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Enhancement of spin polarization induced by Coulomb on-site repulsion between localized p_z electrons in graphene embedded with line defects

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It is well known that the effect of Coulomb on-site repulsion can significantly alter the physical properties of the systems that contain localized *d* and/or *f* electrons. However, little attention has been paid to the Coulomb on-site repulsion between localized *p* electrons. In this study, we demonstrated that Coulomb on-site repulsion between localized p_z electrons also plays an important role in graphene embedded with line defects. It is shown that the magnetism of the system largely depends on the choice of the effective Coulomb on-site parameter U_{eff}. The U_{eff} at the edges of the defect enhances the exchange splitting, which increases the magnetic moment and stabilizes a ferromagnetic state of the system. In contrast, the U_{eff} at the center of the defect weakens the spin polarization of the system. The behavior of the magnetism is explained with the Stoner criterion and the charge accumulation at the edges of the defect. Based on the linear response approach, we estimate reasonable values of U_{eff} to be 2.55 eV (2.3 eV) at the center (edges) of the defects. More importantly, using a DFT+*U*+*J* method, we find that exchange interactions between localized *p* electrons also play an important role in the spin polarization of the system. These results imply that Coulomb on-site repulsion is necessary to describe the strong interaction between localized p_z electrons of carbon related materials.

Introduction

Due to the strong correlation effect, Coulomb on-site repulsion has been extensively studied in systems that contain *d* and/or *f* electrons. It was first introduced to deal with strongly correlated systems[1-5] through integrating the Coulomb correlation term of the Hubbard model into the Kohn-Sham equation: this is the so called DFT+*U* method, in which conventional DFT is used to describe the delocalized electrons of the system, while a Coulomb on-site repulsion term *U* is added for the localized electrons. The DFT+*U* method was developed to provide a broader and more accurate description of the properties of materials in their ground state. The DFT+*U* method was first used to obtain a more accurate band gap of NiO,[6,7] and then was introduced to calculate the ground-state electronic structure of materials containing transition and actinides elements.[8-11]

However, little attention has been paid to the behavior of localized *p* electrons. In fact, for strongly localized *p* electrons, the Coulomb on-site repulsion should also need to be considered. It was found that the charge transfer between carbon atoms and on-top metal atoms is strongly affected by the parameter *U*, and the magnetic moment induced by chemisorption on graphene also depends on the choice of *U*.[12] The DFT+*U* method was also used to investigate magnetic moment formation in fullerene C_{20}.[13] In our previous work,[14] for graphene with hydrogen adsorption, the stability of the ferromagnetic state was found to be very sensitive to the parameter *U* used. Actually, the occupied states can be considerably influenced by Coulomb on-site interaction if the localized *p* electrons strongly contribute to the density of states (DOS) near the Fermi level.

Recently, Lahiri and coworkers[15] have successfully obtained an extended defect that was embedded in otherwise perfect graphene. They found that it is a conductor, because the extended defect provides some localized DOS across the Fermi energy. Many related first-principles calculations[16-21] have focused on the electronic and magnetic character of line defects. However, all of these calculations were performed without considering the Coulomb on-site repulsion.

Since the localized DOS crosses the Fermi energy, the considerable Coulomb on-site repulsion between localized p_z electrons may change the occupied states near the Fermi level and furthermore have an effect on the spin polarization of the system. In this paper, we investigate the effect of Coulomb on-site interactions on the behavior of localized *p* electrons in graphene related materials, e. g., graphene embedded with extended line defects (ELD). We show that there are two kinds of localized *p* electrons in this system: localized π electrons at

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the center of ELDs and localized p_z electrons at the edges of ELDs.

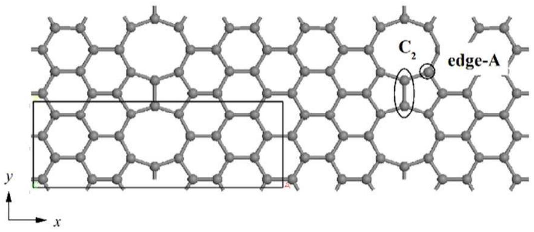

Fig. 1 The geometric structure of graphene with embedded line defect. The central sites of the line defect are denoted C$_2$, and the edge sites of the line defect are denoted “edge-A” sites. The unit cell is shown with straight solid lines.

