnetic properties of ZGNRs, and furthermore provide an avenue to design versatile electronic and spin devices.

Graphene, since its experimental realization in 2004, has attracted considerable amounts of attention due to its interesting physical properties and promising applications in nanotechnology. However, perfect graphene is a zero gap semimetal, which significantly limits the utilization of graphene in nanodevices, for example in p–n junctions or transistors. Thus, it is necessary to have a simple and reliable approach to tune the electronic structure of graphene and make it semiconducting. Several methods have been developed to tailor its electronic or magnetic properties, such as doping, electric field application or by substrate proximity effects. The interaction between transition metal atoms and vacancies in graphene has also been considered in recent experiments and simulations in the context of graphene electronic structure modification.

Graphene nanoribbons (GNRs), one dimensional structures carved from graphene sheets, have fascinating tunable electronic properties depending on different edge shapes. Theoretical studies predict that zigzag graphene nanoribbons (ZGNRs) have special localized edge states, which are antiferromagnetically coupled between the two edges, while armchair GNRs (AGNRs) are nonmagnetic and semiconducting. The capability to control GNRs’ electronic properties is highly desired to build future nanodevice directly on GNRs. The ways to modify the electronic and magnetic properties of GNRs have been extensively investigated, including doping, edge modification, defect, and strain. Recently, the effects of mechanical deformation on the electronic structure and magnetic as well as transport properties of GNRs have received specific attention. For example, Hod et al. investigated the response of GNRs to externally applied mechanical deformations, and found that electronic properties are highly sensitive to the applied stresses. Zhang et al. studied the influence of out-of-plane deformation on the electronic structures of AGNRs and reported semiconductor-to-metal transition. The magnetic properties of small scale curved carbon nanotubes and nanogaphenes were studied as well. The transport properties of the step-shaped and arched GNRs were also investigated in detail. Nevertheless, investigations on large scale curved ZGNR are still lacking.

Here, using first-principles simulations, we demonstrate a simple way to alter electronic and magnetic properties of ZGNRs by large scale bending flat ZGNRs. As the curvature degree increases, the system experiences a transformation from the antiferromagnetic state to a nonmagnetic state and then back to the antiferromagnetic state, while the energy gap first does not considerably change, then decreases monotonically. The diverse electronic and magnetic properties of large scale curved ZGNRs can be used to develop and fabricate electronic and spintronic devices.

Our calculations were performed using the Vienna ab initio simulation package (VASP) code based on density functional theory (DFT). The exchange-correlation potential was chosen to be in the form of a generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The core electrons were accounted for within the projector augmented wave (PAW) approach. The plane wave cutoff energy was set to 500 eV, as further increase showed little effect on the results. The structures were relaxed until the energy and the force on each atom are less than 10^{-6} eV and 0.01 eV/Å, respectively. A 19 × 1 × 1 k-point mesh with Monkhorst-Pack scheme was used for sampling the 1D Brillouin zone. In order to simulate isolated ribbons, the intervals among the ribbons were kept as large as 12 Å for both layer-layer and edge-edge distances.

Following the previous convention, the ZGNRs are defined with m × n indices, where m and n are the numbers of rows and columns across the ZGNR width and length, respectively. Here we choose the ZGNR of m = 4 and n = 7 as the typical system, as shown in Fig. 1(a). The edge carbon atoms are all saturated by hydrogen atoms to avoid dangling bonds. The original structure is constructed by symmetrically bending the ribbon from the middle of the supercell (dashed line in Fig. 1(a)) along the periodic direction. The edge carbon atoms close to the curving sites are indicated by C1, C2 and C3, C4. The degree of curvature can be characterized by...
angle \( \theta \), as denoted in Fig. 1(b). In this study, the curved ZGNRs are named as \( \theta \)-ZGNR. After full relaxation, the geometric structures demonstrate periodic, wavelike geometries, as illustrated in Figs. 1(c) and 1(d) for \( 89^{\circ}/C_{14} \)-ZGNR.

To investigate the effect of curvature on the electronic and magnetic properties of ZGNR, the ground state of the curved ZGNR needs to be calculated. Previous theoretical studies have revealed that flat ZGNR has an antiferromagnetic ground state.\(^{1,11,25} \) To determine the magnetic state of the curved ZGNR, we perform the spin-polarized total energy calculations for different magnetic phases of a series of curved ZGNRs, including nonmagnetic (NM), antiferromagnetic (AFM), and ferromagnetic (FM) ones. Fig. 2 shows the energy difference per supercell between the nonmagnetic state and the magnetic state (both AFM and FM) as a function of bending angle. We found that in the degree range of \( 89^{\circ}/C_{14} - 180^{\circ}/C_{14} \), the energy of AFM state is lower compared to the corresponding FM state, suggesting that AFM is always the ground state for low curvature. Increasing the curvature degree, the energy difference abruptly drops to zero and the ZGNR becomes nonmagnetic, where \( \theta = 88^{\circ} \) is the critical angle which separates the magnetic state from nonmagnetic state. Further curvature does not change the nonmagnetic state until \( \theta = 52^{\circ} \), where AFM state dominates again. Thus, we found a large scale curvature-induced transition from AFM to NM and then back to AFM.

