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# Interaction between single vacancies in graphene sheet: An ab initio calculation

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ABSTRACT

In order to investigate the interaction between single vacancies in a graphene sheet, we have used spin-polarized density functional theory (DFT). Two distinct configurations were considered, either with the two vacancies located in the same sublattice or in different sublattices, and the effect of changing the separation between the vacancies was also studied. Our results show that the ground state of the system is indeed magnetic, but the presence of the vacancies in the same sublattice or in different sublattices and the possible topological configurations can lead to different contributions from the $\pi$ and $\sigma$ orbitals to magnetism. On the other hand, our findings reveal that the net magnetic moment of the system with the two vacancies in the same sublattice move towards the value of the magnetic moment per isolated vacancy with the increase of the distance between the vacancies, which is ascribed to the different contributions due to $\pi$ electrons. Moreover, it is also found that the local magnetic moments for vacancies in the same sublattice are in parallel configuration, while they have different orientations when the vacancies are created in different sublattices. So, our findings have clearly evidenced how difficult it would be to observe experimentally the emergence of magnetic order in graphene-based systems containing randomly created atomic vacancies, since the energy difference between cases of antiferromagnetic and ferromagnetic order decreases quickly with the increase in the distance separating each vacancy pair.



## 1. Introduction

Graphene, a two-dimensional material with a single atomic layer of graphitic carbon, has attracted great attention recently, due to its novel electronic properties and potential device applications [1–3]. Ideal graphene sheet is nonmagnetic, then to use graphene for spintronic applications the major challenge is to make graphene magnetic. In this sense, the experimental observation of magnetic properties in graphene and related materials [4–8] has drawn huge interest, especially considering the applications of these materials in spintronics, quantum information processing and others.

Recently theoretical works [9–14] have revealed that the magnetic properties in graphene-based systems are associated with the occurrence of defects such as atomic vacancies, substitutional and chemisorbed species. In particular, vacancies in graphene sheet giving rise to magnetism depend on the density of defects [15]. Single-atom defects in graphene also lead to the occurrence of quasi-localized states near the Fermi level [13]. The fact that quasi-localized states lie at the Fermi level suggests that itinerant magnetism can be induced due to electron exchange instability [16].

Here, we report a systematic investigation of the effects of changing the spatial arrangement of two vacancies in a graphene sheet on its electronic and magnetic properties; the separation between the vacancies as well as their location (with respect to the distinct sites of the bipartite graphene lattice) were studied, while keeping the density of the defects fixed. Two single vacancies were created in the same sublattice (A0A$i$) or in different sublattices (A0B$i$) with $i$=1, 2, 3 and 4 for different distance between the vacancies. Spin-polarized DFT calculations with full structural relaxation were performed. Our findings show that the ground state of the graphene sheet containing two vacancies is indeed magnetic, with ferromagnetic or antiferromagnetic coupling between the magnetic moments associated with the vacancies. However, depending on the creation of the vacancies on the same sublattice or in different sublattices and on the possible topological lattice distortions, different contributions of the $\pi$ and $\sigma$ orbitals to magnetism are observed.

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## 2. Calculations

In this work, we have investigated the interaction between carbon vacancies in a graphene monolayer, through first-principles calculations, based on the density functional theory (DFT) [17,18]. The spin-polarized DFT calculations were performed using ultrasoft Vanderbilt pseudopotentials [19], and a generalized gradient approximation (GGA) for the exchange-correlation potential [20], as implemented in the VASP code [21–23]. In this calculation we have used a $9 \times 9$ supercell with 160 carbon atoms and two atomic vacancies, which were created by removing carbon atom from an pristine graphene sheet. It is worth stressing that we have also performed calculations for larger supercells, with sizes not fitting into the '$3n \times 3n$' type; although the numerical values of the calculated properties change slightly with the supercell size, the main results and trends observed in our work remain essentially the same (see table S1 in the supplementary Material). Herein, two different vacancy locations were considered: (a) vacancies in the A sublattice and (b) vacancies in the B sublattice. The lattice parameter for graphene obtained from structural optimization was 2.46 Å. We have used a plane-wave-cutoff energy of 400 eV and a Monkhorst-Pack [24] scheme with a $3 \times 3 \times 1$ k-mesh for the Brillouin zone integration. In all calculations the lattice parameter was kept fixed at the calculated value, whereas the atoms were allowed to relax until the atomic forces were smaller than 0.025 eV/Å.

## 3. Results and discussions

In order to study the effect of the interaction between two vacancies in the graphene sheet, we have considered several different configurations as shown in Fig. 1. It is important to stress that the vacancy concentration was kept fixed in all calculations reported herein.

First, a single defect vacancy was created in A0 (as indicated in Fig. 1) and the structure was completely relaxed. The structural relaxation carried out for the entire structure yielded a planar Jahn Teller distorted carbon triangle and local magnetic moment around the vacancy, in accordance with previous work [25]. For the carbon triangle (see Fig. 3), we found two long bonds with a length of 2.55 Å each and a short bond with a length of 1.98 Å (see table table 1), as compared with the value of 2.46 Å for the undistorted structure. The formation of this short bond points to a reconstruction of the two dangling bonds left after the removal of the carbon atom from the A0 site in the graphene sheet [13]. The ground state of the relaxed system exhibited a magnetic moment 1.16 $\mu_B$, in agreement with previous reports [12].