Actually, the strong electron correlations are dependent on two factors: large localization of electronic densities and small overlap of atomic orbitals belonging to different atoms. In the system we studied here, the electronic density is strongly localized at ELD, and the overlap of atomic orbitals between edge of ELD and its neighbor sites is very small. Therefore, relatively strong electron correlations exist at the ELD. What’s more, we carried out first principles calculations for the Coulomb on-site repulsion at ELD, which shows larger Coulomb on-site repulsion than that at other carbon sites. Due to the large localized density of states at ELD and the small overlap between the localized orbitals of ELD with that of ZGR, on-site electron-electron repulsions at ELDs are much larger than the energies associated with the overlap of atomic orbitals belonging to different atoms, indicating that strong electron correlations may exist there. By studying the behavior of the Coulomb on-site repulsion between localized pelectrons, we provide hereby a deeper understanding of spin polarization in graphene related materials.

Computational details and geometric structure

The first-principles calculations in this paper have been performed using the generalized gradient approximation (GGA) exchange-correlation functionals of PBE type[22] as implemented in the SIESTA and SIESTA-LDAU packages.[23-25] The conventional density functional theory (DFT) calculations were carried out with the SIESTA package, while SIESTA-LDAU was used to include Coulomb on-site interaction. The Troullier-Martins parameterized norm-conserving pseudopotentials[26] and the double zeta polarized basis set numeric atomic orbitals (DZP) were employed in the calculations. An equivalent plane wave cutoff of 250 Ry was adopted. The Brillouin zone was sampled with $10 \times 10 \times 1$ and $30 \times 30 \times 1$ Monkhorst-Pork meshes for structural optimizations and electronic property calculations, respectively. The optimized structure was obtained until the force on each atom is less than 0.005eV/Å. Spin restricted and spin unrestricted calculations were performed to describe the magnetic and non-magnetic states, respectively. The charge transfer of the system is estimated using the Mulliken type overlap population.In the DFT+*U* calculations, two parameters, *U* and *J*, should be determined, where *U* is the Coulomb on-site interaction and *J* is the exchange integral. In this paper, following the previous studies focusing on *d* and even *f* electrons, an effective Coulomb repulsion U_{eff} = *U*-*J* was introduced between localized p_z electrons in graphene related systems. In order to study the influence of U_{eff} on this system, we performed a series of calculations with U_{eff} ranging from 2.1 to 4.5eV. Further, first principles calculations have been performed to determine reasonable values of U_{eff} with the linear response approach,[27] as implemented in the Quantum ESPRESSO package.[28] Further, we also investigated the exchange interactions between localized *p* electrons at a C$_2$ site and an edge-A site using a DFT+*U*+*J* method,[29] where *U* is the Coulomb on-site repulsion as discussed above and *J* is the exchange parameter between nearest carbon sites. Normally, the exchange parameter *J* is considerably smaller than the Coulomb on-site repulsion *U*. To study the effect of *J* on the magnetism of the system, by fixing the Coulomb on-site repulsion *U* to be 3.4 eV (at C$_2$ site) and 3.0 eV (at edge-A site), we applied a series of values of *J* ranging from 0 to 0.9 eV to the localized *p* electrons at C$_2$ and edge-A site, respectively.

