Theory of Magnetic Edge States in Chiral Graphene Nanoribbons

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Graphene and derived nanomaterials exhibit a large number of novel electronic properties [1,2]. One of such features is the presence of electronic states localized at the edges of this two-dimensional (2D) nanomaterial [3]. These zero-energy edge states were predicted to give rise to a novel type of magnetic ordering [4] which may lead to practical carbon-based magnetic materials [5]. Even more appealing is the perspective of realizing the theoretical proposals of novel spintronic devices based on graphene [6–10], with chiral edges, and discover a number of structure-property relations. Specifically, we investigate the electronic structure and magnetic properties of chiral graphene nanoribbons. Using a model Hamiltonian approach including electron-electron interactions, we systematically study the electronic structure and magnetic properties of chiral graphene nanoribbons. We show that the presence of magnetic edge states is an intrinsic feature of smooth graphene nanoribbons with chiral edges, and discover a number of structure-property relations. Specifically, we study the dependence of magnetic moments and edge-state energy splittings on the nanoribbon width and chiral angle as well as the role of environmental screening effects. Our results address a recent experimental observation of signatures of magnetic ordering in chiral graphene nanoribbons and provide an avenue towards tuning their properties via the structural and environmental degrees of freedom.

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experimental data [17]. However, we point out that this effective parameter may also incorporate environmental factors such as the enhancement of screening due to the proximity of dielectric or metallic substrate [13]. For this reason we also study the dependence of results on $U/t$.

Two parameters determine the structure of smooth GNRs: (i) the crystallographic direction of the edge, and (ii) the width. In general, the direction of the nanoribbon’s edge is defined by some translation vector $(n,m)$ of the graphene lattice. For high-symmetry zigzag and armchair edges these vectors are $(1,0)$ and $(1,1)$, respectively. Provided that $n > m$, the edge of $(n,m)$ nanoribbon is a repeating structure composed of $n - m$ zigzag units and $m$ armchair units as illustrated for the particular case of a $(4,1)$ GNR in Fig. 1(a). The length of repeat vector $a = (n,m) = a_0\sqrt{n^2 + nm + m^2}$, where $a_0 = 0.246$ nm is the lattice constant of graphene. Alternatively, chirality can be described by the chirality angle

$$\theta = \arcsin \sqrt{\frac{3}{4} \left( \frac{m^2}{n^2 + nm + m^2} \right)}.$$  

Zigzag and armchair edges are characterized by $\theta = 0^\circ$ and $\theta = 30^\circ$, respectively, while for chiral edges $0^\circ < \theta < 30^\circ$. We consider chiral GNRs defined by edge translational vectors $(n+1,1)$ and $(n,n+1)$ ($n \geq 1$). These two series cover the whole range of chirality angles $\theta$ and converge to $\theta = 0^\circ$ and $\theta = 30^\circ$, respectively, with increasing $n$ [Fig. 1(b)]. The configurations of chiral GNRs considered in this study cover $4.7^\circ < \theta < 25.3^\circ$. The width $W = \sqrt{3\omega_0^2 \cos \theta}$ of a GNR is defined by vector $(-w,2w)$ pointing along the armchair direction as shown in Fig. 1(a).

We start our discussion by considering the evolution of tight-binding band structures of GNRs (neglecting $e-e$ interactions, $U/t = 0$) upon the change of chirality from zigzag ($\theta = 0^\circ$) to armchair ($\theta = 30^\circ$) via the series of intermediate chiral configurations at fixed nanoribbon width ($w = 12$). High-symmetry zigzag nanoribbon [Fig. 2 left panel] exhibits a flat band at the Fermi level ($E = 0$) which spans one-third of the 1D Brillouin zone (BZ), that is, the corresponding density of edge states per edge length per spin $\rho(\theta = 0^\circ) = 1/(3a_0)$. Armchair GNRs [Fig. 2 right panel] are either metals or semiconductors with no electronic states localized at the edges. This result can be rationalized within the infinite-width picture by considering the 2D band structure of graphene projected onto the 1D BZ of periodic edge. In the case of an armchair GNR both Dirac points $(K$ and $K')$ of graphene’s band structure are projected onto the $\Gamma$ point of 1D BZ. However, for a zigzag GNR points $K$ and $K'$ are projected onto $k = 2\pi/(3a)$ and $k = -2\pi/(3a)$, respectively, with zero-energy flat band connecting these two points [Fig. 2 insets]. The band structures of chiral GNRs in the infinite-width limit can be obtained by continuous rotation of the band structure of graphene which leads to the known result [13]:

