Non-collinear magnetic moments in graphene with vacancies

Stoyan Pisov, Vladislav Antonov, **Ana Proykova**

University of Sofia, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria
anap@phys.uni-sofia.bg

Abstract
Although Nature does not favor low dimensional crystal growth, self-standing two-dimensional crystal films do exist – single, one-atom-thick layers of carbon and tungstenite are examples of truly two-dimensional materials. Perfect graphene has an amazing band structure [1], which determines its fascinating properties – a zero DOS metal and, simultaneously, a zero gap semiconductor. The full symmetry of the system makes it possible to use the massless two-dimensional Dirac's equation for the low energy state. Since the honeycomb lattice of graphene is a bipartite lattice, it can be partitioned into two mutually interconnected triangular sublattices. Each atom belonging to one sublattice is connected to the atoms in the other sublattice only and vice versa. However, if defects (vacancies) are present then the symmetry between the two sublattices is destroyed, which effectively adds a mass to the Dirac equation. As a result, the gap opens at K-points and new (doping) levels are generated.

In this work we revisit the induced magnetism in defective graphene to focus on frustration that occur after the removal of one or more atoms from a graphene sheet. Graphene is nonmagnetic with negligible spin-orbit coupling that makes it ideal for spin-polarized transport. However, imperfections – impurities or vacancies - change electronic and magnetic properties [2,3,4] and enhance adsorption of gases [5]. 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). Because of this, the position of the missing atom plays an important role in passivation (or not) of the dangling bonds and graphene with vacancies becomes magnetic, either ferro- or antiferromagnetic depending on the vacancy distribution in the graphene sublattices [2,4]. Among physical systems that display collective macroscopic quantum phenomena, interacting spin systems are perhaps the most experimentally informative.

In our computational approach, we consider that a vacancy is formed in a knock-on collision – proton or electron bombardment. The formation a single vacancy in graphene leaves three σ dangling bonds and it removes a π electron. We use spin-polarized density functional theory (Quantum Esspresso, [5]) to monitor the spin polarization. The density functional for exchange-correlation energy of the many electron system is the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). The k-point sets are generated automatically following the Monkhorst-Pack (MP) scheme. The wave-functions at each k-point are represented by the numerical coefficients of a finite set of plane waves, determined by a kinetic energy cut-off at 55 Ry (≅ 748eV). The vacuum layer thickness in the periodic boundary conditions is 12 A. The size of supercell – 16 Bohr radii - is large to minimize self interaction through periodic boundary conditions. The shape of the supercell is hexagonal to preserve the lattice symmetry. Gauge Including Projector Augmented Waves (GIPAW) norm conserving pseudopotential provided by the QE web site http://www.quantum-espresso.org/ was implemented. GIPAW is a DFT based method to calculate magnetic resonance properties, exploiting the full translational symmetry of crystals.

Ab-initio calculations have been performed for different vacancy concentrations – from 12.5% down to 1%. The results show that when high density of k-points 30x30x1 is used then the total magnetization converges as a function of cell size to 1.53 μB for a single-atom vacancy. The maximum magnetic moment of 2 μB (one μB due to the quasilocalized state and one μB due to the dangling bonds) is obtained for the case of non-interacting moments induced at the vacancy positions and if only Γ=0 is used. As it can be expected from symmetry point of view, a double-vacancy defect preserves the zero magnetizaton of graphene.

When the defect concentration is decreased below 3.1%, the spin density becomes non-uniformly distributed among the atoms around the vacancy. The spin density around one of the atoms is higher than the density around the other two atoms that move in a closer distance.