Results and discussion

As shown in Fig. 1, the system was obtained by periodically connecting zigzag graphene ribbons (ZGR) by carbon dimers (C$_2$). Theoretical and experimental studies[19,21,30] have shown that a localized density of states appears at the C$_2$ sites as well

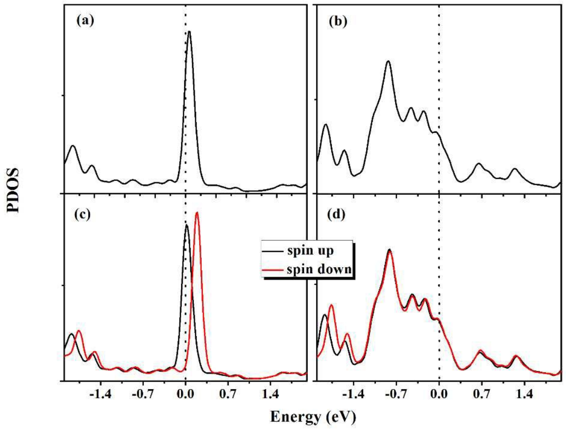

Fig. 2 Left panel: projected density of states (PDOS) of localized p_z electrons at edge-A sites with spin-restricted (a) and with spin-unrestricted (c) calculations; right panel: the PDOS of localized π electrons at C$_2$ sites with spin-restricted (b) and spin-unrestricted (d) calculations. In (c) and (d) the spin up and spin down densities of states are denoted with red and black solid lines, respectively. The Fermi energy is set to zero.

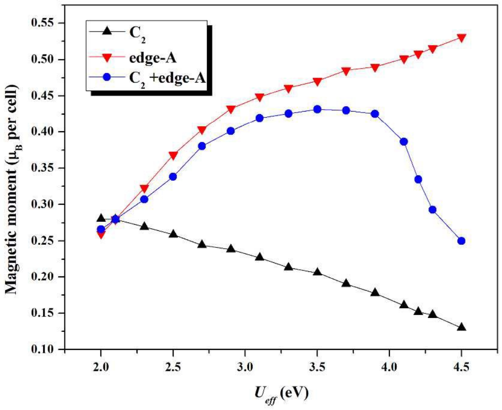

Fig. 3 The total magnetic moment of the system as a function of U_{eff} at C_2 sites alone, at edge-A sites alone, and at both C_2 and edge-A sites, respectively.

as the edges of ZGR (denoted as “C_2” and “edge-A” in Fig. 1, respectively). Both delocalized π electrons in ZGR and localized π electrons (p_z electrons) at C_2 sites (at edge-A sites) exist in this system. Due to the self-interaction error for electrons[31-33], conventional DFT may not appropriately predict the electronic characteristics of this system.

To study the localization of the system, we calculated projected density of states (PDOS) of C_2 and edge-A carbon atoms. Based on normal DFT calculations, a high density of states is localized at both C_2 and edge-A sites, as shown in Fig. 2. To verify the contribution of the localized density of states in the system, we also calculated the PDOS of carbons at the ZGR and found little contribution from the ZGR to the localized DOS near the Fermi energy (as shown in the Supplemental Material). By allowing the system to be spin polarized, a ferromagnetic state is found. Without consideration of Coulomb on-site repulsion, we estimated the magnetism of the system with spin un-restricted calculations.The magnetic moment of the system is found to be 0.19 μ_B per cell. The localized states are fully occupied for carbon at C_2 sites but partially occupied for carbon at edge-A sites. The spin polarization is mainly contributed by the localized p_z electrons at edge-A sites. This is reasonable, because the localized π electrons at C_2 sites are fully paired, and this magnetic moment can be attributed mainly to the splitting of the localized spin density of states at edge-A. Due to the rigidity of π conjugation[34] at C_2 and in ZGR, the p_z electrons at edge-A cannot pair with neighboring π electrons. As seen in Fig. 2, this spin polarization can also be explained by Stoner theory[35]. In the Stoner criterion, if $\mathrm{I_s} \times \mathrm{DOS}(\varepsilon_\mathrm{F}) > 1$, the exchange splitting will occur, where $\mathrm{I_s}$ is the Stoner exchange integral and $\mathrm{DOS}(\varepsilon_\mathrm{F})$ is the DOS at the Fermi energy. The PDOS at edge-A sites crosses the Fermi energy and is largely localized at the Fermi level. It fulfills the Stoner criterion and thus spin polarization occurs.