$$\rho(\theta) = \frac{2}{3a_0} \cos \left( \theta + \frac{\pi}{3} \right).$$  

That is, in the limit of large width only armchair GNRs show no edge states. The density of edge states is largest for zigzag nanoribbons and shows almost linear dependence on $\theta$. The tight-binding band structures of $w = 12$ chiral GNRs [Fig. 2] the $x$-axis scales correspond to the 1D BZ dimensions] confirm this picture. Two important comments should be made: (i) in finite-width GNRs with edge orientation close to the armchair direction zero-energy edge states are partially or even completely suppressed; (ii) in GNRs with edge orientation close to the zigzag direction the flat edge-state band spans whole 1D BZ and becomes multiple degenerate due to band folding.

We now discuss the effects of $e-e$ interactions on the electronic spectra of chiral GNRs. Figure 2(a) shows the band structure and the density of states (DOS) plot for a zigzag GNR ($w = 12$) obtained within the mean-field Hubbard model ($U/t = 1$) compared to the tight-binding results ($U/t = 0$). In the presence of $e-e$ interactions the electronic ground state of the zigzag GNR exhibits an interesting magnetic ordering: ferromagnetic (FM) along the edges and antiferromagnetic (AFM) across the

![FIG. 2: (color online). Evolution of the tight-binding band structures (no $e-e$ interactions) of graphene nanoribbons ($w = 12$) upon the change of chirality from zigzag ($\theta = 0^\circ$) to armchair ($\theta = 30^\circ$) via the series of intermediate chiral configurations. The scales of the plots account for the varying Brillouin-zone dimensions. The insets show the relation between the one-dimensional band structures of zigzag and armchair GNRs and the two-dimensional band structure of ideal graphene.](image_url)
The magnetic moment per edge unit length \( M = 0.313 \mu_B/a_0 \). Spin-polarization lifts the degeneracy of edge states and opens an electronic band gap \( \Delta^0 \). While the tight-binding DOS has only one van Hove singularity related to the presence of 1D edge states at \( E = 0 \), the mean-field Hubbard model solution shows two pairs of peaks split by \( \Delta^0 \) and \( \Delta^1 \). We note that Hamiltonian (1) respects electron-hole symmetry. Splitting \( \Delta^0 \) is related to magnetic correlation between the opposite edges while the larger splitting \( \Delta^1 \) is due to the FM correlation along one single edge of most strongly localized electronic states at \( k = \pi/a \) [19, 20, 21]. Thus, the two splittings \( \Delta^0 \) and \( \Delta^1 \) constitute independent signatures of magnetic ordering across the nanoribbon and along its edge. The rest of electronic spectrum (\( |E| > 0.18t \)) is negligibly affected by the Hubbard term. Van Hove singularities at \( |E| \approx 0.2t \) and higher energies correspond to the bulk-like states subjected to quantum confinement in 1D GNRs of the given width. The mean-field Hubbard model electronic spectra of chiral GNRs show all the features characteristic of zigzag GNRs provided the ground state is spin-polarized. Both splittings, especially \( \Delta^1 \), are reduced in the case of (2.1) GNR (\( \theta = 19.1^\circ \)) due to the smaller magnetic moment \( M = 0.096 \mu_B/a_0 \) [Fig. 3(b)]. Nanoribbons with chirality close to \( \theta = 0^\circ \) show additional pairs of van Hove singularities due to splittings of the multiple degenerate edge-state bands at \( k = 0 \) and \( k = \pi/a \) [Fig. 3(c)] for \( \theta = 7.6^\circ \) (6,1) GNR.

