# Magnetism of bilayer graphene with vacancies

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**Received: 10 August 2017, Revised: 15 August 2017 and Accepted: 06 September 2017**

DOI: 10.5185/amp.2017/914
www.vbripress.com/amp

## Abstract

At the nanoscale defects (vacancies) can be useful for generating novel materials and devices. In this paper we discuss how a bi-vacancy orientation in bilayer graphene influences the total magnetization of the system. The spin-polarized density functional theory as implemented in the Quantum Espresso code is used to calculate the total magnetization for the case of graphene sheets with the same or different vacancy distributions. Important results are obtained: reduction of the magnetic moment due to the interlayer bonding in AA bilayer stack with a double vacancy in each graphene layer on the top of each other; out-off plane arrangement of the carbon atoms in the vicinity of the vacanices; opening of a gap in the band structure due to vacancies. It could be expected that the temperature and the interface will further influence the life-time of the magnetic state but the possibility of switching between non-magnetic, antiferromagnetic and ferromagnetic states as a result of mutual rotation of the defective layers remains. 

**Keywords:** Bilayer graphene, vacancies, magnetic properties, spin-polarized density functional theory.

## Introduction

Graphene is a two-dimensional layer of carbon atoms organized in a hexagonal structure, which causes the $sp^2$ hybridization of the atomic carbon s orbital and the two p orbitals. This enables the formation of a σ bond between neighboring atoms. The σ bond is responsible for the robustness of the lattice structure in all carbon allotropes. Because of the Pauli principle, these bands have a filled shell. As a result, a valence band appears. The pz orbital, which is perpendicular to the graphene plane, binds covalently with carbon atoms nearby. This leads to the formation of a π band. Since every p atomic orbital hosts one extra electron, the π band is half-filled. This is why the perfect graphene is strong and has the best electrical conductivity. These properties make it a dreamed material for high-technological applications – ultra-fast charges of batteries, ultra-thin touch screens, and efficient biosensors – to mention a few. Because the perfect graphene has a zero band gap, it cannot be directly used in an electronic device because of impossibility to switch it off/on. There is a need to introduce non-zero density of states around the Fermi level contributing to charge polarization. This can be done via doping of graphene or via introducing vacancies.

The positive influence of vacancies on the electric and magnetic properties of single-wall carbon nanotubes and graphene has been in our research focus for many years [**1-3**].

Beside the trivial paramagnetism associated with σ dangling bonds of C atoms, a more interesting π magnetism arises in graphene with vacancies [**3,4**]. In [**3**] we demonstrated that in the case of more than one vacancy per supercell, interaction between the total magnetic moments at each defective site occurs. The interaction is ferromagnetic for vacancies in the same sublattices and it is antiferromagnetic for the case of different sublattices.

Monoatomic vacancies in bilayer graphene were computationally studied in [**5**]. For the case of a full σ-bond passivation preventing the reconstruction of the vacancy, a full value of 1 μB for the π extended magnetic moment is recovered for both monolayer and bilayer cases. While the conclusion of [**5**] has been to put on hold claims of vacancy-induced ferromagnetic or antiferromagnetic order in graphene-based systems, recent results, reviewed in [**6**] confirmed our results [**3**] that it is possible to switch between nonmagnetic, antiferromagnetic and ferrimagnetic states.

The bilayer graphene exists in three modifications: AA, AB (or Bernal phase), and twisted bilayer. The simplest form is the AA bilayer - each carbon atom of the second layer is placed exactly above the corresponding atom of the first graphene layer. In the AB bilayer, or

Bernal phase, half of the carbon atoms of the top layer are above the carbon atoms of the lower layer, while the rest are located above the centers of the lower-layer hexagons as it is in graphite. In the third type of bilayer graphene structure, the top carbon layer is rotated with respect to the lower layer by some angle. The electronic properties of the bilayer structures are rather different as it has been reviewed in [**7**]. The electronic structure can be modified by applying a transverse electric field (perpendicular to the layers) [**8**] or through a twist of the layers [**9**]. For finite systems, changing the twist angle causes a gradual crossover between a zero gap and non-zero gap material [**9**]. The review paper [**7**] covers also single-electron properties, effects of static electric and magnetic fields on bilayer-based mesoscopic systems, spin-orbit coupling, direct current transport, optical response, and spontaneous symmetry violation.