Due to the localization of states discussed above, Coulomb

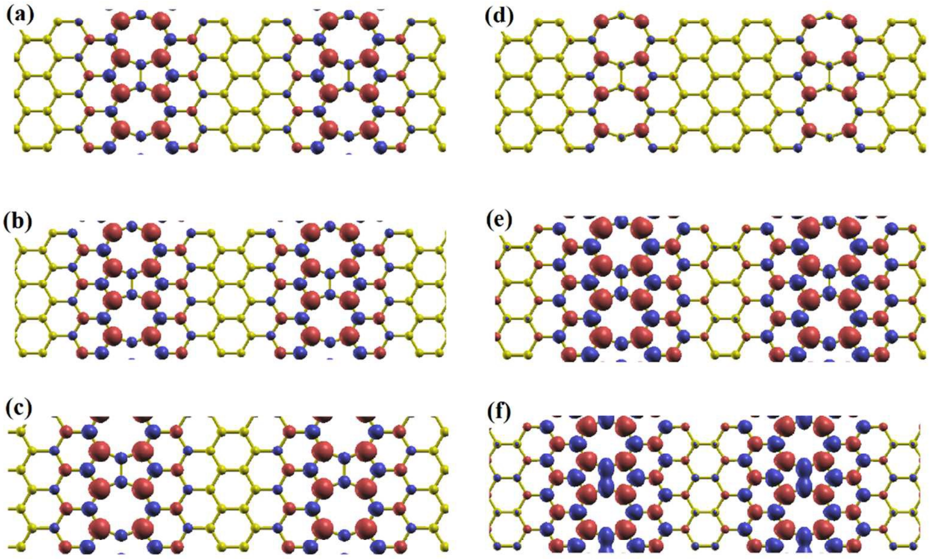

Fig. 4 Left panels: the spin polarization distribution of the system with U_{eff} = 2.5 eV at C_2 sites alone (a), edge-A sites alone (b), both C_2 and edge-A sites (c). Right panels: the spin polarization distribution of the system with U_{eff} = 4.5 eV at C_2 sites alone (d), edge-A sites alone (e), both C_2 and edge-A sites (f). The isosurfaces are drawn for 0.002 eÅ^{-3}.The red and blue isosurfaces represent the spin up and spin down electron densities, respectively.

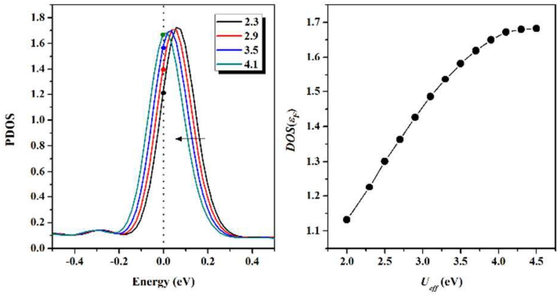

Fig. 5(a) PDOS of localized p_z electrons at edge-A sites from spin-restricted calculations with U_{eff} = 2.3 eV (black line), 2.9 eV (red line), 3.5 eV (blue line), 4.1 eV (green line). The Fermi energy is set to zero. (b) The value of the DOS at the Fermi energy as a function of U_{eff}.

on-site repulsion should be considered. By fitting to experiment, the values of U_{eff} between 2*p* electrons have been determined to be 2.1 eV for graphite and 4.6 eV for carbon nanotubes.[36] For the graphene with line defect considered in this paper, it is reasonable to choose a series of values of U_{eff}. Due to the delocalization of π electrons in the ZGR, the Coulomb on-site repulsion was fixed to be 2.1 eV. In our previous work,[37]the appropriate values of U_{eff} have been determined to be ~2.5 eV at line defect based on linear response *U* approach[27] with first principles calculations. However, in this paper, to investigate the evolution of electronic structures induced by Coulomb on-site repulsion, we change the value of U_{eff} at both C_2 and edge-A sites from 2.1 eV to 4.5 eV to examinethe dependence of the magnetism of the system on the choice of the U_{eff}.

