Quantum magnetism of topologically-designed graphene nanoribbons

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Abstract

Based on the Hubbard models, quantum magnetism of topologically-designed graphene nanoribbons (GNRs) is studied using exact numerical simulations. We first study a two-band Hubbard model describing the low-energy topological bands using the density matrix renormalization group (DMRG) and determinant quantum Monte Carlo (DQMC) methods. It is found the spin correlations decay quickly with distance, and the local moment is extrapolated to zero in the presence of symmetry-breaking terms. The results show that the two-band Hubbard chain is nonmagnetic, which is in contrast to the mean-field calculation predicting a critical interaction for the magnetic transition. We then include the Hubbard interaction to the topological-designed GNRs. For large interactions, the spin correlations remain finite for all distances, and the magnetic order develops. The local moment is extrapolated to almost zero for weak interactions, and begins to increase rapidly from a critical interaction. The estimated critical value is much larger than the realistic value in graphene, and we conclude the experimentally relevant GNRs are nonmagnetic, which is consistent with the experimental results.

Keywords: quantum Monte Carlo, graphene nanoribbon, Hubbard model

(Some figures may appear in colour only in the online journal)
inversely proportional to the widths [21–23]. Recently, the topological properties of the insulating armchair GNRs are investigated, which demonstrates that different widths and end terminations lead to distinct topological phases [24, 25]. The topology is characterized by a $\mathbb{Z}_2$ invariant, and is manifested by localized boundary state between two segments with different topologies. Later experiments confirming the predictions are reported [26, 27]. Furthermore, the junction states are successfully used as building block to engineer the famous Su–Schrieff–Heeger topological model [26–28].

The armchair GNRs have no edge states, and the critical interaction to antiferromagnetism is similar to that of bulk graphene. In the topologically-designed GNRs, there are zigzag-edge segments at the boundary, which suggests the possibility of magnetic ordering at weak interactions. While the mean-field (MF) calculation finds a critical interaction smaller than that of bulk system ($U_c = 2.23t$) [8], it is still larger than the realistic value in graphene, and supports that the experimentally realized structures are nonmagnetic. Since the quantum fluctuation is strong in two dimensions, it is very necessary to perform an exact numerical study of the effect of interactions, and validate the absence of the magnetism.

In the manuscript, we study quantum magnetism of topologically-designed GNRs based on the Hubbard models using exact numerical simulations. We first derive a two-band model for the low-energy topological bands, and study the corresponding 1D Hubbard model using DMRG and DQMC methods. It is found the spin correlations decay quickly with the distance, and the local moment is extrapolated to zero in the presence of symmetry-breaking terms. The results show

![Figure 1](image1.png)

**Figure 1.** (a) Schematic structure of a pristine 7-AGNR. (b) The geometry of a topologically-designed GNR based on the pristine 7-AGNR. In (a) the pristine 7-AGNR with a zigzag termination is a 1D topological insulator, and the wavefunction of the zero boundary mode is plotted (red filled circles with the radius denoting the wavefunction amplitude). In (b) we also show the wavefunction of the designed topological band, which is mainly distributed on the two outmost sites of each zigzag shoulder. The unit cell is enclosed by green dashed lines, which have 14(48) sites in (a) and (b).

![Figure 2](image2.png)

**Figure 2.** The band structures for (a) the pristine 7-AGNR, and (b) the topologically-designed GNR based on the pristine 7-AGNR. In (b), the two bands near the Fermi energy are well fitted using a 1D chain with alternating hopping amplitudes $t_1 = 0.1493t$ and $t_2 = -0.1824t$ (orange open circles).
that the two-band Hubbard chain is nonmagnetic. We then include the Hubbard interaction to the topologically-designed GNRs, and calculate the spin correlations and the local moments in the presence of symmetry-breaking terms. We find the magnetic order develops from a critical interaction, which is much larger than the realistic value in graphene. We conclude the experimentally relevant GNRs is nonmagnetic, which is consistent with the experimental results.

