Interaction of iron clusters \((\text{Fe}_n; n \leq 6)\) with a divacancy in graphene

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Abstract

In this work, we have studied the chemical and magnetic interactions of Fe$_n$; $n \leq 6$ clusters with a divacancy site in a graphene sheet by ab-initio density functional calculations. Our results show significant chemical interactions between the cluster and graphene. As a result, a complex distribution of magnetic moments appear on the distorted Fe clusters in presence of graphene and results in a lower average magnetic moments compared to the free clusters. The presence of cluster also prevents the formation of 5-8-5 ringed structure known to exhibit in a graphene sheet having a divacancy defect. The clusters induce electronic states primarily of $d$-character near the Fermi level.

1 Introduction

Graphene has been a subject of immense investigation since its discovery in 2004 as it has a great potential for future electronics. It is a one-atom-thick planar sheet of sp$^2$-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes, fullerenes as well as recently synthesized graphane. Measurements have shown that graphene has a breaking strength 200 times greater than steel, making it the strongest material ever tested.

Despite its strength, graphene is prone to the impurities and defects as any other material. The nature and types of defects in graphene have been discussed by Castro Neto et al in their extensive review. Among a number of defects and disorders seen in graphene, ripples or topological defects are intrinsic while cracks, vacancies, charged impurities, atomic adsorption etc. are extrinsic. In particular graphene is prone to the formation of vacancy defects. Divacancy defects are quite probable to form as strong reactive centers. It is shown theoretically how different defect structures can be engineered in graphene. It is known that such defects can affect the electronic structure and hence transport properties of graphene.

One of the important points in graphene research is to explore the possibility of having spin-dependent transport in graphene. As the mobility of graphene is extraordinarily high, electronic
transport with selective spin is an interesting topic of study. The relevant question is how to make graphene magnetic. One idea is to deposit magnetic adatoms on graphene and study the range of spin polarization in the host lattice arising from the exchange coupling between the adatoms. One can make use of the defects for trapping the adatoms. It is known that the chemisorption energies at vacancy sites are very high. So it is possible to trap the magnetic adatoms or clusters at various defect sites and hope to have an effective spin polarization. In an interesting theoretical work based on density functional theory (DFT) the magnetism of different transition metal adatoms on single and divacancy centers has been studied. In a work based on DFT, Wang et al have studied the interaction between a single adatom and graphene containing a Stone-Wales defect. They have observed a reduction in local magnetic moment on iron atom and a substantial modulation of electronic states near the Fermi level. Instead of a single adatom, a flux of adatoms may generate various sizes of magnetic nanoclusters trapped in defect sites. As already noted, the divacancies are quite frequently form on a graphene sheet and hence we investigate the interaction of small clusters of Fe with a divacancy. Thus, a comparison of geometric and magnetic structure between adsorbed and free Fe clusters will be made.

2 Computational details

All the calculations have been performed on a monolayer graphene with a divacancy using plane-wave based density functional code VASP. The generalized gradient approximation as given by Perdew, Burke and Ernzerhof has been used for the exchange-correlation potential. The energy and the Hellman-Feynman force thresholds are kept at $10^{-5}$ eV and $10^{-3}$ eV/Å respectively. For geometry optimization, a $4 \times 4 \times 1$ Monkhorst-Pack $k$-grid is used. Total energies and electronic structures are calculated with the optimized structures on $11 \times 11 \times 1$ Monkhorst-Pack $k$-grid.

The supercell is generated by repeating the primitive cell by six times in $a$ and $b$ direction of the cell and then removing two carbon atoms in the vicinity to create the divacancy. Such large cell, containing 70 atoms is required to avoid the interaction between the clusters. Further interactions
in vertical direction is avoided by taking a vacuum of more than 15 Å.

To determine the ground state geometries, several initial structures of iron clusters are placed on divacancy and are fully optimized. We wish to point out that a special care has to be taken to achieve the correct magnetic moment by starting the optimization procedure with several possible guesses of magnetic states.

## 3 Results and discussion

### 3.1 Geometries

We begin our discussion by presenting the ground state geometries of the systems studied. Our aim is to find out the possible evolution of the geometries of clusters on the divacancy. [figure][1][1] depicts all the geometries of clusters on a divacancy, starting from Fe\(_1\) to Fe\(_6\). Also shown in the insets are the geometries of free clusters.

As reported earlier\(^{16}\), the single iron atom diffuses almost to the interior of the vacancy as seen in [figure][1][1](a). The four Fe-C bonds are identical with the bond lengths of 1.97 Å. It is interesting to note that not only for a single atom but in general, the underlying vacancy does not undergo any significant structural rearrangement. This is in contrast with the vacancy in absence of iron atoms where the carbon atoms are known to move close to each other to form in-plane \(\sigma\) bonds, resulting in a 5-8-5 ringed structure\(^{7}\). This indicates that even a single iron atom can be used to maintain the structure of underlying lattice despite the presence of the vacancy.