As seen in Fig. 3, whenthe values of U_{eff} at C_2 sites and edge-A sites increase, opposite trends were found. The total magnetic moment of the system increases with increasing the values of U_{eff} at edge-A sites while the spin polarization is weakened when the Coulomb on-site repulsion increases at C_2 sites. For comparison, we also calculated the magnetism of the system by gradually increasing the value of U_{eff} in the ZGR. It is found that the parameter U_{eff} then has no effect on the magnetism of the system. This is reasonable, since the π electrons in the ZGR are quite delocalized and the effect of the Coulomb on-site repulsion can be ignored. However, when the Coulomb on-site repulsion increases simultaneously at C_2 and edge-A sites, the value of the magnetic moment of the system at first increases but then decreases, depending on the strength of the Coulomb on-site repulsion. We will discuss the mechanism of this phenomenon in the following.

To study the localization of magnetic moment, the spin polarization distribution of the system was calculated. As shown in Fig. 4, for small values of U_{eff} the spin polarization is mainly localized at edge-A sites, similar with that of zigzag graphene nano-ribbons.[38] However, for zigzag graphene nano-ribbons, the direction of spin polarization is opposite from one edge to the other; for graphene with line defect, the spin polarization of the two "edges" have the same direction. In Fig. 4, it can be clearly seen that the Coulomb on-site interaction between p_z electrons at edge-A sites enhances the spin polarization at the line defect, and the spin polarization decays deeply into the ZGR. This indicates that the Coulomb on-site interaction at edge-A sites induce a large and long range magnetic interaction between line defects. However, the Coulomb on-site repulsion at C_2 weakens the spin polarization of the whole system, as shown in Fig. 4. When the Coulomb on-site repulsion increases simultaneously at C_2 and edge-A sites, competition occurs between the spin polarization at both sites: for small U_{eff}, the spin polarization at edge-A sites dominates the magnetic moment of the system, while for large U_{eff}, the spin polarization at C_2 sites becomes evidently larger, which decreases the magnetic moment of the system.

To explain the trends of the magnetic moment of the system, we focus on the behavior of the localized states close to the Fermi energy. As discussed above, the magnetism of the system is mostly attributed to the spin polarization of the localized p_z electrons at edge-A sites. In order to further study the effect of Coulomb on-site repulsion at edge-A sites, we first investigated the PDOS of edge-A carbon with spin-restricted calculations for a series of U_{eff} values. As shown in Fig. 5a, large densities of states are localized near the Fermi energy. With increasing U_{eff} a rigid left-shift of the PDOS occurs at the Fermi energy. This indicates that more electrons tend to occupy the localized states as U_{eff} increases.

To study the behaviors of the electrons as a function of U_{eff}, we calculated the trends of charge distribution with increasing U_{eff} at edge-A and C_2 sites, respectively. As shown in Fig. 6, with increasing value of U_{eff} at edge-A sites, the amount of charge increases almost linearly for the carbons at edge-A sites while charge depletion occurs for the carbons at C_2 sites. Due to the charge accumulation at A sites, the value of $\mathrm{DOS}(\varepsilon_\mathrm{F})$ increases monotonously with increasing U_{eff}, as shown in Fig. 5b. Therefore, based on the Stoner criterion, the spin polarization is enhanced. In contrast, by increasing the values of U_{eff} at C_2 sites, charge accumulation occurs there. Since the localized states of C_2 are fully occupied, they contribute little

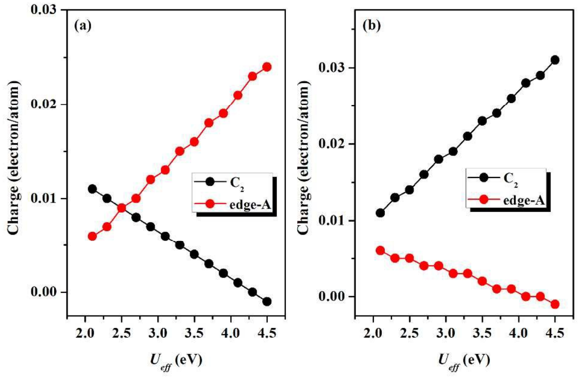

Fig. 6 Charge of the carbon atoms at C_2 sites and edge-A sites as a function of U_{eff} at edge-A sites (a) and at C_2 sites (b), respectively.

to the Stoner type of spin splitting. Furthermore, because charge depletion occurs for carbons at edge-A sites, the spin polarization is gradually weakened in this case.