2. The model and method

We consider a nearest-neighbor (NN) tight-binding Hamiltonian on a topologically-designed GNR with the geometry shown in figure 1,

$$H_0 = -\sum_{\langle ij \rangle \sigma} t c_{i\sigma} c_{j\sigma}^\dagger,$$  \hspace{1cm} (1)

where \(c_{i\sigma}\) and \(c_{j\sigma}^\dagger\) are the annihilation and creation operators at site \(j\) with spin \(\sigma = \uparrow, \downarrow\). The hopping amplitudes between the NN sites \(l\) and \(j\) are \(t\), which is about 3 eV in graphene.

The geometry in figure 1(b) is obtained by adding small segments with zigzag edges periodically on the pristine armchair GNR with the width \(N = 7\) (7-AGNR). The resulting geometry is a superlattice of alternating unit cells of 7-AGNR and 9-AGNR. The topological property of the 7(9)-AGNR composed of such unit cells (see shaded region in figure 1(b)) is described by a \(Z_2\) invariant: \(Z_2 = \frac{1}{2}[(-1)^{\sum_{j}(-1)^{1+n_j}} + 1],\) where \([x]\) is the floor function and the sign is negative (positive) for \(W = 7(9)\) [24]. The \(Z_2\) value is 0(1) for 7(9)-AGNR, and the topological and trivial unit cells alternate along the chain. Thus the localized boundary states between adjacent unit cells may form low-energy dispersing bands in the gap.

Performing Fourier transformation, the Hamiltonian in equation (1) becomes \(H_0 = \sum_{\mathbf{k}} \psi^\dagger_{\mathbf{k}} H(\mathbf{k}) \psi_{\mathbf{k}}\), where the basis is \(\psi_{\mathbf{k}} = (c_{1,\mathbf{k}}, c_{2,\mathbf{k}}, ..., c_{N,\mathbf{k}})^T\) (\(N_i\) is the number of sites in a unit cell), and \(H(\mathbf{k})\) is the \(N_r\)-by-\(N_i\) Hamiltonian matrix in the momentum space. By diagonalizing \(H(\mathbf{k})\), the band structures are directly obtained, and are shown in figure 2. Figure 2(a) shows the band structure of the pristine 7-AGNR for comparison, which has been known to be a semiconductor with the gap size about 0.5\(t\). By including small segments, two new dispersing bands appear in the gap (see figure 2(b)), and their wave functions mainly distribute on the zigzag sites of the small segments.

Since the two low-energy bands in figure 2(b) are isolated from other bands, an effective model for them can be constructed using maximally localized Wannier functions [29], which is a 1D chain containing hoppings of different ranges. The main contribution is from the NN ones, and the corresponding hopping amplitudes are \(t_1 = 0.1493t\) and \(t_2 = -0.1824t\), respectively. It is found that the low-energy two bands are fitted quite well only using the above NN hoppings (see figure 2). Thus the designed GNR realizes an effective 1D tight-binding model analog to the famous Su–Schrieffer–Heeger one.

It has been known that the pristine 7-AGNR supports a topological phase. The topological invariant depends on the shape of its termination, and the zigzag termination yields a nontrivial topological invariant. It is also desirable to know the topological class of the above topologically-designed GNR. The 1D topological property is characterized by the Berry phase[30–34],

$$\gamma = \int \langle \psi_k | \frac{d}{dk} | \psi_k \rangle dk,$$ \hspace{1cm} (2)

where \(k\) varying from 0 to \(2\pi\) is the wave vector, and \(\psi_k\) is the periodic part of the Bloch wave function corresponding to \(k\). The Berry phase of the Hamiltonian equation (1) on the geometry shown in figure 2 has a nontrivial value \(\pi\), corresponding to which a pair of zero boundary modes appear under open boundary condition.

To study the magnetic property of the topologically-designed GNR, we consider the Hubbard interaction, which writes as,

$$H_U = \sum_{i} U(n_{i\uparrow} - \frac{1}{2})(n_{i\downarrow} - \frac{1}{2}),$$ \hspace{1cm} (3)

where \(n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}\) is the number operator of fermion and \(U\) is the strength of the on-site interaction. In the following discussions, we include the Hubbard term into both the Hamiltonian in equation (1) and the two-band effective model, and study the induced magnetism.

