



Influence of the structural configuration on the stability and magnetism in multivacancy graphene systems



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ABSTRACT

This manuscript reports a comprehensive study of the stability and magnetism in graphene multivacancy systems, using Density Functional Theory (DFT) calculations, by means of the concept of the complementary figure, i.e. the sequence of carbon atoms removed to produce these defected graphene structures. We studied the role of the relative positions of the pentagonal rings that form after optimization in the resulting defected graphene structure, the occurrence of dangling bonds, their steric hindrance and the magnetic arrangements formed. The results here reported give an interesting approach to understand complex multivacancy graphene systems and contribute to this field by going further in the use of the complementary figure to characterize and predict the properties of such systems.

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1. Introduction

Carbon materials have been intensively studied since the discovery of fullerenes [1], the preparation of carbon nanotubes [2] and the pursuit of new properties in graphite [3–9]. More recently, graphene has attracted great interest due to its very unusual physical properties derived from its electronic structure [10–17] and the potential applications that could have devices based on this material, such as field-effect transistors, single molecule gas detection or quantum information processing devices.

The search for new properties in graphene-based materials includes the study of nanoribbons [18] and the field of the metamaterials [19], i.e. materials with the design of artificial periodic nano- or micro-scale modifications.

The study of vacancies in nanotubes [20,21] and graphene [20,22] have been carried out due to the potential influence that such defects could cause on the pristine materials. Particularly, vacancies in graphene have been studied, either in mono- or divacancies [21,23–25] or in more complex multivacancy systems [26–29]. The use of graphene-based materials due to their potential applications could be very much enhanced if a gap in the electronic structure of pristine graphene could be opened through any modification that could be introduced in such structure. It has

been demonstrated that a gap could be achieved in graphene through the creation of vacancies [30–36].

Recent reports describe the creation of defects by etching at high temperature and controlled atmosphere [37], the improvement of the defects creation at the nanoscale in graphene [38] and the production of antidot lattices using ebeam lithography and oxygen beam etching [39–47], increasing the interest of theoretical work in this subject, to explain and to predict properties of new defected materials.

Recently, a set of rules that could help in the prediction of net magnetic moment in multivacancies in graphene, based on the shape of the complementary figure (i.e. the geometric figure of the atomic arrangement that is extracted from graphene when the multivacancy is created) were reported [48]. The complementary figure gives a new insight to understand the multivacancies structures and their properties. For this reason we think that further work could be done in graphene multivacancies systems, regarding the different shapes that complementary figure can adopt.

In this manuscript we study the stability of simple multivacancy graphene systems by means of the first principles-based calculations of the formation energies of these defected systems, disregarding the approach of reconstructed vacancies, 585 and 555–777 double vacancies or Stone Wales defects [49], just focusing in the vacancies formation without any rearrangement. In order to carry out this study, we performed Density Functional Calculations, DFT [50,51].

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2. Computational methods

Periodic spin polarized band structure calculations were performed on graphene multivacancies systems with the use of the DFT program VASP (Vienna *ab initio* simulation package) [52]; pseudopotentials were applied with a plane-wave basis, using the supercell approach. The exchange correlation potential was chosen as the generalized gradient approximation (GGA-PBE) [53] in a projector augmented wave (PAW) method [54,55]. An energy cutoff of 500 eV was used to expand the Kohn–Sham orbitals into plane wave basis sets. In all of the calculations reported here the k -point mesh was taken equivalent to $4 \times 4 \times 1$ for the full (reducible) Brillouin Zone, allowing the convergence of total energy, stress components and ionic forces, with a tolerance for the total energy of 10^{-6} eV/cell. Supercell parameters and ions positions were allowed to optimize, until residual forces and stress tensor components were positioned down to 0.01 eV/Å and 5 kbar respectively.

Due to the differences in the size and shape of the multivacancies, different supercell parameters were considered, for example for three atom vacancies a supercell of 6×6 where considered, defined in terms of pristine graphene, giving place to $a \sim b \sim 14.4$ Å, with a vacuum distance of $c = 30$ Å. In the case of high order vacancies, supercells of 12×12 where considered, with $a \sim b \sim 29.0$ Å. The proximate values are presented here because the geometrical optimization leads to asymmetrical distortions in the original cell parameters. An important point to mention here, is that actual supercell parameters ensures the convergence of the further formation energies, with an accuracy of 0.01 eV, as obtained for a same vacancy obtained for two supercell as $n \times n$ and $(n+1) \times (n+1)$. This methodology have been successfully applied to close related defective graphene system, as published for our group [16,48].

3. Discussion and results

3.1. Structure and stability

The formation energies per carbon atom, showing the stability in these multivacancy systems, were calculated in the following way:

$$E(k) = E_k - NE_1$$

where N is the number of carbon atoms in the graphene supercell after the vacancy has been created, k is the number of carbon atoms extracted to create the vacancy, E_k is the energy of the optimized structure for a k -order vacancy and E_1 is the energy per carbon atom in regular graphene.