Figure 4 summarizes the calculated magnetic moments and energy splittings for GNRs of various chiralities and widths, and different magnitudes of \( U/t \). At \( U/t = 1 \) spin-polarized ground states of few-nm-wide GNRs span almost full range of chiralities [Fig. 4(a)]. The magnetic moments per unit length \( M \) follow closely the dotted curve which corresponds to the complete spin-polarization of edge states in the infinite-width limit [22], but appear to be negatively shifted by nearly constant amounts which are moderately dependent on width. Splitting \( \Delta^1 \) shows a similar dependence on \( \theta \) and it is independent of \( w \) [Fig. 4(b)]. On the contrary, the magnitude of \( \Delta^0 \) is largely insensitive to the variations of \( \theta \) in broad ranges of this parameter, but shows a clear dependence on \( w \) analogous to the case of zigzag GNRs [19]. As the chiral angle \( \theta \) approaches 30° magnetic moments vanish and the tight-binding band gaps \( \Delta_g \) quickly rise reaching their maximum values for the corresponding armchair GNRs [22]. Figure 4(c) reveal a moderate dependence of \( M(\theta) \) on the strength of \( e-e \) interactions. However, the magnitudes of \( \Delta^0 \) and \( \Delta^1 \) are both approximately proportional to \( U/t \) [Fig. 4(d)].

Finally, we turn our attention to the spatial variation of electronic spectra of magnetic graphene edges in relation...
to the experimental observations. As a case study we investigate the mean-field Hubbard model \((U/t = 1)\) local density of states (LDOS) evaluated across the \((6,1)\) chiral GNR \((w = 12, W = 5 \text{ nm})\) [Fig. 2(a)] and along its edge [Fig. 2(b)]. We find that both pairs of contributions to the total DOS due to the edge states seen in Fig. 2(c) are localized at the edge. However, the higher-energy LDOS peak at \(E = 0.1t\) decays very fast being confined within the 1-nm-wide edge region while the lower-energy feature at \(E = 0.035t\) penetrates deep into the middle of GNR. The series of peaks at \(E \gtrsim 0.2t\) repeated in energy by \(\approx 0.1t\) correspond to the bulk-like graphene states subjected to quantum confinement. The total density of edge states from the tight-binding calculations shows pronounced oscillations along the GNR edge [dashed curve in Fig. 2(d)]. The oscillation period corresponds to the edge periodicity \(a = 1.6 \text{ nm}\). The \(E = 0.1t\) LDOS peak from the mean-field Hubbard model follows this trend. In contrast, the lower-energy peak \((E = 0.035t)\) shows weak variations of LDOS. This behavior was found to be generic to all studied chiral and zigzag magnetic GNRs.

To summarize, our model Hamiltonian study of the electronic structure and magnetic properties of chiral graphene nanoribbons revealed a number of structure-property relations. The described relations can serve as unambiguous signatures of edge-state magnetism in graphene nanoribbons and provide an avenue towards controlling their magnetic and electronic properties.

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**FIG. 5:** (color online). Variation of the local density of states (LDOS) \((a)\) across the \((6,1)\) chiral GNR \((x\)-axis is oriented along the edge; \(y = 0\) corresponds to the outermost edge atom) and \((b)\) along its edge obtained using the mean-field Hubbard model \((U/t = 1)\). \((c),(d)\) Log-linear plots of LDOS at the energies indicated in panel \((a)\) across the \((6,1)\) chiral GNR and along its edge, respectively. The dashed lines correspond to the tight-binding LDOS at \(E = 0\). The inset in panel \((d)\) superimposes the edge structure with the plot.

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