The interacting Hamiltonian is solved numerically by means of the DQMC and DMRG methods [35–37]. In the DQMC approach, one decouples the on-site interaction term through the introduction of an auxiliary Hubbard–Stratonovich field (HSF). The fermions are integrated out analytically, and then the integral over the HSF is performed stochastically. The only errors are those associated with the statistical sampling, the finite spatial lattice and inverse temperature discretization. All are well-controlled in the sense that they can be systematically reduced as needed, and further eliminated by appropriate
extrapolations. The DMRG method is most efficient for the ground state of 1D systems [38]. We use it to solve the effective model directly at zero temperature. In the following calculations, we focus on half-filled bands, when the DQMC method is free of the infamous ‘minus-sign problem’.

To study the magnetic behavior, we measure the local moment
\[ m_{\text{z}}^j = \langle S^z_j \rangle \]
with
\[ S^z_j = \frac{1}{2} (n^+_j \downarrow n^+_j) \]. Since the original Hamiltonian preserves the \( SU(2) \) symmetry, a symmetry-breaking term should be included to induce the magnetism. We break the symmetry of the magnetic phase to \( z \)-axis by adding an alternating Zeeman term
\[ H_B = \sum_j B_j (n^+_j \downarrow n^+_j) \]
with
\[ B_j = \pm B \] depending on the sublattices. The value of the local moment is extrapolated to the limit \( B = 0 \), and a nonzero value marks the existence of the magnetism. The equal-time spin correlation function is also calculated, which is given by
\[ c_{\text{spin}}(i) = \langle S^+_j S^-_{j+i} \rangle + \frac{1}{2} \left( S^+_j S^-_{j+i} + S^+_j S^-_{j-i} \right) \].

3. Magnetism of the effective model for the topologically-designed GNRs

We first study the magnetic property based on the effective two-band Hubbard model, which writes as,
\[ H_{\text{eff}} = - \sum_{j,\sigma} (t_{1j}^\dagger c^\dagger_{j,\sigma} c_{j+1,\sigma} + H.c.) + H_U, \]
where the spin raising and lowering operators are
\[ S^+_j = c^\dagger_{j,\uparrow} c_{j,\downarrow}, \quad S^-_j = c^\dagger_{j,\downarrow} c_{j,\uparrow}, \] respectively.

![Figure 4](attachment:figure4.png)

**Figure 4.** The equal-time spin correlation as a function of distance at \( U = 4t \). Insets are the log plots for the left (b) and right (c) parts. The 1D lattice has 40 sites.

![Figure 5](attachment:figure5.png)

**Figure 5.** The equal-time spin correlation function between the NN sites connected by the bonds with the hopping amplitude (a) \( t_1 \) and (b) \( t_2 \). The lattice size is the same as that of figure 4.
\[ \langle n_{\uparrow,A} \rangle = \frac{1}{2} + m_A, \quad \langle n_{\downarrow,A} \rangle = \frac{1}{2} - m_A \]
\[ \langle n_{\uparrow,B} \rangle = \frac{1}{2} - m_B, \quad \langle n_{\downarrow,B} \rangle = \frac{1}{2} + m_B. \] (7)

Then the Hubbard term becomes,

\[ \sum_i n_{\uparrow} n_{\downarrow} = E_0 + \sum_{i \in A} (-m_A n_{\uparrow} + m_A n_{\downarrow}) + \sum_{i \in B} (m_B n_{\uparrow} - m_B n_{\downarrow}) , \] (8)

where \( E_0 = \frac{1}{2}NU + \frac{NU}{2}(m_A^2 + m_B^2) \) (\( N \) is the total number of the sites). The MF Hamiltonian writes as,

\[ \mathcal{H}_{mf}^\sigma(k) = \begin{pmatrix} \mp \sigma m_A & l_1 + t_2 e^{-ik} \\ l_1 + t_2 e^{ik} & \pm \sigma m_B \end{pmatrix} \] (9)

where \( \sigma = 1(-1) \) represents up (down) spin. For a uniform antiferromagnetic order, we suppose \( m_A = m_B = m \). The energy spectrum is directly obtained by diagonalizing the above Hamiltonian, which is \( \pm E_k \) with