As the size of the cluster increases some trend is discernible. In all the cases we note that one of the carbon atom is at the center of the vacancy. In other words the structures evolve as a gradual addition of atoms on the geometry of single iron system.

Iron dimer has also been studied earlier\(^{16}\) and our results are in agreement with theirs. As seen from [figure][1][1](b), the geometry is obtained by adding an atom to the optimized geometry of Fe\(_1\). The dimer bond length is 2.20 Å which is about 10% enhanced over the bond length found in a free cluster (2.02 Å). We recall that a single iron atom is just out of plane, but forming four bonds
Figure 1: Ground state geometries of Feₙ (n ≤ 6) clusters on the graphene sheet with a divacancy. Insets show the geometries of corresponding clusters in free space.
with nearest neighbour carbon atoms, thus maintaining the 5-8-5 ring structure. Thus after one atom is accommodated in this lattice, there is no more scope for any additional Fe atoms. Hence the single atom remains with lattice plane and the additional Fe atoms are out of the plane with the first atom as an apex.

It is worth mentioning that this system has a few isomers. The closest one is the geometry where the dimer resides parallel to the plane of the graphene and none of the iron atoms goes inside the vacancy. The energy difference between this structure and ground state is $\sim 0.3$ eV. This isomer is important because all the larger clusters ($n > 2$) have at least one isomer with the basic unit as a dimer parallel to the graphene plane. The second isomer is obtained by changing the orientation of the dimer with respect to the graphene plane. In this case the energy difference is about 0.4 eV.

It is interesting to point out that, in the ground state, one of the atoms is outside the vacancy which is in contrast with a nitrogen dimer placed on a divacancy center. In that case both the nitrogen atoms of the dimer become a part of the graphene lattice by occupying the vacant places of carbon atoms thereby completely healing the topological disorder.

Clusters evolve systematically as we go on adding an atom on Fe dimer. Fe$_3$ forms a triangle which is tilted with respect to vertical axis and none of the sides are identical to each other. The bond lengths are 2.22 Å, 2.11 Å and 3.05 Å. The tilt occurs due to the optimization of the interactions with underlying carbon atoms. Also, as the nearest carbon neighbours are not same the sides of the triangle are not identical.

When we add the fourth iron atom to the system, the triangle aligns vertically and the fourth adatom positions from a side to form a distorted prism. Clearly the distortion is brought about by the carbon lattice. As can be inferred from the figure, the addition of the fifth atom is rather straightforward change from prism to pyramidal structure with the added atom going on top. The sixth atom distorts this pyramid and forms a complex structure as shown in [figure][1][1]. Although distorted, the four-atom structure can still be seen near the graphene plane. As we shall see later, the prism formed by four atoms is a very stable system and we believe that in more complex
clusters with large $n$ this prism may serve as the building block.

Clearly the geometries of iron clusters on graphene are remarkably different than those studied in free space.\textsuperscript{17} As said earlier the dimer bond length is slightly reduced in presence of divacant graphene. The trimer in the free space is reported to be isosceles triangle\textsuperscript{17,18} while the trimer on vacancy is a distorted isosceles triangle with the bond lengths differing substantially from that in free space. Fe\textsubscript{4} also forms a prism in free space with the bond lengths ranging from 2.22-2.41 Å. However in our case the bond length varies substantially from 1.6 Å to 2.6 Å. The change in the trigonal bipyramid of isolated Fe\textsubscript{5} is seen in the vertical four-atom plane where the bond lengths are increased with respect to those in free space. Fe\textsubscript{6} undergoes a substantial change from octahedron to a more complex structure seen in \textsuperscript{[figure][1][1][f]}.

### 3.2 Energetics and Magnetic structure

Iron in a body centered cubic structure is known to be ferromagnetic in its bulk phase as well as in a cluster form. It is thus interesting to see the nature of magnetism in the studied systems. It is also helpful to discuss the energetics with the same.

![Figure 2: Binding energies and total magnetic moments as a function of cluster size (Fe\textsubscript{n}).](image)

Before we proceed we define the binding energy $\Delta E$ of the iron cluster in presence of the
divacancy as:

\[ \Delta E = (E_{GD} + E_{Fe}) - E_{GD+Fe} \]  

(1)

where \( E_{GD+Fe} \) is the total energy of the system (i.e. the cluster on graphene with a divacancy), \( E_{GD} \) is the total energy of the graphene with a divacancy and \( E_{Fe} \) is that of an isolated iron cluster. Higher binding energy indicates a more stable system.

shows the binding energies and total magnetic moments for all the systems. Two observations can be made immediately. Firstly, the binding energy slowly increases from one to four atoms-cluster and then slowly decreases. Secondly, the plot of total magnetic moment steadily increases except for the five-atom cluster. Thus from the observation of binding energies, it is not surprising that we see a four-atom prism staying almost intact in larger clusters. It also indicates that the \( Fe_4 \) is the most stable structure on the divacancy center in graphene, however there is no indication of \( Fe_4 \) being the most stable in the free space.