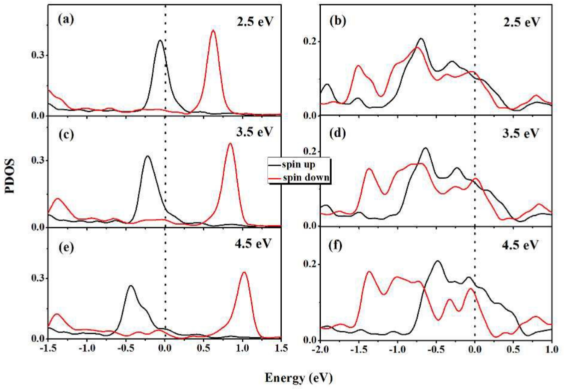

Fig. 7 Left panel: PDOS of localized p_z electrons at edges-A sites applying U_{eff} at both edge-A and C_2 sites with values of 2.5 eV (a), 3.5 eV (c) and 4.5 eV (e), respectively. Right panel: (b), (d), (f): same for π electrons at C_2 sites. The Fermi energy is set to zero.

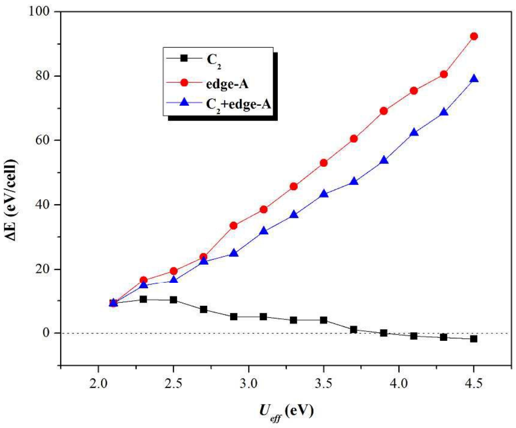

Fig. 8 The ferromagnetic (FM) stability of the system as a function of U_{eff} at C_2 sites alone, at edge-A sites alone, and at both C_2 and edge-A sites, respectively. ΔE is defined as $\Delta\mathrm{E} = \mathrm{E}_{\mathrm{NM}} - \mathrm{E}_{\mathrm{FM}}$, where E_{NM} is the total energy of the system in the NM state and E_{FM} is the total energy of the system in the FM state.

However, when Coulomb on-site repulsion increases at both C_2 and edge-A sites, the magnetic moment of the system at first increases but then decreases along with the increasing U_{eff}. This behavior can be explained by the exchange splitting effect at C_2 and edge-A sites. As shown in the left panel of Fig. 7, the state below the Fermi energy corresponds to the highest occupied molecular orbital (HOMO) of p_z electrons at an edge-A site, while the state above the Fermi energy is related with the lowest unoccupied molecular orbital (LUMO) of p_z electrons at an edge-A site. By contrast, in the right panel, the state crossing the Fermi level is the HOMO of the localized π electrons at a C_2 site. In Fig. 7, opposite exchange splitting occurs at C_2 and edge-A sites. When U_{eff}< 3.5 eV, the exchange splitting of p_z electrons of edge-A carbons plays the main role in the magnetism of the system. However, when U_{eff}> 3.5 eV, the opposite spin splitting isstrongly enhanced at C_2 sites. Therefore, the total magnetism of the system shows different behaviors with increasing U_{eff}.