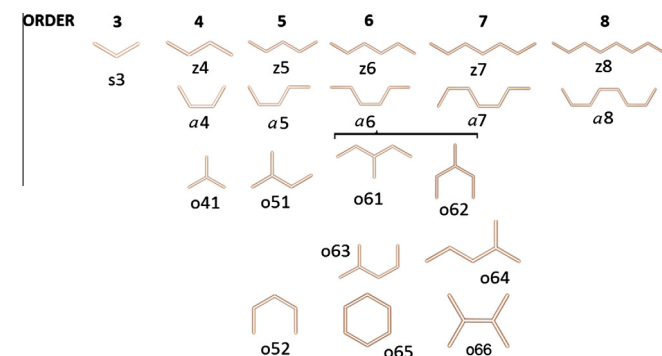


Fig. 1. Complementary figures for graphene multivacancy systems. z, a and o, stands for zigzag, armchair and other configurations.

Fig. 1 shows a scheme where the evolution of the complementary figure can be seen when the order of the vacancies (k) increases. The nomenclature zk and ak stands for zigzag and armchair growth of the complementary figure and ok for other configurations. Additional number n as in okn is just an ordinal number to identify different configurations among k -order vacancy systems.

As an example, Fig. 2 shows $z4$ (a) and $a4$ (b) optimized structures, with their respective complementary figures. The planar distortion of the lattice to form pentagons where terminal points of the complementary figures are located is evident, as predicted previously [48].

The formation energies per carbon atom for the z, a and o systems, are shown in Table 1.

Fig. 3 shows a steady trend for increasing $E(k)$ with the order of the vacancy, in armchair or zigzag complementary figures configurations. Linear fittings could be performed for these curves, both with acceptable $R^2 = 0.96$. Although there are some differences between calculations and the linear fit, it is possible to establish that for $k > 5$ the multivacancy systems built on the basis of an armchair complementary figure could be more stable than the ones based on zigzag configurations.

A closer inspection suggests that the curves are not really linear, but adopt a distorted staircase form, since the energy differences $E(k) - E(k-1)$ are smaller for even k than for odd k – a similar effect

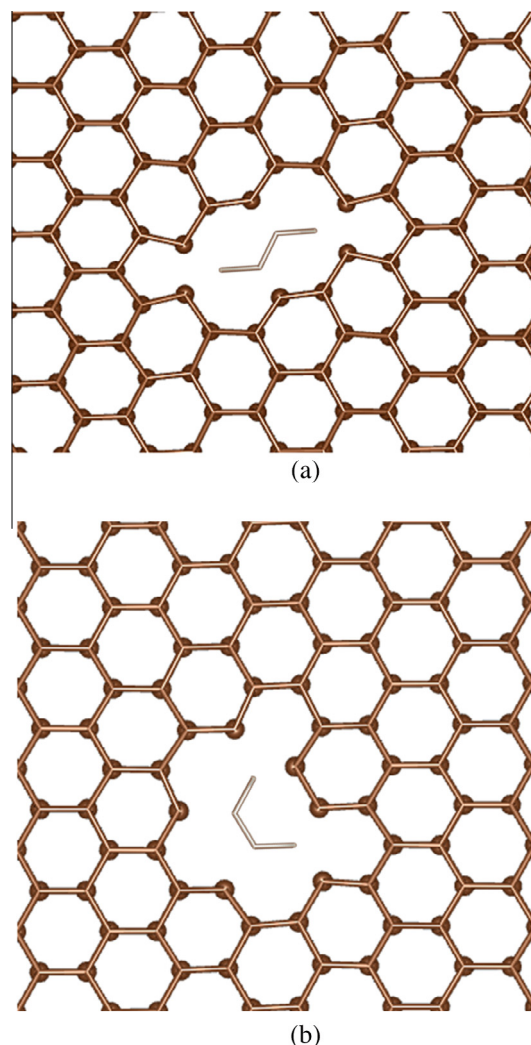


Fig. 2. Structure of $z4$ and $a4$ configurations, with their complementary figures.

Table 1

Energy per carbon atom for defected graphene structures, differences with a single carbon atom extraction and with the extraction of two carbon atoms, for zigzag and armchair complementary figures.

Vacancy system	$E(k)$ (eV)	$[E(k)-E(k-1)]/[E(k)-E(k-2)]$ (eV)	Vacancy system	$E(k)$ (eV)	$[E(k)-E(k-1)]/[E(k)-E(k-2)]$ (eV)
z3	8.194		a4	14.103	5.909
z4	10.793	2.599	a5	15.330	1.227
z5	16.154	5.361/7.960	a6	15.744	0.414/1.641
z6	17.800	1.646/7.007	a7	18.473	2.729/3.143
z7	21.878	4.078/5.573	a8	19.314	0.841/3.570
z8	22.727	0.849/4.927	a10	23.513	-/4.199