To illustrate this phenomenon, we present the ground state spin density distributions of the curved ZGNRs for \( 89^{\circ}/C_{14} \)-ZGNR, \( 88^{\circ}/C_{14} \)-ZGNR, and \( 52^{\circ}/C_{14} \)-ZGNR. Fig. 3(a) shows spin distributions of \( 89^{\circ}/C_{14} \)-ZGNR, which is similar to that of the flat ZGNR,\(^{11} \) with the FM ordering at each edge and AFM ordering between the opposite two edges. Finite spin density is present over the whole nanoribbon and decays from the edges to the middle. Fig. 3(b) shows that the spin density of \( 88^{\circ}/C_{14} \)-ZGNR completely disappears and the system becomes nonmagnetic. In Fig. 3(c), \( 52^{\circ}/C_{14} \)-ZGNR displays the AFM spin distributions again, but the spin density is no longer distributed over all carbon atoms. Instead, it is mainly localized in the border region of the supercell.

In addition to the magnetic transformation, it is of importance to examine the electronic properties of the large scale curved ZGNRs. The variation of the energy gap as a function of the bending angle \( \theta \) is given in Fig. 4. The red upward and blue downward triangles denote the AFM and NM ground states, respectively. We first consider the case with \( \theta = 180^{\circ} \), i.e., the flat ZGNR, which presents an energy gap with 0.60 eV and is in good agreement with previous study.\(^{12} \) Following, ZGNRs with \( \theta = 165^{\circ}, 150^{\circ}, 135^{\circ}, 120^{\circ}, \) and \( 105^{\circ} \) are calculated, we find the energy gap remains essentially the same, and the system displays the AFM ground state. When \( \theta = 88^{\circ} \), the energy gap undergoes a sudden drop to 0.56 eV and the system becomes a NM semiconductor. High sensitivity of the energy gap upon curvature is found. With the bending angle decreasing, the band gap decreases monotonically. For \( 52^{\circ} \)-ZGNR, the system exhibits the AFM ground state and has an energy gap of 0.10 eV.
Specifically, we present the detailed analyses for the electronic structure of $89^\circ$-ZGNR and $88^\circ$-ZGNR. Fig. 5(a) shows the band structure of $89^\circ$-ZGNR, which has the AFM ground state and a band gap of 0.62 eV is opened at the Fermi level, where the gap results from the spin splitting of the localized edge states. The states of opposite spin orientation are degenerate in all bands. Charge density distributions of the lowest conduction band (LCB, indicated by olive line) are similar to that of the flat ZGNR, which are highly localized on the two edges of the ZGNR, and the spin-up states are mainly located on the upper edge while the spin-down states are distributed on the opposite edge, as shown in Figs. 5(b) and 5(c). The small scale curvature does not give rise to noticeable changes in the localization of the electronic states. Thus, the energy gap remains essentially the same for the small scale curvature of $89^\circ$-ZGNR.

In the case of $88^\circ$-ZGNR, the system presents the NM characteristic, so the energy gap is different from the gap caused by spin splitting in $89^\circ$-ZGNR. From Figs. 3(a) and 3(b), we can clearly see that the geometric structure of relaxed $88^\circ$-ZGNR has obvious change compared to $89^\circ$-ZGNR. The distance between C1 and C2 (C3 and C4) atoms suddenly decreases to 1.66 Å and there is the wave functions overlap between them (see Fig. 6(b)). The band structure and charge density of the LCB (indicated by olive line) are presented in Figs. 6(a) and 6(c). Charge density distribution of the LCB is different from that of $89^\circ$-ZGNR. Although a significant part of the LCB still comes from the two edges of the ZGNR, there is no contribution to the LCB from C1, C2 and C3, C4 atoms, the $\pi$ bonding states of which have been transformed into the $\sigma$ bonding states due to the wave functions overlap between them. Thus, the C1, C2 and C3, C4 atoms have no $\pi$ orbital states contributing to the states near the Fermi level, which removes the edge states. So the energy gap can be mainly attributed to the wave functions overlap between C1 and C2 (C3 and C4) atoms due to the strong curvature.

As the bending angle decreases further, the band gap decreases monotonically. For comparison, Fig. 7 presents the band structures of $88^\circ$-ZGNR, $72^\circ$-ZGNR, and $56^\circ$-ZGNR. We suppose the decreasing of band gap is related to the variation of the distance between two bending faces. When decreasing the bending angle, the distance between them decreases, and the interlayer coupling is enhanced, which lead to the LCB (indicated by olive line) moving downwards and the highest valence band (HVB, indicated by pink line) moving upwards, so the band gap decreases. We also carried out the calculation for several different curvature degrees of ZGNRs with $m = 6, 8,$ and $10$, the same trend is found although the critical angle is changed. So taking into account the high sensitivity of the band gap on the curvature, one could envisage fabrication of strain sensors based on ZGNRs.

In summary, we have found that the electronic and magnetic properties of ZGNRs are not sensitive to the small scale curvature for $89^\circ \leq \theta < 180^\circ$, while they are sensitive to the large scale curvature for $\theta \leq 88^\circ$, which leads to a curvature-induced magnetic transitions from the AFM state to a NM state and then to the AFM state. Correspondingly, the energy gap first remains essentially the same and then decreases monotonically. The significant variation can be mainly attributed to the overlap of wave functions localized on carbon atoms at curving sites as well as to the interlayer coupling induced by the strong curvature. Our results provide a simple way to manipulate the electronic and magnetic properties of ZGNRs, which are helpful to construct and design versatile electronic and spin devices.
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