As seen from shows all the systems studied are effectively magnetic in nature. Our analysis of local magnetic moment has revealed that in all the cases none of the carbon atoms has any significant local moment. Almost all the contribution towards total magnetic moment is from iron atoms. Unlike the isolated clusters it is inappropriate to calculate the magnetic moment per atom as the atoms in the cluster may not have strictly iron neighbours.

\[ \text{Figure 3: Local magnetic moment on individual iron atoms for six clusters.} \]

From it is clear that, up to the \( Fe_4 \) cluster, as the number of atoms increases,
the magnetic moment also increases as the atoms are ferromagnetically coupled to each other. However as the cluster size increases, the hybridization of Fe $d$ orbitals inside the clusters results in the lowering of total magnetic moment. To ascertain that we also plot the local magnetic moments on individual atoms. [3] shows the magnetic moments on individual atoms for all the clusters. It can be deduced from the figure that as the cluster increases in size the variation of the local moments becomes non-monotonous [2]. Except Fe$_5$, all the other clusters studied show aligned local moments on Fe atoms though they vary in size. In Fe$_5$ cluster, one of the iron atoms has the moment flipped with respect to the other atoms. So, the average moment on iron in this cluster is smaller than the others.

Naturally in the presence of iron clusters the density of states (DOS) of the graphene lattice undergoes a substantial change. Particularly interesting is the fact that the contributions from the iron atoms occur directly at the Fermi level. (a) shows the total DOS in the presence of a single iron atom while (b) shows the local DOS (LDOS) on an iron atom. LDOS is resolved into its angular components. It should be mentioned that the single atom case is the simplest of all the cases studied however the features seen here are similar for all the clusters. So, we present only the DOSs for a single iron atom.

![Figure 4](a): Total DOS and (b) the local DOS of an iron atom on the divacancy. Only the $d$-components of LDOS are shown. The upper and lower parts of the graph depict the spin-up and spin-down components respectively. Iron clearly induces electronic states on the Fermi level which is marked by a vertical line.
Our angular momentum based analysis of LDOS on iron atom ([figure][4][4] (b)) shows that the contribution from the components except \( d \) is negligible. Also, the characteristics of the electronic structure are very different from that of pure graphene. The presence of midgap states of \( p \) orbital character in presence of a divacancy was discussed before.\(^{7,8}\) Here, these states are mainly of \( d \) character. So, the characteristics of transport properties are expected to be different. As seen from the figure that the contribution from the \( d \) orbital is concentrated in the energy interval of about 6 eV downwards from the Fermi energy. More interestingly, the contribution from spin-up and spin-down channels of iron atom is substantially different. The contribution near the Fermi level arising from the orbital with \( d_{z^2-r^2} \) character increases, maintaining the difference in the spin channels as the cluster size increases. Such features are of particular interest in spintronics applications where the spin-dependent transport properties are discussed heavily.

![Figure 5](image)

**Figure 5:** Charge density isosurface of a state near the Fermi level. The system consists of a single iron atom on which a \( d \)-like state is clearly seen and \( p \)-states on nearby carbon atoms are heavily distorted. Isosurface is shown at one tenth of its maximum value.

Thus it is clear that iron atoms induce a substantial number of states on the Fermi level and it is seen that those are mainly \( d \)-like. This becomes further evident from ([figure][5][5]) which shows the charge density isosurface for a state close to Fermi energy for a single iron atom. This feature is general and is present in all the clusters. The state represents a complex of \( d \) states on central iron atom and heavily distorted \( p \) orbitals on neighbouring carbon atoms. Interestingly it is only the nearest carbon atoms those contribute towards the charge density. It is the interaction between
the four carbon atoms with the iron cluster which is responsible for the strong binding.

4 Conclusions

We have systematically investigated the geometries and electronic structures of Fe$_n$ ($n \leq 6$) clusters on a graphene sheet with a divacancy using DFT. When a divacancy is created in graphene, the underlying structure undergoes structural rearrangements to form a 5-8-5 ringed structure. The presence of an iron cluster, however prevents the formation of 5-8-5 ring and maintains the pristine hexagonal structure. The geometries of iron clusters also undergo significant changes due to the interaction between their $d$ orbitals with $p$ orbitals of the neighbouring carbon atoms. Individual atom in the iron cluster possesses different magnetic moment and in general the atom closest to carbon matrix has the lowest magnetic moment. However as the cluster size increases, more complex patterns of magnetic moments emerge. The iron clusters in free space has an average moment $\sim 3 \mu_B$, however in presence of divacant graphene the average moment is reduced to $\sim 2.5 \mu_B$. The iron cluster also has an important contribution in DOS, as most of the $d$ states of iron contribute within $\pm 3$ eV around the Fermi level. Our spin polarized calculations also reveal that the contribution of up and down channels are not identical making the system a candidate for spintronics materials.

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