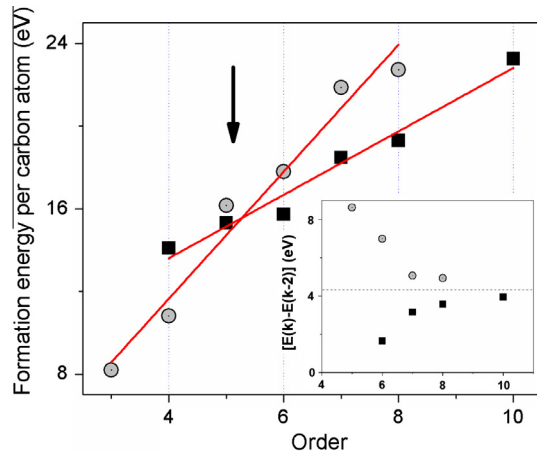


Fig. 3. Evolution of the formation energy per carbon atom with the order of the multivacancy (black square symbols, armchair complementary figure; hollow circle symbols, zigzag complementary figure). Inset: differences in formation energy per carbon atom, among alternate order vacancy structures. The dashed line is guide to the eye for the trend for higher order vacancies.

for the stability depending on the odd or even vacancy order was previously seen for carbon nanotubes defected systems [20]. The behavior of this distorted staircase effect led to the inset of Fig. 3 with very clear trends for $E(k)-E(k-2)$, for zigzag and armchair complementary figure configurations, that suggest a convergence at high order vacancies. This convergence confirms that the linearity in the curves in Fig. 3 was apparent and did not precisely describe the evolution of the formation energy with the order of the vacancy.

3.2. Magnetism and stability

Fig. 4 shows the energy cost to extract a carbon atom from the defected graphene system o51. In Fig. 4(a), four different places where the defect could be enlarged are shown – there is a different case, showed in Fig. 4(b), which will be discussed later. The difference in energy indicates that o64 is the most stable vacancy, with $\Delta E = 0.416$ eV, followed by o62, $\Delta E = 1.852$ eV, and that o63 and o61 are the less stable ones, with $\Delta E = 2.099$ and 2.648 eV, respectively. This can be explained through the effects caused by the steric hindrance between the two dangling bonds that oppose the vertices of the complementary figure, according to the rules previously established [48], and the local ferro-, ferri- or antiferromagnetic configurations. This effect can be seen in Fig. 4(a). The possible ferro-, ferri- or antiferromagnetic configurations are easier to be determined through the shorter path of the complementary figure than through the longer path of the defected graphene itself. This is a secondary benefit of the use of the complementary figure when studying multivacancy systems. Thus, the o63 system is created from the o51 one, by extracting a carbon atom from the

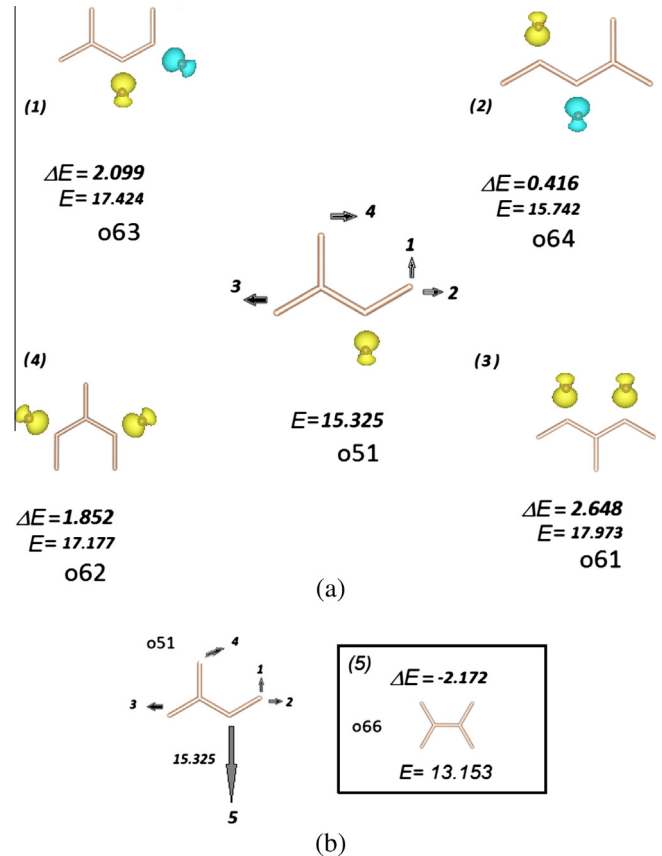


Fig. 4. Effect of the position where a vacancy is grown from 5- to 6-order one. (a) Large font values are $E(o6n)-E(o51)$ in eV and the small font values below are the $E(o6n)$ energies. The dangling bonds correspond to the vacancy opposed to the complementary figure – the one which is exhibited. The defected graphene is omitted for clarity. Spin density configurations are shown by different colors. (b) The o66 case is framed and the energy difference ($E_{o66}-E_{o51}$) is shown with an arrow. Energies in eV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

already defected graphene structure, with the occurrence of a second dangling bond, sterically perturbed by the original one, both in antiferromagnetic configuration. In comparison, the o61 system shows a less favoured ferromagnetic arrangement in a still sterically perturbed configuration. The o62 system shows no sterically perturbed dangling bonds configuration, but the ferromagnetic arrangement yields a non-favoured structure. The o64 structure is the more stable one in this figure, with no steric hindrance and antiferromagnetic arrangement.

Another example can be seen in Fig. 5, where the evolution of the vacancy – i.e. the complementary figure – from a4 to o65 through o52. While the a4 system has antiferromagnetic character, with steric hindrance, the o52 one is also sterically hindered but with ferrimagnetic arrangement for the three dangling bonds.