For a quantitative description of the magnetic instability, the energy difference (ΔE) between the non-magnetic (NM) and the ferromagnetic (FM) states has been plotted in Fig. 8. The stabilization of the FM state is larger for stronger Coulomb on-site interaction at edge-A sites while the FM state becomes unstable when increasing the Coulomb on-site repulsion at C_2 site. However, the Coulomb on-site repulsion at A sites plays the dominate role in the stability of the FM state of the system, as clearly seen in Fig. 8. This can be explained by considering the exchange splitting of localized density of states at edge-A sites. As shown in Fig. 5a, the localized DOS crosses the Fermi energy. By introducing exchange interaction, spin splitting occurs at the Fermi energy, which shifts the localized DOS to a lowerenergy. When the Coulomb on-site repulsion increases at edge-A sites, larger spin splitting occurs. Consequently, the FM state becomes more stable.

As discussed above, the values of U_{eff} play an important role on the strength of spin polarization and the stability of the magnetic configurations of the system. However, the question arises that which U_{eff} is reasonable for the localized *p* electrons in this system. To estimate the reasonable values of U_{eff}, we have performed first principles calculations to study the strength of Coulomb on-site repulsion based on linear response method.[27] This method provides a self-consistent procedure to obtain reasonable values of U_{eff} without introducing any empirical parameters. It has been extensively applied for systems containing *d* and/or *f* electrons.[39-42] For the system we studied here, we calculated the values of U_{eff} for localized *p* electrons. As a comparison, we firstly calculated the value of U_{eff} for π electrons in graphene. The theoretical value of U_{eff} in graphene is 4.6 eV, which is considerably larger than that of experimental value (2.1 eV).[36] This overestimate may be attributed to the neglect ofnonlocal Coulomb interactions in graphene.[43] To achieve a simple correction, we performed a rigid shift of 2.5 eV for all the values of U_{eff} obtained. As a result, we can show that the reasonable values of U_{eff} is 2.55 eV for localized π electrons at C_2 sites and 2.3 eV for localized p_z electrons at edge-A sites.

To verify the validity of the DFT+*U* method for this system, we compared the magnetic moment based on DFT+*U* calculations (the values of U_{eff} have been chosen to be 2.55 eV (2.3 eV) at the center (edges) of the defects and 2.1 eV for the other sites) with the results obtained by the HSE method.[44] The magnetic moment of the former is ~0.38 μ_B/cell and of the latter ~0.36 μ_B/cell. Both of the results are considerably larger than that from GGA (~0.25 μ_B/cell), indicating that it is reasonable to introduce Coulomb on-site repulsion for the localized *p* electrons in this system.

Further, the additional Coulomb on-site *U* also requires a “double-counting” correction term in the energy function to

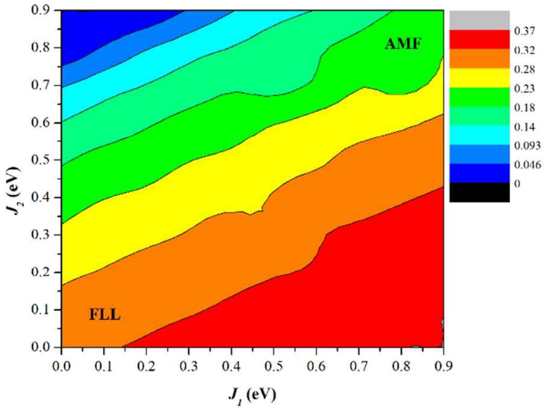

Fig. 9 Magnetic moment of the system as a function of the exchange parameter *J* at C_2 and edge-A sites. J_1 is the value of the exchange parameter at the C_2 site and J_2 is its value at the edge-A site. The values of the magnetic moment are presented with different colors.