These properties of bilayer graphene alter in the presence of defects – zig-zag/arm-chair edges, add-atoms or vacancies.

The present paper presents results for the AA bilayer stack with two vacancies per cell. The AA stack is thought to be less stable than the AB arrangement due to the difficulties to produce it in practice.

The paper answers the following important questions: what is the role of vacancies and their distribution in the AA structure on the magnetic moment of the system and how does the vacancy-vacancy interaction change the type of magnetism.

The importance of the addressed topic is related to both technological applications of bilayer graphene and fundamental understanding of the symmetry breaking in finite-size systems exhibiting phase transformations. In molecular clusters we have developed a method to include the symmetry even in finite-size clusters [**10**], which will navigate the research on spin phase transitions in the bilayer graphene with vacancies, which violate the symmetry of the infinite carbon bilayer and, by this, induce magnetic moments. The bilayer magnetism offers compelling prospects for the future development of graphene-based spintronics

## Model of the bilayer graphene with vacancies

We consider vacancies in each graphene layer to study the spin-polarization as a function of vacancy-vacancy interaction within each layer and between the layers. In practice such vacancies can be produced in knock-on collisions, which involve direct transfer of kinetic energy from high-energy incident beam (say protons from an accelerator) to the individual atoms in graphene sheets. In the model system, the initial distance between the parallel graphene sheets was 3.3 Å and the C-C bond length - 1.41 Å.

The position of the missing atom plays an important role in passivation (or not) of the dangling bonds. The passivation can be understood by looking at the local arrangement of the carbon atoms. Since the honeycomb lattice of a graphene layer is a bipartite lattice, it can be represented with two mutually interconnected sublattices. Each atom belonging to one sublattice is connected only to the atoms in the other sublattice and vice versa. The carbon atoms have either three (perfect hexagonal arrangement) or two nearest neighbors (in the case of a neighboring vacancy or if it is an edge atom).