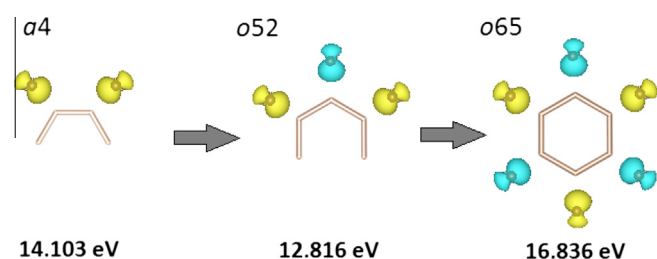


Fig. 5. Evolution of the vacancy from a4 to o65 through o52, formation energies are presented in eV.

According to the previous discussion, the a4 system should be more stable than the o52 one, which is not the case. The special feature for o52 and according to the rules already defined [42], the adjacent position of two pentagonal rings, which are located opposite to the terminal carbon atoms of the complementary figure, yields to a medium range low-stressed structure along the defected graphene system. This configuration, where the optimized structure is ruled by the competition among neighboring pentagonal rings, stabilizing the rest of the system seems to play a key role, more important than the other mentioned factors, i.e. the dangling bonds magnetic arrangement or their steric hindrance. When removing one more carbon atom and evolving to o65, an antiferromagnetic arrangement is formed but at the cost of the occurrence of three extra dangling bonds, and with no pentagonal rings to further stabilize the structure, yielding to a more unstable structure.

Fig. 6 presents the partial density of states for a5, z5, a6 and z6. In all the cases the densities of states look asymmetric as consequence of the spin polarization, where σ - and π -states contributions are very different. The σ -states present more localization due to presence of the multi atom vacancies, establishing a pseudo

gap higher than 0.8 eV. In the case of π -states their contribution is present in a wider energy range, in comparison with σ -states. This is a consequence of the better p_z hybridization between carbon atoms close to the edge of the multivacancy, which additionally exhibit an important contribution of states at the Fermi level. These results can be complemented by inspection of the corresponding spin-density maps, as presented in Fig. 7.

In Fig. 4(a), there is one case that was not discussed yet, which is the removal of the dangling bond in o51. This is shown in Fig. 4(b). The negative value of the subtraction $E(o66)-E(o51)$ deserves a special consideration.

When going from o51 to o66, there is no longer any dangling bond and instead, four pentagons are formed. This can be seen in Fig. 8(b). According to the rules previously defined [48], terminal carbon atoms at the complementary figure, imply the formation of pentagons in the defected graphene structure that remains after the removal. In the case of o66 there are no vertices exposed in the complementary figure, so no dangling bond should occur after the vacancy creation, according to the same rules.

We found this extra stabilization after the disappearance of dangling bonds and the reorganization of the remaining graphene structure with the occurrence of pentagons harmonically separated by hexagonal rings. The absence of exposed vertices and the proliferation of terminal carbon atoms in the complementary figure, is very characteristic of a dendritic-like figure.

3.3. Dendritic structures

In order to evaluate our hypothesis about the cause for the stability of the o66 configuration and the dendritic character that could act as a stabilizing factor for the formation of multivacancies, we tried to study other vacancies with dendritic-like complementary figures. The simplest dendritic-like complementary figure corresponds to the symmetric 4-order vacancy, shown in Fig. 8(a),

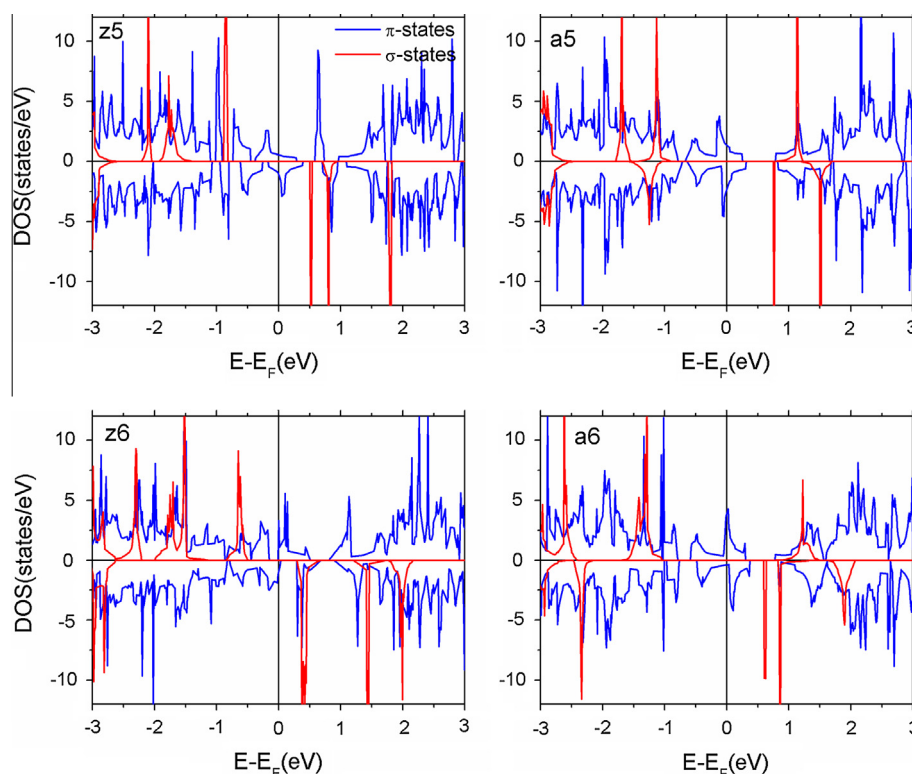


Fig. 6. Partial density of states for: z5, a5, z6 and a6; indicating σ and π contributions. Blue and red lines represents π - and σ -states respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