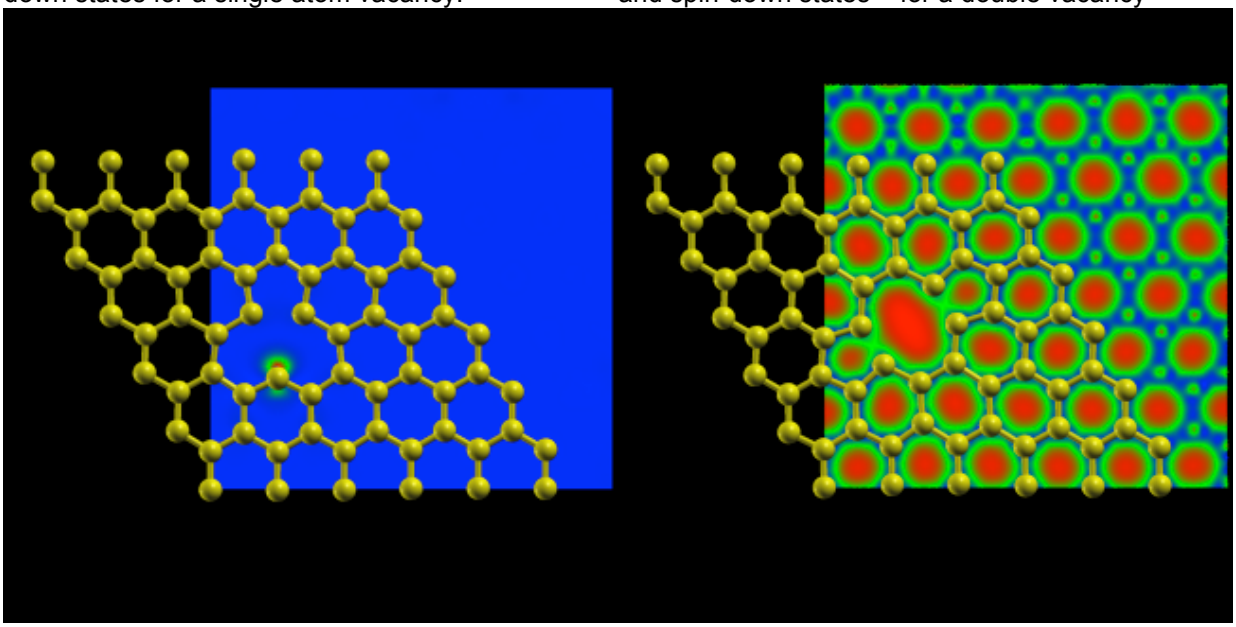
Finally, we discuss whether the ‘‘multi-sublattice structure’’ is required for the occurrence of non-collinear arrangements in a quantum spin system.

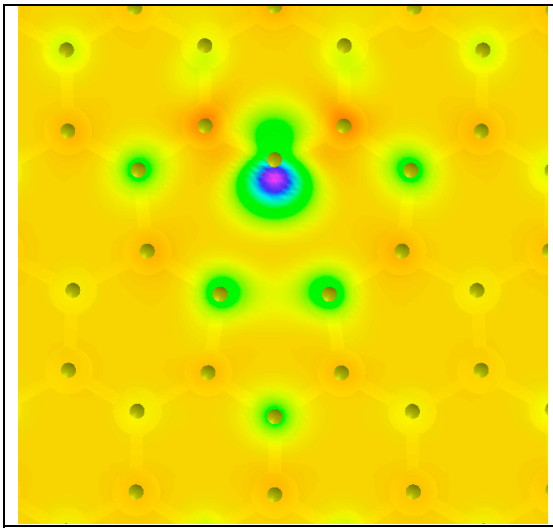
References

[1] Novoselov, K., Geim, A., Morozov, S., Jiang, D., Katsnelson, M., Grigorieva, I., Dubonos, S. and Firsov, A., Nature 438(7065) (2005) 197–200.
[2] Yazyev O., Rep. Prog. Phys. 73 (2010) 056501.
[3] Terrones, H.,Lv, R.,Terrones and Dresselhaus, M., Rep. Prog. Phys. 75 (2012) 062501
[4] Antonov, V., Borisova, D., Proykova, A., IJQC 113(6) (2013) 792–796 (Article first published online: 24 MAR 2012) DOI: 10.1002/qua.24078)
[5] Giannozzi, P., J. Phys. Condens. Matter. 21 (2009) 395502-395521.
[6] Antonov, V., Borisova, D., Pisov, S., Proykova, A., Nanoscience & Nanotechnology, 11 (2010) 17-19.

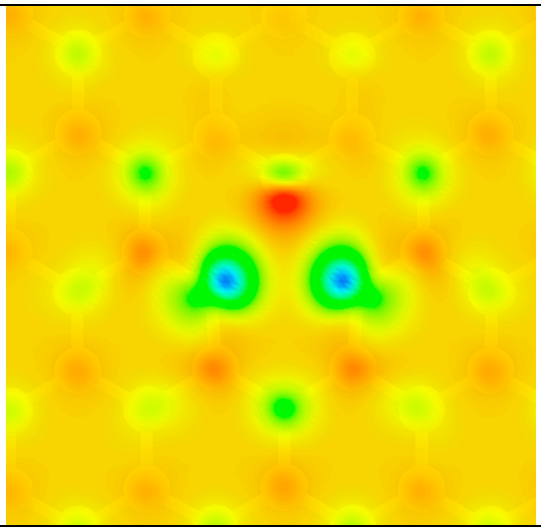
A plot of the difference between spin-up and spin-down states for a single atom vacancy.

The total electron density – a sum of the spin-up and spin-down states – for a double vacancy





1.0% vacancies: the magnetic moment is perpendicular to the graphene plane



2.0% vacancies: the magnetic moments are not collinear (frustration)