subtract the Coulomb energy that is already included in the LSDA (or GGA) functional. These DFT+*U* functionals are generally referred to as being around-mean-field (AMF) and the fully localized limit (FLL), of which the latter is used in this paper. However, the localized electronic states at C_2 and edge-A sites (especially at the C_2 site) do not fully exhibit atomic characteristics, and the exchange interactions between localized *p* electrons should be considered. To introduce the exchange interactions, magnetic (exchange) interactions between nearest localized *p* electrons are estimated based on the DFT+*U*+*J* method. For the system we studied here, we sequentially increase the exchange parameter *J* from 0 to 0.9 eV at C_2 and edge-A sites, respectively. As shown in Fig. 9, the largest spin polarization occurs for the system with large J_1 (C_2 site) and small J_2 (edge-A site); by contrast, almost no magnetic moment appears in this system. This can be explained as follows. On one hand, the bonding states between p_z electrons at C_2 and edge-A sites are different. Due to the rigidity of π conjugation,[34] the un-paired p_z electron at an edge-A site cannot couple with its nearest p_z electrons, while the localized p_z electrons at a C_2 site pair up and form a non-spin-polarized localized π electronic structure. On the other hand, different values of J_1 and J_2 may induce charge transfer between C_2 and edge-A site. For large J_1 and small J_2, electrons prefer to be located at an edge-A site. Therefore, the spin polarization is enhanced there. However, for large J_2 and small J_1, more electrons transfer to C_2 sites, where no spin polarization occurs. As a result, the magnetic moment decreases. The FLL is reached with small J_1 and J_2, as shown in Fig. 9, which possesses a similar magnetic moment as that calculated using the DFT+*U* method (with U_{eff} ~2.5 eV), while when using large J_1 and J_2, the localized *p* electrons are described with the AMF approximation. This is easy to understand, because the value of *J* represents the exchange interaction between localized electrons. The larger is the exchange parameter, the more delocalization of the localized *p* electrons occurs.

Localized *p* electrons can be induced by vacancies, distortions and adsorptions in carbon related materials. Coulomb on-site repulsion should be considered not only in the system we studied here but also other systems containing localized *p* electrons. As a comparison, we apply the DFT+*U* method to graphene with a single vacancy, where the un-paired *p* electron and localized π electrons determine the magnetism of the system. By increasing the Coulomb on-site repulsion for these localized *p* electrons, the magnetic moment increases correspondingly (see Supplemental Materials). For a deeper understanding of Coulomb on-site repulsion between localized *p* electrons, we will in future work study the effect of Coulomb on-site repulsion induced by un-paired p_z electrons in carbon materials.

Conclusions

In this paper, the quite significant Coulomb on-site repulsion between strongly localized p_z electrons is studied in graphene embedded with line defects by use of the *DFT+U* method. We found that the spin polarization of the localized p_z electrons is very sensitive to the values of U_{eff}. If U_{eff} is applied to the edge of the line defect (edge-A sites), the exchange splitting is increased, and therefore the magnetism as well as the stability of the FM state are enhanced. However, if U_{eff} is applied to the center of the line defect (C_2 sites), the spin polarization of the system is weakened. More importantly, the Coulomb on-site repulsion also induces a charge accumulation with increasing U_{eff}. Due to the high value of the localized DOS originating from the p_z orbitals of carbon atoms at edge-A sites, the Stoner criterion is satisfied, and thus exchange splitting occurs. Based on linear response approach, we estimate reasonable values of U_{eff} to be 2.55 eV (2.3 eV) at the center (edges) of the defects. With these values of U_{eff}, we calculated magnetic moment of the system based on DFT+*U* method, which is considerably enhanced compared with the result of normal DFT calculation. More importantly, our DFT+*U* results are consistent with the results obtained with HSE method, indicating that it is reasonable to consider Coulomb on-site repulsion for the localized *p* electrons in this system. Further, the magnetism of the system is also influenced by the exchange interactions, i.e., exchange interaction between localized *p* electrons. We find that the full localized limit and the around-mean-field approximation can be reached by tuning the exchange parameter *J* for the localized *p* electrons. Our finding provides a new insight into the spin polarization of graphene related materials, where the Coulomb on-site repulsion between localized p_z electrons plays an important role in the magnetism and magnetic stability of the system.

Acknowledgements

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