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Graphene nanoflakes in external electric and magnetic in-plane fields

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ABSTRACT

The paper discusses the influence of the external in-plane electric and magnetic fields on the ground state spin phase diagram of selected monolayer graphene nanostructures. The calculations are performed for triangular graphene nanoflakes with armchair edges as well as for short pieces of armchair graphene nanoribbons with zigzag terminations. The mean field approximation (MFA) is employed to solve the Hubbard model. The total spin for both classes of nanostructures is discussed as a function of external fields for various structure sizes, for charge neutrality conditions as well as for weak charge doping. The variety of nonzero spin states is found and their stability ranges are determined. For some structures, the presence of antiferromagnetic orderings is predicted within the zero-spin phase. The process of magnetization of nanoflakes with magnetic field at constant electric field is also investigated, showing opposite effect of electric field at low and at high magnetic fields.

1. Introduction

Graphene, being the first truly two-dimensional material, exhibits highly unusual electronic properties, and offers, in addition to novel, unique physics, also a promising platform for applications in spin electronics [1–4]. As a consequence, intense studies of magnetic properties of graphene are highly encouraged [5]. Within this field, recent experimental findings concerning the existence of magnetically polarized edge state in graphene nanoribbons [6] provide a sound motivation for theoretical studies of magnetism in geometrically constraint graphene. The presence of edge and further reduction of dimensionality of graphene below two significantly modifies its electronic structure, causing the emergence of early-predicted [7] and experimentally observed [8–10] edge states. On the other hand, it also enables the design of the energy spectrum [11], which crucially shapes the magnetic behaviour.

Magnetism arising in zero-dimensional graphene-based nanostructures (nanoflakes, quantum dots, and nanoribbons) as a result of the presence of edge and modification of electronic structure has recently collected rich literature [12–32]. The potential for spintronics applications has been proven by the proposals of numerous graphene nanoflake-based devices (e.g. [33–35]). In particular, the description of spin-polarized transport through graphene nanostructures was already a goal of numerous studies [36–43]. This supports hopes for development of carbon-based spintronics.

The key feature for spintronics is the ability to control the magnetic properties. Therefore, one of the flourishing fields of exploration is the influence of external fields on the magnetic properties of graphene and nanographenes. Within this scope of studies, the electric field focuses dominant attention, both in the context of graphene itself [44–51], its cousin systems [52–55] as well as for derivative nanostructures, like monolayer and bilayer graphene nanoflakes (quantum dots) [21,56–67], nanoribbons [35, 68–76] or nanotubes [77]. The effect of magnetic field on magnetism in graphene-based structures has also been investigated [24,78–82]. However, it is rather rare to study the common influence of both fields on the properties of graphene [83,84].

In order to extend our previous theoretical works concerning the sole effect of electric field [63] or magnetic field [81] on selected aspects of magnetism in some graphene nanoflakes, we perform the present study. For example, Ref. [63] was focused strongly on indirect coupling between external magnetic planes mediated by a graphene nanostructure and mainly on the possibility of controlling it with electric field. Therefore, our present aim is to investigate the combined effect of external in-plane electric and magnetic fields and to construct the ground state spin phase diagram of some monolayer graphene nanostructures. The calculations presented in the paper are based on the tight binding model with the Hubbard term (in MFA), supplemented with electrostatic potential term and the Zeeman term.

Our systems of interest belong to a class of very small graphene quantum dots, so that the strategy to obtain them experimentally is likely a bottom-top approach, i.e. a procedure based on some molecular precursors. In such context, it should be strongly

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emphasized that some of the nanographenes with shapes and sizes corresponding to our interest in the present work have been recently synthesized within such scheme, what paved the way towards characterization of their magnetic properties [85,86] and served as a motivation for the present research. The experimental development of the class of carbon-based nanostructures under discussion would allow to extend the range of systems in which the control over magnetism by electric field was proven in experiment beyond 'classical' semiconducting systems (see e.g. [87,88]).

The system of interest as well as theoretical model and numerical results will be discussed in details in the following sections of the paper.

2. Theoretical model

The system of interest in the present paper is a monolayer graphene nanostructure (nanoflake or quantum dot) in external in-plane electric and magnetic fields. The schematic view of the studied structures is shown in Fig. 1(a), where the orientation of nanoflakes with respect to the electric field (provided by the gates) along the direction x is sketched. Also the example magnetic field direction is shown (however, it can be an arbitrary other in-plane direction). Each nanostructure is composed of N carbon atoms, belonging to two interpenetrating sublattices (marked with filled and empty symbols). Our interest is focused on two classes of graphene nanoflakes (GNFs). The first one is a triangular nanoflake with armchair edges, each one consisting of M hexagons, what defines the size of the structure (see Fig. 1(b)). The second class of structures is an ultrashort section of armchair nanoribbon with zigzag terminations (shown in Fig. 1(c)). This nanoflake is characterized by N_x atoms constituting a zigzag termination and N_y atoms along each armchair edge. We assume that all the edge carbon atoms are passivated.

We have selected such shapes of graphene nanostructures in general to avoid studying the commonly discussed case of spin-polarized zigzag edge state, e.g. in zigzag-edged triangular nanoflakes [21] or in zigzag-edged nanoribbons [5,68]. We would rather concentrate on the structures possessing armchair edges to avoid zero-field magnetic polarization. Moreover, the present calculations [73] indicate that for some shapes and orientations of the nanostructures the screening effects for the electric field are particularly weak. The same factor limits our interests to nanostructures of small sizes (see also the discussion in our work [63]). We should emphasize here that in order to avoid metallic character of our structures, we consider the smallest, molecular-like nanoflakes with well-separated energy states and with a significant gap between highest occupied state and lowest unoccupied electronic state.

