Metal Adatom Adsorption on Graphene Sheet: A First-principle Study

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The adsorption on graphene of two different metal adatoms, K and Cu, is studied using first-principles density-functional theory with the generalized gradient approximation. Three different adsorption sites are considered. For individually adsorbed adatoms, we have the most favored adsorption sites by comparing the adsorption energies. The equilibrium geometry, adsorption energy, electronic structure in terms of density of states, and charge transfer are calculated for each adatom-graphene system in the minimum energy configuration. The calculation shows that the interaction between alkali-metal adatoms and graphene has a large ionic character. We also calculated, in few specific cases, the lateral interactions, i.e., the interaction between pairs of coadsorbed atom.

1. Introduction

Carbon based nanostructures are among the most prominent nanoscale materials currently studied. The confinement to one or two dimensions and the high symmetry of most of these structures lead to interesting new physics and many potential applications, specially involving their electronic structure. This work is focussed on graphene, a new exciting material with many novel properties, which are associated with its truly two-dimensional structure, leading to a zerogap semiconductor behavior. The single-layer graphene is a one-atom thick sheet of hexagonally arranged sp^2-bonded carbon atoms . The aim of this work is to investigate the adsorption of two different adatoms on graphene, namely of K and Cu, which are very different, the former leading to ionic bonding and the latter to covalent bonding. The geometry and the adsorption energy of both adatom-graphene systems are calculated, together with charge rearrangement. The lateral interactions, i.e., the interactions between adsorbed atoms, which to our knowledge have not yet been studied by first-principles, is needed if we want to predict trends concerning the aggregation of adatoms on graphene on different sites are shown in Fig. 1.

2. Method

Graphene has two Carbons atoms arranged in a two-dimensional honeycomb lattice with a hexagonal primitive unit cell. Our calculations are performed within the first-principles DFT under the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE), including spin polarization. The Quantum Espresso ab-initio simulation package is used to perform all calculations. The semicore $3d$ states of Cu are treated explicitly as valence. A plane-wave basis set with a maximum plane-wave energy of 30 Ry is used for the valence electron wave functions. A Gaussian smearing with a width of σ=0.025Ry is used for the occupation of the electronic levels. During all of the calculations, except for the band structure, the partial occupancy of the electronic states has been allowed and the tetrahedron method for Brillouin zone integration has been used. The k-point mesh, Γ point-centered was (4 4 1) except for the density of states (DOS) and the band calculations. In the first case, the DOS was calculated using a (12 12 1) mesh. With the parameters listed

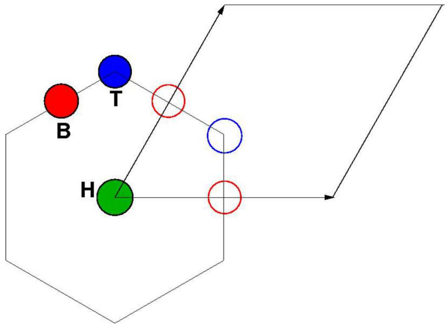

FIG. 1: Sketch of the primitive cell of graphene with the different inequivalent high symmetry absorption sites: hollow (H), top (T) and bridge (B).

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above, the calculated equilibrium lattice parameter for pure graphene is 4.65 a.u., slightly larger than the experimental value of 4.63 a.u., with a numerical uncertainty of 0.02 a.u. The distance between two adjacent graphene layers is fixed at 22.68 a.u.

The adatom-graphene system is modeled using a 4x4 hexagonal graphene supercell (Fig. 2). This setup corresponds to a coverage of 1 adatom per 32 C atoms. Calculations for the 4x4 clean graphene and the 4x4 adatom-graphene system are performed with the same-sized hexagonal supercell (in-plane lattice constant of 18.6 a.u., and distance between layers of 22.68 a.u.). The Brillouin zone is sampled with a (7 7 1) Γ-centered k-point grid. We consider the binding of the adatom on three sites of high symmetry (Fig. 1): the hollow (H) site at the center of the hexagonal, the bridge (B) site at the midpoint of a carbon-carbon bond, and the top (T) site directly above a carbon atom. For each adsorption site for the adatom-graphene system, the adatom is relaxed along the z direction and the C ions in graphene in all directions until forces on the ions are less than 0.001 Ry/a.u. The supercell dimensions are kept fixed for all calculations. To calculate adsorption energies, we also require the total energy of an isolated atom, which is approximated by using a simple cubic supercell of side of 25 a.u. We only consider the Γ point for the integration in the Brillouin zone. For more accurate results, we have calculated some electronic properties, such as the density of state (DOS) and the charge transfer, by using denser k-point mesh, (12 12 1) and (27 27 1), with the other parameters like in the previous calculations. Finally, to study the adsorption of atomic pairs and their lateral interaction, we also used a 4x4 supercell with some selected configurations according to the favorite sites for K and for Cu, with the same parameters of the individually adsorbed adatoms.