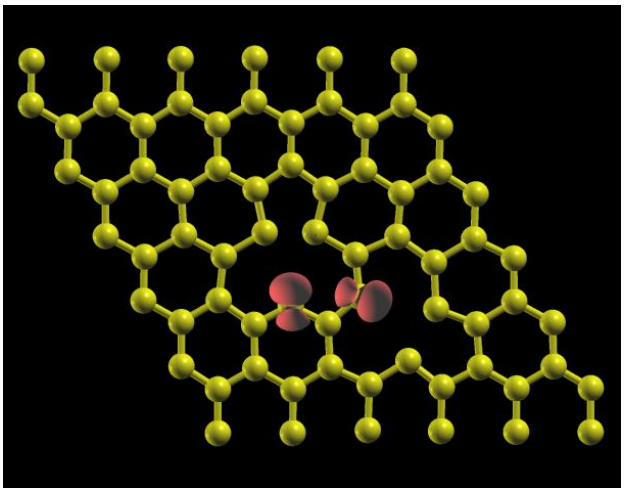

**Fig. 1.** The top view of one graphene sheet with two vacancies in a ferromagnetic state.

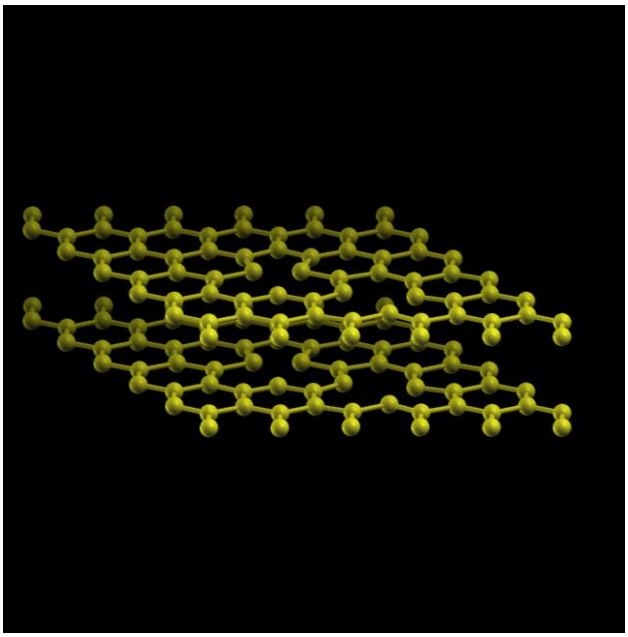

**Fig. 2.** AA bilayer stack: the distance between the sheets was initially set to 3.3 Å.

**Fig.1** and **Fig. 2** show the system immediately after the removal of two carbon atoms belonging to the same sublattice. Such a bilayer graphene, before the relaxation, is in a ferromagnetic state with a total magnetization of 4.87 μB/cell. The total moment is calculated along an axis perpendicular to the bilayer surface. The magnetization induced by vacancy defects is opposite for the two sublattices in each graphene sheet. The system is subjected to a relaxation before the production run.

 

## Computational procedure

We have implemented the spin-polarized Density Functional Theory in the Quantum Espresso version - espresso/5.4.0 that contains programs for electronic structure calculations and density functional perturbation theory, using a plane-wave basis set and pseudopotentials [11]. We run the parallel computations on 128 cores. The density functional for exchange-correlation energy of the many electron system is the Perdew-Burke-Ernzerhof generalized gradient approximation [12]. As the important quantity when discussing k-points is not the number but their spacing in reciprocal-space, we have generated an equal spaced mesh following the Monkhorst-Pack scheme [13]. The k-point grid for the non-self consistent field was 12x12x3; for the self-consistent field the k-point grid was 3x3x1. The wave functions at each k-point are represented by the numerical coefficients (weights) of a finite set of plane waves determined by a kinetic energy cut-off at 80 Ry. The weight of the k-points describes the contribution of data at a single k-point to the data for the whole Brillouin zone and accounts for the symmetries. Because of the vacancies, the symmetry of the pristine graphene sheets is reduced and we are obliged to use a denser grid than in the case of a full symmetry. The vacuum layer thickness in the periodic boundary conditions was 23.35 Å.

## Results and discussion

The vacancy defects in graphene induce local magnetic moments caused by quasilocalized states and dangling bonds of the atoms surrounding a vacancy. A quasilocalized state contributes one Bohr magneton per one vacancy in a supercell as the Lieb's theorem predicts. A single vacancy leaves three σ dangling bonds and removes a π electron. The magnetic moments of the three atoms around the vacancy are summed up and the total magnetization is obtained from:

$$M_{total} = \int (n_{up} - n_{down}) d^3 r$$

where $n_{up}$ and $n_{down}$ are the number of spins in up and down orientation. The total magnetization varies from zero to a maximum value that depends on the boundary – zigzag, armchair, or a mixture of the two.

Due to high chemical reactivity of the dangling bonds, it is seen that they are coupled in the vicinity of vacancies when these are very close, **Fig. 3.** The **Fig. 3** presents the top view of iso-surface (0.25 level) distribution of the electron density in an AA stack with vacancies on the top of each other. The electron distribution is not uniformly distributes and the atoms that are less bound within the plane become outward and bind with the respective atoms of the other layer, **Fig.4** left side.

Because of the interlayer bond seen in the **Fig.4** left side the total magnetization of the system drops down from 4.87 to 1.65 μB/cell. The interlayer C-C bond length is 1.34 Å, i.e. even shorter than the C-C bond length of 1.41-1.42 Å in the carbon hexagonal structure. It is seen in the Fig.3 that only one pentagon is formed with a bond length of 1.35 Å. This pentagon keeps the bond length of 1.41 Å where it is in contact with hexagon.

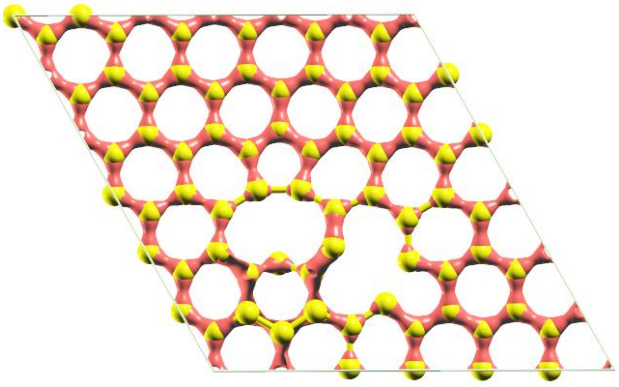

**Fig. 3.** The top view of the iso-surface distribution of the electron density in the AA bilayer graphene with vacancies on the top of each other.