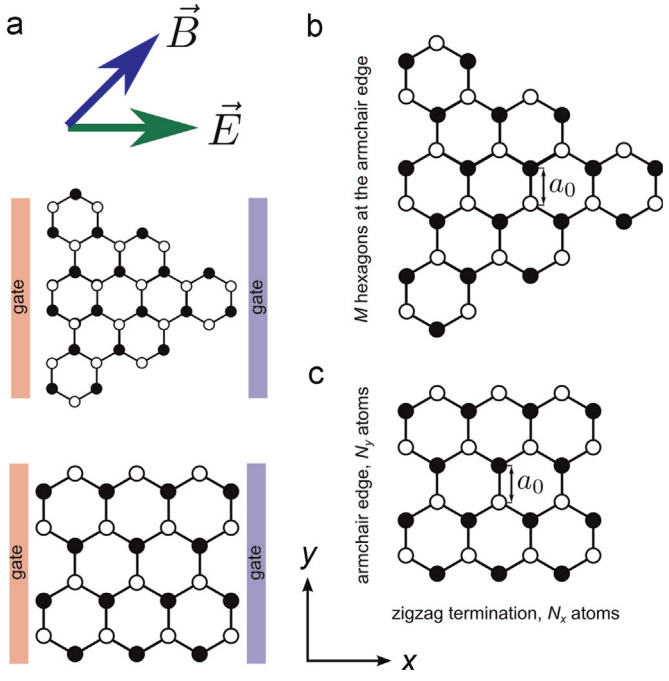

Fig. 1. (a) Schematic view of graphene nanoflakes in external in-plane electric and magnetic fields. (b) Schematic view of triangular graphene nanoflake with armchair edge composed of M hexagons. (c) Schematic view of a short section of armchair graphene nanoribbon with zigzag terminations, width equal to N_x and length equal to N_y.

The goal of the model we use is to capture magnetic properties which result from the behaviour of p^z electrons in graphene nanostructures. These electrons contribute the energy states close to the Fermi level for charge-neutral nanoflakes. In the present work we describe the behaviour of the mentioned charge carriers by means of the following tight-binding based Hamiltonian in real space [81,63]:

$$\begin{aligned}\mathcal{H} = &- \sum_{\langle i,j\rangle,\sigma} t_{ij}(c^{\dagger}_{i,\sigma}c_{j,\sigma} + c^{\dagger}_{j,\sigma}c_{i,\sigma}) \\ &+ U\sum_i (\langle n_{i,\uparrow}\rangle n_{i,\downarrow} + \langle n_{i,\downarrow}\rangle n_{i,\uparrow}) - U\sum_i \langle n_{i,\uparrow}\rangle\langle n_{i,\downarrow}\rangle \\ &+ eE\sum_{i,\sigma} x_i n_{i,\sigma} + \frac{\Delta_B}{4}\sum_i (n_{i,\uparrow} - n_{i,\downarrow}).\end{aligned} \tag{1}$$

In the first term, t_{ij} is the hopping integral between nearest-neighbour carbon sites. We assume that $t_{ij} = t$ for all nearest-neighbour bonds in triangular graphene nanoflakes with armchair edges. On the contrary, for ultrashort pieces of graphene nanoribbons with armchair side edges and zigzag terminations, we assume that $t_{ij} = t(1+\Delta)$ with $\Delta = 0.12$ for outermost bonds at the armchair edges [68,63]. For the remaining nearest-neighbour pairs we take $t_{ij} = t$. The value of t is usually set as 2.7 eV [89]. The value of t can serve as an useful energy scale in further considerations. The operators $c^{\dagger}_{i,\sigma}$ ($c_{i,\sigma}$) create (annihilate) an electron of spin $\sigma = \uparrow, \downarrow$ at lattice site i, while $n_{i,\sigma} = c^{\dagger}_{i,\sigma}c_{i,\sigma}$ is the number of such electrons.

The tight-binding term is supplemented with the Hubbard term, which is considered within MFA, thus neglecting the products of fluctuations $\left(n_{i,\uparrow} - \langle n_{i,\uparrow}\rangle\right)\left(n_{i,\downarrow} - \langle n_{i,\downarrow}\rangle\right)$. The on-site effective energy is taken as $U/t = 1.0$ (see [90], where such an assumption is justified for both charge-neutral and weakly doped structures). It should be emphasized that graphene and graphene nanoflakes do not belong to strongly correlated systems.

In order to account for the external in-plane electric field E along x direction, the electrostatic potential term is added. Moreover, the external in-plane magnetic field H is introduced by means of the Zeeman term, where $\Delta_B = g_e\mu_B H$ is the Zeeman energy parameter. Let us mention that the in-plane orientation of magnetic field does not lead to the Peierls substitution [91], because the hopping integrals are only modified in the presence of in-plane component of the vector potential of the magnetic field.

The horizontal electric field is assumed to originate from the gates between which the graphene nanostructure can be placed. In our considerations we use the normalized electric field, Ea_0/t. It might be useful to mention that for graphene nanostructures, the unity value of this normalized field would correspond roughly to 2 V/Å. Regarding the magnetic field, let us mention that the source of Zeeman term present in our model may be either external magnetic field or, even more likely, it can result from exchange bias originating from the magnetic substrate on which graphene nanostructures can be deposited. Let us focus on the second possibility, being particularly interesting in the light of recent experimental achievements concerning growth of graphene on