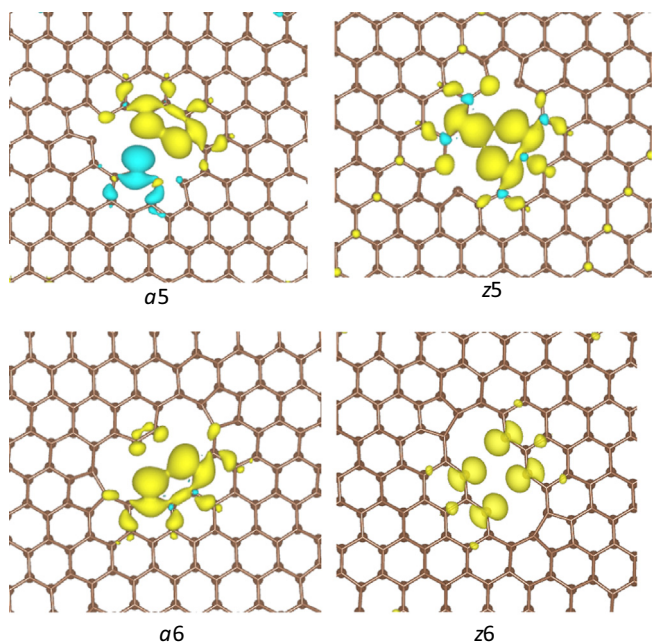


Fig. 7. Spin-density maps for a5, z5, a6 and z6, indicating majority and minority contribution in yellow and cyan respectively. All the graphs were obtained for an iso-density of $0.01 \text{ e}/\text{\AA}^3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

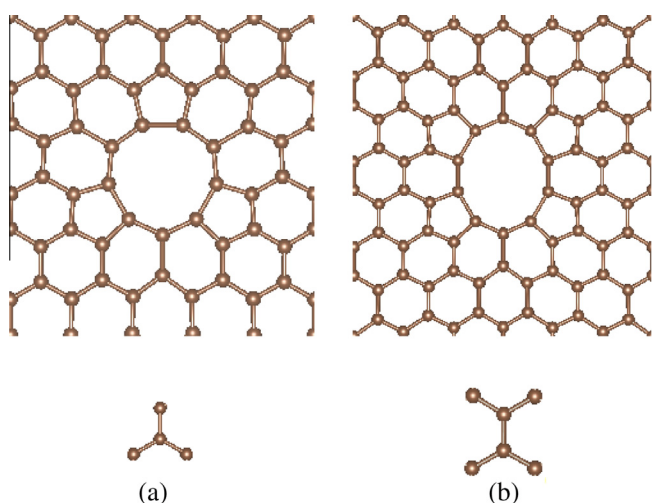


Fig. 8. (a) 4- And (b) 6-order vacancy systems (up) with complementary figures with dendritic shapes (down).

already studied from the magnetic point of view [48], that has an energy of 9.566 eV, lower than the other 4-order vacancy systems, the zigzag (10.793 eV) and armchair (14.103 eV) ones, what would suit with our hypothesis, as can be seen in Fig. 9.

After this, we tried to check the validity of the hypothesis of the dendritic-like complementary figure, as a general trend for stable multivacancy systems, and for this reason we studied multivacancies with dendritic-like complementary figures (i.e. with no exposed vertices, and many terminal carbon atoms), for 8-, 18-, and 30-order vacancies. These cases are shown in Figs. 10 and 11, respectively, with the complementary figure and the defected graphene structure after it has been removed, explicitly exhibited, and the multivacancy system after optimization.

The 8-order vacancy system is obtained when an 8 carbon atoms, aliphatic-like complementary figure is removed. Although this complementary figure is symmetric, as can be seen in

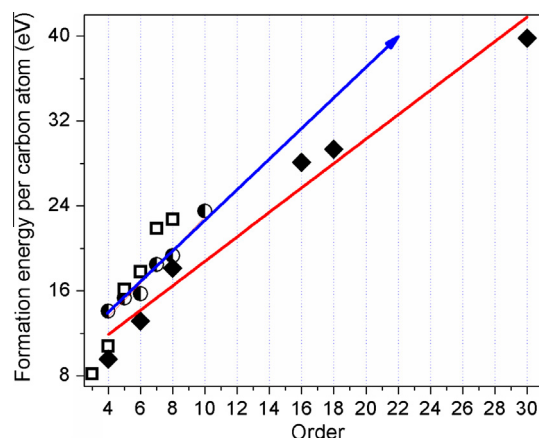


Fig. 9. Formation energy per carbon atom as a function of the order of the vacancy. Square and circle symbols correspond to zigzag and armchair complementary figures, previously discussed and diamonds symbols, to dendritic complementary figures. The thick arrow shows the trend of the armchair complementary figure, to make clear how the dendritic structures are more stable for increasing order. The solid line shows the linear fit for the dendritic structures ($R^2 = 0.96$).