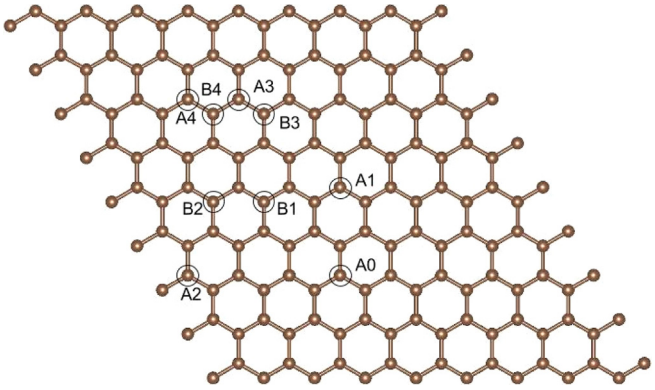


**Fig. 1.** (Color online) Topological configurations of two vacancies on single graphene, where A*i* and B*i* indicate the position of the vacancies created on A and B sublattice, respectively.

**Table 1**
Bond lengths in the carbon triangles formed around each single vacancy in the relaxed graphene structure. The symbols dA0 and LA0 represent the short bond and the two long bonds in the triangle formed around the A0 site, whereas dX *i* and LX *i* represent the corresponding bond lengths in the triangle formed around the second vacancy (X can indicate an A or B site and *i* ranges from 1 up to 4.)

| System | dA0(Å) | LA0(Å) | dX*i*(Å) | LX*i*(Å) |
|---|---|---|---|---|
| A0 or B0 | 1.98 | 2.55 2.55 | 1.98 | 2.55 2.55 |
| A0A1 | 1.73 | 2.54 2.52 | 1.90 | 2.58 2.65 |
| A0A2 | 1.79 | 2.52 2.56 | 1.86 | 2.60 2.68 |
| A0A3 | 1.87 | 2.54 2.54 | 1.93 | 2.57 2.57 |
| A0A4 | 1.89 | 2.55 2.58 | 1.95 | 2.58 2.65 |
| A0B1 | 1.91 | 2.61 2.64 | 1.91 | 2.61 2.64 |
| A0B2 | 1.84 | 2.53 2.60 | 1.82 | 2.56 2.57 |
| A0B3 | 1.97 | 2.57 2.59 | 1.95 | 2.55 2.55 |
| A0B4 | 2.08 | 2.57 2.64 | 1.93 | 2.55 2.57 |

The formation energy of a single vacancy in the graphene sheet at the ground state of the system was calculated as

$$E_f = \frac{1}{n}\left(E_v - \frac{N-n}{N}E_g\right), \quad (1)$$

where $N$ denotes the number of C atoms in the defect-free graphene sheet, $n$ represents the number of vacant C atoms (i.e., $n=1$ for a single vacancy) and $E_g$ and $E_v$ are the total energies of the defect-free and the vacancy-containing graphene sheets, respectively. The formation energy of the graphene sheet containing a single vacancy calculated according to Eq. (1) was found to be 7.6 eV, which is in good agreement with the experimental value of 7.0 eV [26] and also with previous results of DFT calculations [27,28].

However, when we created the second vacancy in the graphene sheet the formation energy was found to be 7.50 eV, which is a value somewhat smaller than the one corresponding to a single isolated vacancy [13]. A Jahn-Teller distorted triangle was again observed around each vacancy (see Fig. 3). The values of the bond lengths in these triangles for a graphene sheet with two vacancies separated by varying distances after a full relaxation of the whole topological configuration (see Fig. 1) are given in Table 1, with the symbols d and L standing for the short bond and the two long bonds, respectively.

From the data displayed in Table 1, one can note that the average lengths of the two long bonds are in general larger than 2.55 Å (value corresponding to a single isolated vacancy) for all configurations. Also, for systems with two vacancies, it can be verified that the length of the short bond in the carbon triangles increases with the increase of the distance between the vacancies; however, the average length of this short bond calculated from the lengths associated with each vacancy (dX*i* and dA0) remains in most cases below the value corresponding to an isolated vacancy (1.98 Å).

In order to investigate the effect of the creation of the second vacancy on the ground state of the system and on its total magnetic moment, different configurations were considered in terms of the relative location of each vacancy (A0A*i* or A0B*i* configurations) and of the separation between the vacancies (different *i* values), as indicated in Fig. 1. In this sense, the total energy difference between states with distinct magnetic couplings involving the magnetic moments associated with each vacancy was determined. The values of the calculated total energy differences considering ferromagnetic (FM) and antiferromagnetic (AFM) coupling for all configurations studied herein are shown in Fig. 2.

The results plotted in Fig. 2 clearly show that the FM state is more energetically stable than the AFM state for the case of the two vacancies created on the same sublattice (A0A*i* configuration). The ferromagnetic coupling between the magnetic moments associated