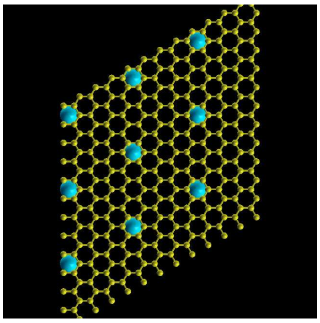

FIG. 2: Stick-and-ball model of 4x4 repeated supercells describing one adatom in hollow (H) site.

3. Results

3.1. Pure graphene

Our calculations reproduced well the main features for pure graphene that are reported in the literature. The band structure along the high symmetry directions is shown in Fig 3. This figure indicates the same trend reported in Ref. [2].

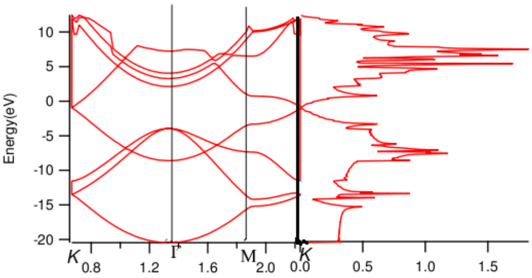

FIG. 3: Band structure for graphene using GGA: band dispersion along high symmetry directions (left panel) and density of states (right panel).

3.2. Adsorption of individual atoms

3.2.1. Adsorption energy and geometry

We define the adsorption energy as

$$E_{ads} = -(E_{ag} - E_g - n_a E_a) \tag{1}$$

Where, E_{ag} is the total energy of the 4x4 supercell with adatom on graphene, E_a is the total energy of an isolated atom, n_a is the number of adsorbed atoms which is just 1 in this calculations, and E_g is the total energy of the isolated graphene per 4x4 supercell (containing 32 C atoms). From this definition a larger E_{ads} indicates a stronger adsorption. Since we can have unpaired electrons, we allow for spin-polarization. The distance (d_{AC}) is defined as the distance between the adatom A and the nearest carbon atom C. For the three adsorption sites considered, the site with the largest adsorption energy (maximum total energy) is referred to as the favored site. The high-symmetry site with the next largest adsorption energy is representative of a transition state along a diffusion path connecting two lowest energy adsorption sites. The energy difference between these sites is an estimate of the diffusion barrier (E_{diff}). Adsorption energies and structural properties for the three sites considered are summarized in the following table.

TABLE I: Adsorption energy, adatom-carbon distance d_{AC}, total and absolute magnetization for one adatom on graphene in a 4x4 supercell, with a (7 7 1), Γ-centered k-point mesh. Spin-polarized calculations are performed, but without fixing the occupation of the states.

Atom	*sites*	$E_{ads}(eV)$	$d_{AC}(\AA)$	$\mu_{tot}(\mu_B/\text{cell})$	$\mu_{ab}(\mu_B/\text{cell})$	Δq
K	H	0.80	2.70	0.00	0.00	0.84
	B	0.73	2.83	0.00	0.00	
	T	0.73	2.85	0.01	0.01	
Cu	H	0.07	2.04	-0.83	0.89	0.20
	B	0.23	2.10	-0.72	0.77	
	T	0.23	2.13	-0.73	0.85	