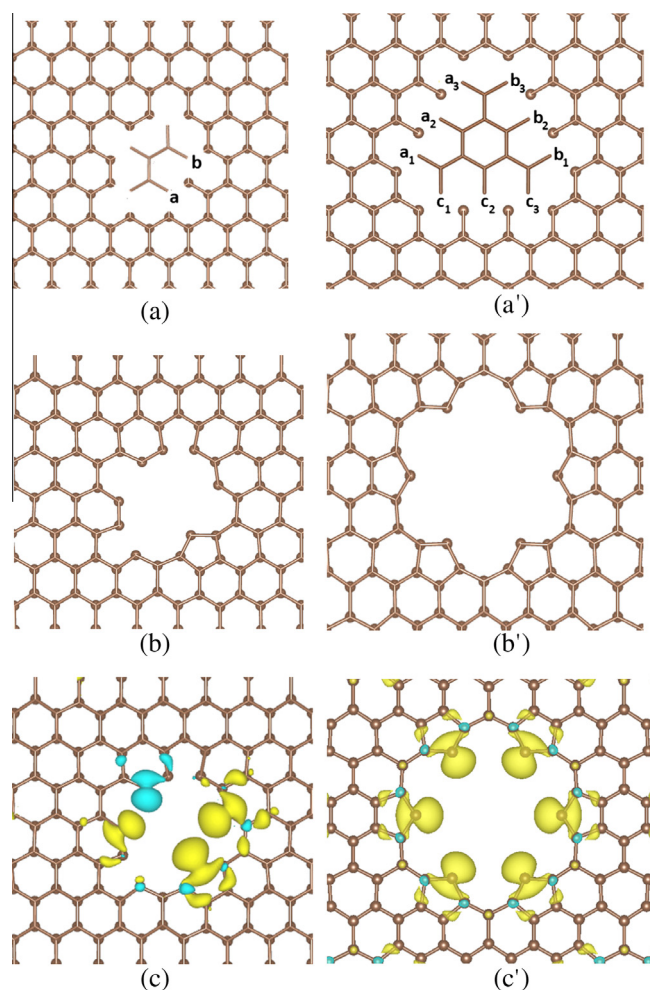


Fig. 10. (a) Complementary figure for 8-order vacancy, (b) vacancy after optimization and (c) differences between the spin-up and spin-down populations, (a') complementary figure for 18-order vacancy, (b') vacancy after optimization and (c') differences between the spin-up and spin-down populations.

Fig. 10(a), after optimization, the symmetry is broken. This effect is due to the close position of the terminal carbon atoms, labeled as *a* and *b*. This two terminal atoms removed, generate a competition

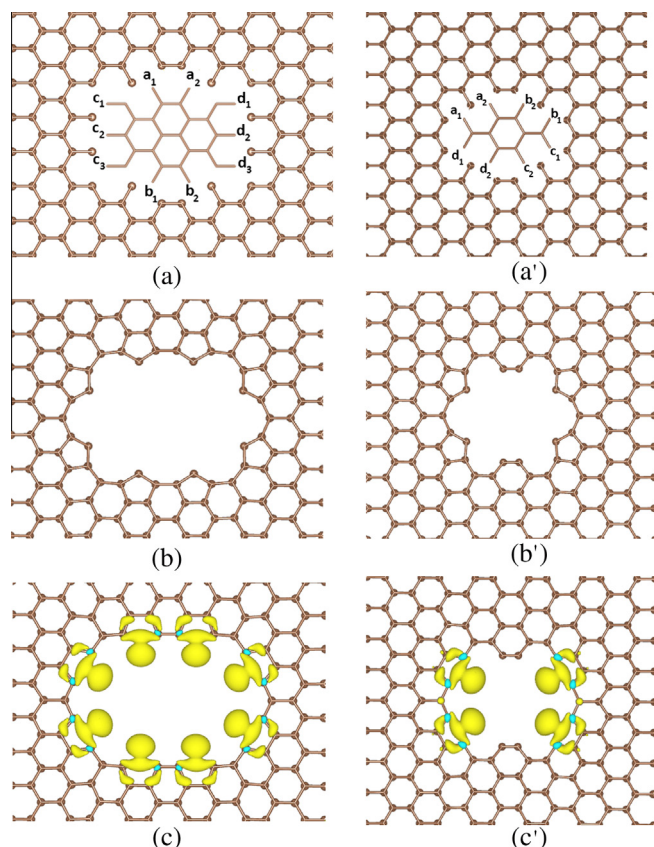


Fig. 11. (a) Complementary figure for 30-order vacancy, (b) vacancy after optimization, (c) differences between the spin-up and spin-down populations, (a') complementary figure for 16-order vacancy, (b') vacancy after optimization and (c') differences between the spin-up and spin-down populations.

for the pentagon occurrence, either where a or b was located, yielding to a clearly non-symmetric vacancy after the optimization of the structure. This kind of competition when a multivacancy system is formed is new to our knowledge and leads to unexpected results, that were not included in the rules previously postulated [48]. This 8-order vacancy shows a net magnetic moment, in spite of the absence of exposed vertices in the complementary figure, as can be seen in Table 2, where formation energies per carbon atom and magnetic moments for the systems here presented are exhibited. The non-symmetry of the vacancy allows the occurrence of a magnetic system where the spin-up and spin-down charge density in the hole is driven only by the alternation in consecutive atoms, as can be seen in Fig. 10(b). The difference between spin-up and spin-down population is shown in Fig. 10(c).

