Electric Field Effects in Zigzag Edged Graphene Nanoribbons

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Abstract. We investigate the magnetic ordering in zigzag edged graphene nanoribbons under cross-ribbon electric fields by using the Hubbard model within the unrestricted Hatree-Fock approximation. In the absence of applied electric field, the ground state is an “edge-magnetized state” with magnetic moments mainly localized on the edges, where the moments on the two edges are mutually antiparallel. Under electric fields, we find that the band gap near the Fermi level becomes spin dependent. On increasing the strength of the electric field, the biased charge distribution decreases or increases the band gap with respect to the majority spin on each edge. Increasing the strength further, the system becomes half-metallic, and finally the magnetization completely disappears.

1. Introduction
Graphene, an isolated monolayer of graphite, has many characteristic features arising from the conical low energy bands. The electrons acts as a massless Dirac particle, and have unusual transport properties such as anomalous half integer hall effect [1]. Long ribbon-like strips made of graphene, especially the ones with zigzag edges are called zigzag graphene nanoribbons (ZGNRs), additionally have some striking properties which are studied extensively.

The lowest energy bands of ZGNRs are partially flat bands which corresponds to the surface states localized on the edges. This structure leads to an almost complete electron current blocking for long range potentials with certain height [3]. The Scatterings by the barrier potentials have band selection rules [4], and this property has the potential to make ZGNR an attractive future device material.

Another topic which arises from the flat band structure is the magnetism of a ZGNR. The flat bands are expected to enhance the effects of the interaction. Fujita et. al. [2] have used a Hubbard model within the unrestricted Hatree-Fock approximation, and have shown that the system is an “edge-magnetized state” despite the small $U$. The spin densities are localized on the edges, and have opposite sign on the opposite edges. Using this unique magnetic ordering, ZGNR can show half-metallicity [5]. The electric field which is applied across the ribbon splits the spin-degenerated bands. With a strong field strength, one of the gaps can be completely suppressed. However when the electrons move freely, they destroy the magnetization and the half-metallicity. Recently, this property has been argued by numerical calculations based on the density functional theory (DFT) [5,7,8].

In the present work, we investigate this property by a rather simple but explicit tight-binding model shown in Sec. 2. In Sec. 3, we show that half-metallicity and the magnetization disappear.
Figure 1. (a) The lattice structure of a ZGNR, the width can be indicated by the number of the zigzag chains $N$. (b) A schematic picture of the magnetic ordering of the “edge-magnetized state”. The color and radius of the circles denote the sign and size of the spin polarization, respectively.

for sufficiently strong cross-ribbon electric fields. A summary is shown in Sec. 4.

2. Model
We consider an infinitely long ZGNR with finite width [see Fig. 1(a)] in an electric field applied across the ribbon. The width of the ribbon is characterized by the number $N$ of zigzag chains, and can be written as $W = a(0.75N - 1)$ where $a = 1.42\text{Å}$ is the lattice constant for graphene. The lowest energy $\pi$ bands are nearly flat for $2\leq k \leq 3$.

We are interested in the magnetism of such a system. The large density of states in the vicinity of the Fermi level induces magnetic instability due to electron-electron interaction [2]. This instability arises from the flat band nature of the $\pi$ bands, and thus we use a single band Hubbard model, where only interactions between electrons are taken into account. Early works by Fujita et. al. [2] have predicted a magnetic ordering on the edges by treating the Hubbard term within the unrestricted Hatree-Fock approximation. Similar results are earned from density functional calculations [5,6] in the low energy region. We employ the Hatree-Fock approximation in order to treat the Hamiltonian as in Ref.2. The Hamiltonian including the electric field is the following:

$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c_i^{\dagger} c_j + U \sum_i \left( \langle n_{i,\uparrow} n_{i,\downarrow} \rangle \langle n_{i,\downarrow} \rangle - \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle \right) + \sum_i v_i n_{i,\uparrow},$$

where $t$ is the nearest-neighbor hopping integral, and $U$ is the on-site Coulomb repulsion. The hopping integral $t$ is approximately $2.7\text{eV}$ for graphene [9]. $U$ should be smaller than $t$, and is set to $U = 0.1t$ throughout the calculation. The site potential $v_i$ describes the onsite energies from the electric field, and we write it as a linear function of $i_y$,

$$v_{i_x,i_y} = V \left( \frac{1}{2} - \frac{i_y - 1}{2N - 1} \right),$$

explicitly. For $V = 0$, the ground state is an “edge-magnetized-state” [2] [see Fig. 1(b)]. $v_i$ is a local potential which changes sign on the opposite side of the ribbon ($v_i = -v_{2N+1-i}$), and since the edge localized spin density also changes its sign on the opposite edge, the electrostatic
potential for each spin changes. By this means, the electric field can couple with the electron spin through the spacial distribution, and this results in the splitting of the bands. To see how the ground state changes, we employ the usual formulation. First, we diagonalize the Hamiltonian using Fourier and canonical transformation. Then by rewriting the mean fields with the diagonalized operators, we derive a set of self-consistent equations for $m_i = \langle n_{i,\uparrow} \rangle - \langle n_{i,\downarrow} \rangle$, and solve it iteratively. In the following, we consider the case of $T = 0$ and half-filling.

Figure 2. The electric field dependence of the local magnetic moments for $U = 0.1t$ and $N = 10$.

Figure 3. The band structures for various values of $V$ with $U = 0.1t$ and $N = 10(W = 9.23\,\text{Å})$. The solid and dashed lines denote the bands for spin up and down electrons. Only the highest occupied and the lowest unoccupied bands are shown.

3. Results
The electric field dependence of the local magnetic moments for $U = 0.1t$ and $N = 10$ ($W = 9.23\,\text{Å}$) is shown in Fig. 2. The magnetic moments slowly decreases first, and then
rapidly drops until it completely disappears at \( V = V_m \). We also show the band structure for various field strengths in Fig. 3. The electron bands for each spin are degenerate in the absence of the electric field, and for a certain value of \( V \), the band gap for spin-up electrons closes while the gap for spin-down electrons is still open. The former completely closes at \( V = V_b \), and the system becomes half-metallic. With stronger \( V \), the magnetic moments disappear and the band degeneracy will recover. In the half-metallic regime (\( V_b < V < V_m \)), the local magnetic moments fall rapidly, which is attributed to the fact that the spin-up electrons can move freely. It should be noted that the charge polarizations grows rapidly at the same time. For \( V > V_m \) the system will be an “edge-polarized state” [10]. The two critical voltages are \( V_b = 0.048 \text{eV} \), and \( V_m = 0.049 \text{eV} \) for the ribbons with \( W = 9.23 \text{Å} \) (\( N = 10 \)).

4. Summary
In summary, we have studied the magnetic property and the band structure of ZGNR under cross-ribbon electric fields using single-band Hubbard models. We see that half-metallicity can be obtained with sufficiently large \( V \). With further increase of \( V \), the half-metallicity and the magnetization disappear simultaneously. Our results can be compared qualitatively with the results in Ref. 8. The semi-half-metal structure is expected to be earned by including terms breaking particle-hole symmetry, such as next-nearest-neighbor hoppings.

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