Figure 6. (a) The local moment \( m \) as a function of temperature for several values of \( U \). The pinning Zeeman field is along the z-axis with the strength \( B = 0.1 \). (b) The local moment \( m \) as a function of \( B \). Solid curves are from the fitting function \( y = a(1 - e^{-bm}) \). Open (solid) symbols in both figures represent DQMC (DMRG) results. The lattice size is the same as that of figure 4.

Figure 7. The spin correlations on a lattice containing three unit cells (144 sites) for several values of \( U \). The star marks the reference site, and the radius of the circles denote the values of the spin correlations. The crosses mark the sites with too large values or error bars.

Figure 8. (a), The spin correlation as a function of the indexes of the sites. (b), The spin correlation as a function of the distances along several typical directions. Here the interaction is \( U = 4t \). The lattice size is the same as that of figure 7.
When the temperature is lowered, the thermal fluctuation is reduced and the local moment increases. Near the lowest temperatures $T = 0.05$, accessed by our DQMC simulations, the value of $m$ begins to be saturated. The saturated values are in good agreement with those from the DMRG method. It is noted that the case of $U = 0$ also becomes a magnet with $m \sim 0.1$, which is a natural result of the inclusion of a staggered Zeeman term. An extrapolation to $B = 0$ is necessary to know the intrinsic magnetic property of the system. We carry out DMRG simulations with several different $B$ and the data are shown in figure 6(b). They are well fitted using $y = a(1 - e^{-b x})$, a function exponentially rising to maximum. So as large as $U = 4t$, the extrapolated local moment is zero, and the long-ranged antiferromagnetic order is absent in a strictly 1D system. It is in great contrast to the MF theory, where the antiferromagnetism develops above a critical interaction through a first-order phase transition.

4. Magnetism of topologically-designed GNRs

Next we study the experimentally relevant topologically-designed GNRs, which usually contain several unit cells. We first perform a MF analysis, and decouple the Hubbard term in the same channel described in equation (8),

$$\begin{align*}
    n_{\sigma}n_{\sigma} = \langle n_{\sigma} \rangle n_{\sigma} + \langle n_{\sigma} \rangle n_{\sigma} - \langle n_{\sigma} \rangle \langle n_{\sigma} \rangle \\
    &= -m_{\sigma}n_{\sigma} + m_{\sigma}n_{\sigma} + \frac{1}{4} + m_{\sigma}^2, \\
    \end{align*}$$

where the average density on each site writes as $n_{\sigma(i)} = \frac{1}{2} \pm m_{\sigma}$. We obtain the following MF Hamiltonian,

$$\begin{align*}
    H_{\text{mf}} &= -\sum_{\langle \sigma \rangle} \tau_{\sigma} c_{\sigma} + U \sum_{i} (-m_{\sigma}n_{\sigma} + m_{\sigma}n_{\sigma}) \\
    &+ \frac{1}{4}NU + \frac{U}{n_{\sigma}} \sum_{i} m_{\sigma}^2, \\
    \end{align*}$$

where $N$ is the total number of sites, and each unit cell has $n_{\sigma} = 48$ sites. Minimizing the free energy $F$ with respect to $m_{\sigma}$, we obtain a set of self-consistently equations $m_{\sigma} = -\frac{m_{\sigma}}{2\xi N \frac{\partial F}{\partial m_{\sigma}}}$.