In order to achieve higher order vacancies that follow the dendritic character, complementary figures based in a phenyl-like structure, were designed. In the case of the 18-order vacancy, the complementary figure has D_{3h} symmetry, and the competition of terminal carbon atoms is present too. As can be seen in Fig. 10(a'), the x_2 terminal atoms are in clear competition against x_1 and x_3 , for pentagon formations when optimization is processed ($x = a, b$ and c). The result after the optimization can be seen in Fig. 10(b'), and even though in the complementary figure there is no exposed vertex – i.e. the idea of a dendritic structure, the final

carbon defected graphene system still shows a net magnetic moment as can be seen in Table 2. The occurrence of dangling bonds on the exposed vertices of the pentagonal rings formed after the optimization through a novel pentagonal configuration, resembling the pyrrole rings configuration in porphyrins, not previously seen in simpler, non-dendritic complementary figure based multivacancy systems (see Fig. 10(c')).

In this case, the phenyl-like core relieves the stress that the removal of the complementary figure causes, yielding a vacancy system that holds the symmetry of this figure. The ferromagnetic structure that arises due to the spin polarization of the charge density is driven by the alternation in the hole of the system as well as the preserved symmetry of the system, due to the already mentioned low stress.

In an effort to study higher order vacancy systems, we designed a 30-order one, which is shown in Fig. 11(a). As can be seen, the complementary figure is based on a pyrenyl-like core, with aliphatic terminal segments to yield the dendritic character. This complementary figure correspond to the D_{2h} symmetry, which is centrosymmetric if constrained to the plane, introducing an axial anisotropy. In this case, the x_1 and x_2 terminal carbons of the complementary figure, are in competition for the formation of pentagonal rings, due to their close vicinity ($x = a, b$). In the orthogonal direction, the central y_2 terminal carbon atoms are in competition with the y_1 and y_3 atoms ($y = c, d$). The pyrenyl-like core of the complementary figure relieves the stress in the vacancy optimization, and the final multivacancy system keeps the symmetry of the complementary figure (Fig. 11(b)). The magnetic moment for this system is $4.89 \mu_B$, corresponding to a spin-up density based on the dangling bonds at each loose vertex of the pyrrole-like pentagonal rings. If this magnetic arrangement was only driven by the alternation of spin character in successive carbon atoms, the final structure should exhibit no net magnetic moment, and four dangling bonds with spin-up arrangements at the left of Fig. 11(c) would oppose the other four dangling bonds with spin-down configuration at the right. This possibility is ruled out by symmetry considerations, since the vacancy has the same symmetry as the complementary figure due to the eccentricity of the hole formed by the strong influence of the pyrenyl-like core. The centrosymmetric point group that result from removing such complementary figure leads to the need of a full spin-up configuration to keep the invariance of the magnetic moment through the symmetry operations that originates that group [56,57]. The anisotropy in orthogonal directions of this example, offers new insights of the magnetic behavior of the multivacancy systems. Additionally, the symmetry of the complementary figure rules on the magnetic arrangements in the dangling bonds system against the alternation of spin in successive carbon atoms, when a minimal eccentricity of the remaining hole is achieved – i.e. there is a stress relief caused by the aromatic core in the dendritic-like complementary figure.

In order to check this new concept, we designed a 16-order vacancy system, as shown in Fig. 11(a'). The complementary figure shows a D_{2h} symmetry, with axial anisotropy, as in the already discussed 30-order vacancy system. For this reason, this example could be a good test to the key role of symmetry when orthogonal anisotropy is present in the complementary figure. In this case the competition for pentagonal ring formation is among x_1 and x_2 positions of the terminal carbon atoms of the complementary figure ($x = a, b, c, d$).

Table 2
Formation energy per carbon atom and magnetic moment for defected graphene structures.

Vacancy system	z3	o66	o8	o16	o18	o30
$E(k)$ (eV)	8.194	13.153	18.138	28.101	29.341	39.802
Magnetic moment (μ_B)	1.04 [48]	0	1.16	2.34	6.21	4.89