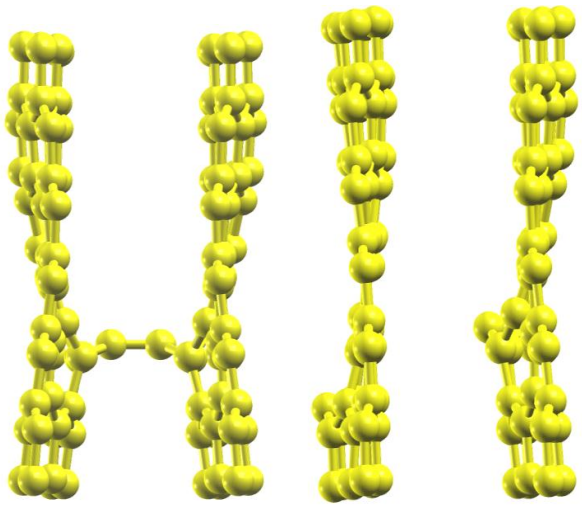

**Fig. 4.** There is a bond between the two layers when the defects are located on the top of each other (left figure); the layers are not bound when the vacancies are opposite to each other (right figure) although there are outward carbon atoms.

This deformation contributes to non-homogeneous distribution of the electron density. The other vacancy does not form a pentagon because the distance between the neighboring carbon atoms is 1.7 Å, which is longer than the longest C-C bonds. The reason is the out-off plane arrangement of the atoms.

The reduction of the magnetic moment due to the interlayer bonding is an important result. It shows that if the vacancies are very close and let a bond between the atoms with dangling bonds in the different graphene layers, the magnetic moment of the system can be reduced even more than it has been observed in a single graphene sheet with 2.93 μB magnetic moment for the same vacancy distribution [**14**]. This observation opens the avenue of technological development of magnetic devices.

 

If the two graphene layers, each with a double-vacancy, are rotated at the $180^0$, i.e. the configuration contains opposite vacancies, the total electron density at 0.39 level is as it is plotted in the **Fig. 5.** The side view is shown in the **Fig. 4** – right side. There are no interlayer bonds because the closest distance between the two layers is 3.44 Å (initially the distance was set to 3.3 Å). The largest distance (upper and lower parts of the sheets in the **Fig. 4** right side) is 5.03 Å.

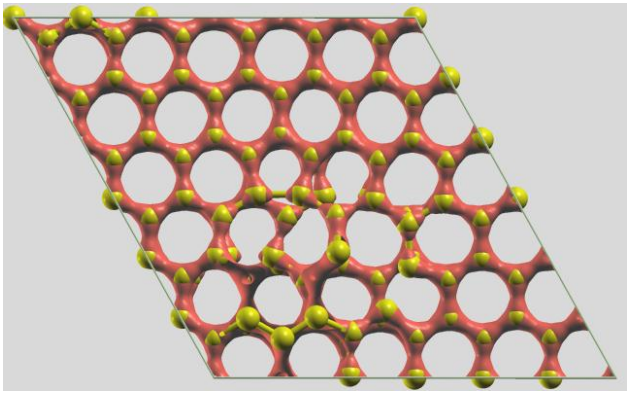

**Fig. 5.** The top view of the iso-surface distribution of the electrons in a bilayer graphene – the two graphene sheets are rotated at $180^0$.

## Conclusion

The spin density is non-uniformly distributed among the atoms around the vacancies and the nearest neighbors contributing to non-zaro magnetic moment of AA bilayer graphene. The Fermi level of the system is 1.5243 eV and there is an opening in the vicinity of the Fermi level, which classifies this stack as a semiconductor.

The reduction of the magnetic moment due to the interlayer bonding is an important result, which opens the possibility of various technological applications of such a system.

It will be very interesting to compare in the future the adsorption ability of bilayer graphene with double-vacancies with the results for mono-vacancy defective bilayer graphene [**15**].

#### Acknowledgements

This work was supported by the ERDF Project No. BG161PO003-1.2.05-0001-C0001 - Sofia Tech Park (the HPC laboratory), http://nestum.phys.uni-sofia.bg

#### Author's contributions

DD, SP performed the computer simulations and plot the data; AP brought the idea and wrote the paper: Authors have no competing financial interests.

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