Figure 9. (a) The local moment $m$ as a function of $B$. Solid curves are from the fitting formula $y = c + a(1 - e^{-b x})$. (b) The extrapolated local moment as a function of $U$. Here the temperature is $T = 0.05t$. The lattice size is the same as that of figure 7.

$$\begin{align*}
    E_k = \sqrt{(U m)^2 + (t_2 \sin k)^2 + (t_1 + t_2 \cos k)^2} \\
    \text{(the dispersion is degenerate for both spin copies). Minimizing the free} \\
    \text{energy } F = -2 \sum_k E_k + E_0, \text{ the self-consistent equation for} \\
    \text{the order parameter } m \text{ is } 1 = U \sum_k \frac{1}{E_k}. \\
    
    \text{Figure 3 shows the self-consistent order parameter as a} \\
    \text{function of } U. \text{ The value of the order parameter } m \text{ is zero} \\
    \text{for small interactions and the 1D chain is nonmagnetic. From a} \\
    \text{critical interaction, we have a finite self-consistent solution} \\
    \text{for } m, \text{ implying the magnetism develops in the system. As } U \\
    \text{is increased, } m \text{ also increases and the magnetism is strengthened.} \\
    \text{As shown in figure 3, the curve } \frac{d m}{d U} \text{ tends to be divergent} \\
    \text{at the critical interaction, from which we get } U_c = 0.29t. \\
    
    \text{While the MF study provides a qualitative understanding of} \\
    \text{the magnetic behavior, the quantum fluctuation is strong} \\
    \text{in 1D, and the MF approximation may be not accurate. So we} \\
    \text{next perform exact numerical simulations on the Hubbard} \\
    \text{model in equation (5). The equal-time spin correlation function} \\
    \text{of the ground state is calculated using DMRG, and the result at } U = 4t \\
    \text{is shown in figure 4. The spin correlations decay with the distance, and the signs of} \\
    \text{their values are alternating, implying the correlations are antiferromagnetic.} \\
    \text{In log plot, the curve for each sublattice slightly deviates from a} \\
    \text{straight line, suggesting that the decay is slightly slower than an} \\
    \text{exponential law. It has been known that the antiferromagnetic} \\
    \text{correlation is critical for a homogeneous Hubbard chain [39]. The} \\
    \text{difference may be due to the 1D chain with alternating hopping amplitudes has a} \\
    \text{gapped spectrum. The spin correlations at finite temperatures are also} \\
    \text{obtained using DQMC. In figure 5, we plot the spin correlation between the} \\
    \text{NN sites as a function of temperature. It shows that the curves} \\
    \text{become saturated at low temperatures, and the values steadily} \\
    \text{tend to those obtained with DMRG at zero temperature. The} \\
    \text{consistence further validates the accuracies of both methods.} \\
    \end{align*}$$
(i = 1, …, n_i). The order parameters m_i are self-consistent solved, and the result is shown in figure 3(b). The order parameters become nonzero from a critical interaction U_c ≈ 1.66t, from which the magnetism develops in the ribbon. Then the interactions are exactly dealt with using the DQMC method. Figure 7 shows the spin correlations on a lattice containing three unit cells for several values of U. Their values grow as the interactions are increased, implying the interactions strengthen the spin correlations. We plot the values at U = 4 as functions of the indexes of the sites and the distances along several typical directions. As shown in figure 8, the spin correlations keep finite for all distances in the range of the lattice, implying the magnetism develops for large interactions.

Next we study the intrinsic magnetism of the system by extrapolating a symmetry-breaking term to its vanishing limit. As shown in figure 9(a), the local moment as a function of \( B \) is best fitted using an exponentially-increasing formula \( y = c + a(1 - e^{-bB}) \). The extrapolated local moments are almost vanishing for weak interactions, and then increase rapidly from a critical interaction. The behavior is consistent with the MF approximation. The critical interaction estimated is between 2t and 3t, which is larger than the MF one. Since the realistic value of the Hubbard interaction in graphene is about t, the experimentally relevant GNRs should be nonmagnetic, which is consistent with the experimental results [26, 27].

5. Conclusions

Quantum magnetism of topologically-designed GNRs is studied based on the Hubbard models using exact numerical simulations. We first study a two-band Hubbard model describing the low-energy topological bands using DMRG and DQMC methods and show that it is nonmagnetic. We then include the Hubbard interaction to the topologically-designed GNRs, and find the local moments develop from a critical interaction between 2t and 3t. Compared to the realistic value in graphene, we conclude that the experimentally relevant GNRs are nonmagnetic, which is consistent with the experimental results.