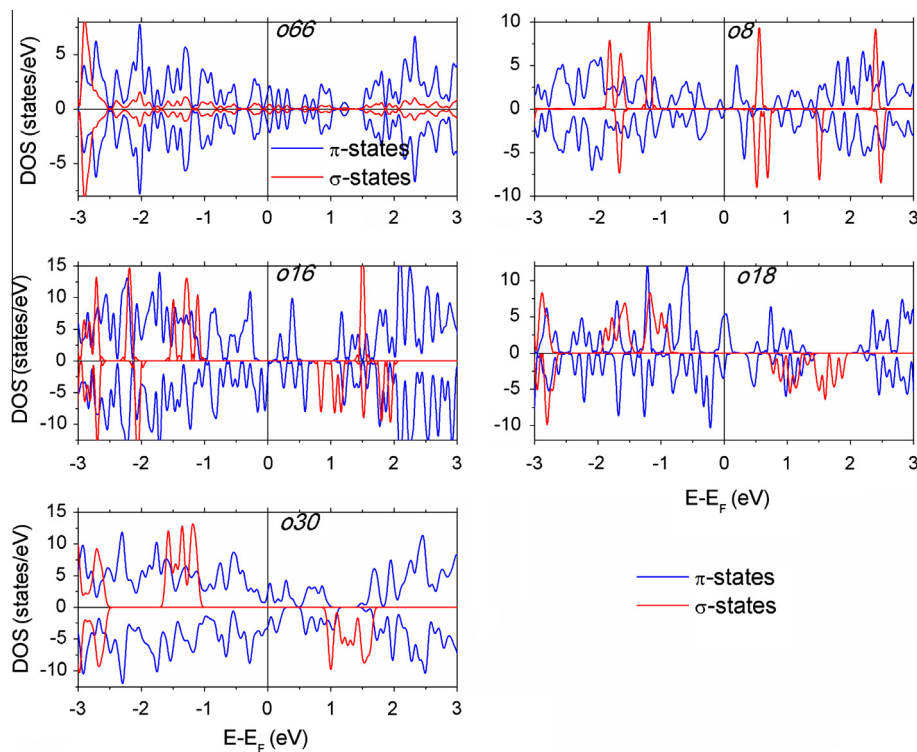


Fig. 12. Partial density of states for: o66, o8, o16, o18, o30; indicating σ and π contributions. Blue and red lines represents π - and σ -states respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The phenyl-like core, as in other cases, is providing relief against the stress of the atoms removal on the vacancy formation. As a consequence, the final optimized defected carbon graphene keeps the D_{2h} symmetry, which is centrosymmetric (see Fig. 11(b')). There is a net magnetic moment after the optimization, as can be seen in Table 2, which is not expected in terms of the alternation of the spin character in adjacent carbon atoms in the hole. If the magnetic arrangement was driven by this effect, two subsets of opposite spins would occur and the calculated magnetic moment clearly imply that it is not the case. As in the 30-order vacancy case, the symmetry of the defected graphene, with a center of inversion that drives the invariance of the magnetic moments on each dangling bond to present only spin-up character, yields to a ferromagnetic local arrangement at the edge of the vacancy (see Fig. 11(c')).

Fig. 12 presents the partial density of states for the o66, o8, o16, o18 and o30 cases. As expected and already mentioned, the only case where there is no spin polarization corresponds to o66, where the density of states looks symmetric along the energy axis, with σ - and π -states contributions at the Fermi level. In the case of o8, o16, o18 and o30, the densities of states look asymmetric as consequence of the spin polarization, where σ - and π -states contributions are very different. In one hand, σ -states present more localization due to presence of atom vacancies, establishing a pseudo gap of about 1.8 eV. On the other hand, the π -states contribute in a wider energy range in comparison with σ -states, this is a consequence of the better p_z hybridization between carbon atoms close to the edge of the multivacancy; which additionally present an important contribution of states at the Fermi level.

4. Conclusions

Zigzag complementary figures, yield to extended vacancies, unstable for $k > 5$. Our results suggest that armchair complementary figures could be more stable than zigzag ones, except for $k = 4$.

The stability of multivacancies could be explained through the relative positions of the pentagonal rings formed in the resulting defected graphene structure, as the more relevant factor. In fact the presence of two adjacent pentagons is suggested to yield an extra stabilization.

Other secondary factors that affect the stability of a graphene multivacancy system are the dangling bonds magnetic arrangements and their steric hindrance.

For complex multivacancy systems, the optimization led to flower-like defected graphene structures, very stable and with fullerene-like resemblance in the structural role that pentagonal rings and their conjugation with hexagonal ones exhibit.

The dendritic-like complementary figures yield to the most stable multivacancy systems configurations studied so far. This would be in agreement with recent results [37] that show that the dendritic growth of vacancies in graphene by etching, in the macroscale, that could be driven by this preferred route from the nanoscale. The aliphatic dendritic complementary figures could lead to distortions that could decrease the symmetry of the optimized final vacancy structure. The removal of a dendritic complementary figure based on a phenyl- or pyrenyl-like core, suggested to contribute with a eccentricity of the vacancy that could relieve the stress of the defected structure. The consequence of such complementary figure is the preservation of the symmetry of this figure after the optimization process. We found that it plays a key role in the arrangement of the spins located at the dangling bonds at the vacancy. We designed two orthogonal anisotropic cases to check the importance of this factor on the final magnetic moment of the systems.

Due to the stress that the competition for the formation of pentagonal rings in adjacent positions, multivacancy systems constructed from the removal of dendritic-like complementary figures, are the exception to the rules previously suggested [48].

The complementary figure has proved again to be useful for the characterization of multivacancy systems and to help to predict

their properties, now with the perspective of more complex cases than previously studied.

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