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References

[1] Yazyev O V 2010 Rep. Prog. Phys. 73 056501
[2] Son Y, Cohen M L and Louie S G 2006 Nature 444 347
[3] Yazyev O 2013 Acc. Chem. Res. 46 2319
[4] Nakada K, Fujita M, Dresselhaus G and Dresselhaus M S 1996 Phys. Rev. B 54 17954
[5] Kimouche A, Ervasti M M, Drost R J, Halonen S, Harju A, Joensuu P, Sainio J and Liljeroth P 2015 Nat. Commun. 6 10177
[6] Ruffieux P et al 2016 Nature 531 489
[7] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109
[8] Sorella S and Tosatti E 1992 Europhys. Lett. 19 699
[9] Paiva T, Scalettar R T, Zheng W, Singh R R P and Oitmaa J 2005 Phys. Rev. B 72 085123
[10] Meng Z, Lang T, Wessel S, Assaad F and Muramatsu A 2010 Nature 464 847
[11] Sorella S, Otsuka Y and Yunoki S 2012 Sci. Rep. 2 992
[12] Feldner H, Meng Z Y, Lang T C, Assaad F F, Wessel S and Honecker A 2011 Phys. Rev. Lett. 106 226401
[13] Hikihara T, Hu X, Lin H H and Mou C Y 2003 Phys. Rev. B 68 035432
[14] Feldner H, Meng Z Y, Honecker A, Cabra D, Wessel S and Assaad F F 2010 Phys. Rev. B 81 115146
[15] Luitz D J, Assaad F F and Schmidt M J 2011 Phys. Rev. B 83 195432
[16] Schmidt M J and Loss D 2010 Phys. Rev. B 82 085422
[17] Golor M, Lang T C and Wessel S 2013 Phys. Rev. B 87 155441
[18] Hagymási I and Legeza O 2016 Phys. Rev. B 94 165147
[19] Joly V L J et al 2010 Phys. Rev. B 81 245428
[20] Magda G Z, Jin X, Hagymási I, Vancso P, Osvath Z, Nemescincze P, Hwang C, Biro L P and Tapaszo L 2014 Nature 514 608
[21] Son Y W, Cohen M L and Louie S G 2006 Phys. Rev. Lett. 97 216803
[22] Brey L and Fertig H A 2006 Phys. Rev. B 73 235411
[23] Ezawa M 2006 Phys. Rev. B 73 045432
[24] Cao T, Zhao F and Louie S G 2017 Phys. Rev. Lett. 119 076401
[25] Lin K S and Chou M Y 2018 Nano Lett. 18 7254
[26] Groning O et al 2018 Nature 560 209
[27] Rizzo D J, Veber G, Cao T, Bronner C, Chen T, Zhao F, Rodriguez H, Louise S G, Crommie M F and Fischer F R 2018 Nature 560 204
[28] Su W P, Schrieffer J R and Heeger A J 1979 Phys. Rev. Lett. 42 1698
[29] Marzari N, Mostofi A A, Yates I and Vanderbilt D 2012 Rev. Mod. Phys. 84 1419
[30] Guo H and Shen S Q 2011 Phys. Rev. B 84 195107
[31] Guo H, Shen S Q and Fang S 2012 Phys. Rev. B 86 085124
[32] Wang Z and Zhang S C 2014 Phys. Rev. X 4 011006
[33] Resta R 1994 Rev. Mod. Phys. 66 899
[34] Xiao D, Chang M C and Niu Q 2010 Rev. Mod. Phys. 82 1959
[35] White S R, Scalapino D J, Sugar R L, Loh E Y, Gubernatis J E and Scalettar R T 1989 Phys. Rev. B 40 506
[36] Hirsch J E 1985 Phys. Rev. B 31 4403
[37] White S R 1992 Phys. Rev. Lett. 69 2863
[38] Bauer B et al 2011 J. Stat. Mech. 2011 P05001
[39] Paiva T and dos Santos R R 2000 Phys. Rev. B 62 7007