Table I summarizes the adsorption energies E_{ads}, the equilibrium distances d_{AC} for the cases of the two adatoms (Cu and K)and the total and absolute magnetization.The relative stabilities of different adatom-graphene systems are determined by the adsorption energies. The largest absolute values of the adsorption energy mean strong binding of the adatom to the surface of graphene. According to Table I, we see that the hollow position (H) is favored for K with an adsorption energy, which is 0.80 eV and the equilibrium distance is 2.70 Å. The same study has been done for Cu and we find that the adsorption energies in the top (T) and bridge (B) positions are very similar, i.e., 0.23 eV. This table indicates some remarkable differences between the adsorption of K and Cu. Not only that their favored adsorption sites are different but also their adsorption energies are different, K resulting more strongly bound to graphene than Cu. Furthermore, a spin polarized calculation (with allowed fractional occupational occupation of states) gives almost zero spin polarization for adsorption of K and a sizeable polarization for Cu, with a magnetic moment of the cell ranging from $0.77\mu_B$ for B to $0.89\mu_B$ for T. The three adsorption sites are characterized by small differences in the d_{AC} equilibrium distances, both in the case of K and Cu. The numerical accuracy is of about 0.02 eV for adsorption energies and 0.02 Å for distances, which means a relative numerical accuracy of few % for the relevant energetic and geometric quantities. Many results for adatom adsorption are already available in literature. Ref. [1] reports DFT calculations for Cu on C nanotubes; ref. [2] for K on graphene, but at a too high coverage; therefore, we exclude them from a direct comparison with our results.

Ref. [3] and Ref. [4] report a systematic work for different adatoms, but giving only a few details in terms of technical parameters of the calculations. Ref. [5] is systematic work for different adatoms, but uses supercells 3x3 with only 4 k points (too few), mixing results with LDA and GGA, giving only E_{ads} and no other information. Moreover, it is not specified whether the calculations are spin polarized or not. Much more details are found in other references, such as Refs. [6–10], but in these papers we can find results for K or Cu only, so that it is difficult to compare them on the same ground. To our knowledge, only Refs. [3–5] treat both K and Cu.

We see that our results are in agreement with those reported in Refs. [5–7] for K. The results from Refs. [5, 8, 9] are quite spread: only the relative order of H, T and B positions is reproduced, but the values of the adsorption energies are similar to ours only in Ref. [9]. We think that in this case the spin polarization has an important effect and the results could also depend on the constraint on the occupation of the states. We also see that accounting for van der Waals interactions, as it is done for instance in Ref. [10] by the vdW-DF and the PBE+D2 methods, but not in our calculations, has a non negligible effects on the results. However, remarkably, the order of the absorption sites remain the same within the numerical accuracy of the calculations.

We calculate the projection of occupied Bloch states on pseudo-atomic orbitals in order to determine what is called the *Löwdin charge* to study possible charge transfer. We must remark that since the pseudo-atomic orbitals that are considered are arbitrary to some extent and not orthormal to each other, the projection cannot be done exactly, but there is some *missing* charge that is delocalized. The spilling parameter [13], which is the relative value of the missing charge, measures the ability of the basis provided by the pseudoatomic wavefunctions to represent the occupied Bloch states by measuring how much of the subspace of the Hamiltonian eigenstates falls outside the subspace spanned by the atomic basis. We did, therefore, some tests by increasing the number of k points in the non self-consistent cycle: (14 14 1) and (27 27 1) points. With the latter choice, we obtained a spilling parameter of the order of 0.01, which means that we miss about 1% of the charge with respect to the total valence charge, which is a reasonable amount.

For K absorbed on graphene on the H site, we found that it gives to graphene 0.84 electrons. These extra electrons on graphene are distributed all over the 32 C atoms of the simulation cell. In particular, the 6 C atoms nearest neighbor to K gain each about 0.06 electrons and all the remaining C atoms gain about 0.02 to 0.03 electrons. The case of Cu absorbed on graphene is a bit different. In this case also, the adsorbed atom gives electrons to graphene, but by a smaller amount (the total charge given to graphene is 0.20 electrons for our test considering H site) and more localized on the 6 C atoms nearest neighbor to Cu that gain about 0.06 electrons each, whereas all the other C atoms remain practically neutral. These estimates of charge transfers indicate that the bonding of K with graphene has a dominant ionic character, as expected since K is an alkali atom with the external electron that can be quite easily extracted. The bonding of Cu with graphene has also an ionic component, but much less pronounced. Comparing our results for charge transfer with those from literature for K (Refs. [6, 7]), we see that there is quite a large spread of results. This is due to different methods used to calculate this transfer, which is somehow arbitrary. However, the qualitative results are in agreement, confirming an important ionic character of the K-graphene bonding. The charge transfer for Cu on graphene can be compared with the results in Ref. [8], and they are in good agreement.

3.2.2. Density of States

We complete the description of the effect of adatom adsorption on the electronic structure of graphene by calculating the density of states. We remark that these calculations are obtained by allowing fractional occupation of electronic states. A more complete investigation should include also calculations with fixed occupation. However, within the description chosen, we obtain the results shown in Figs. 4 and 5 for K and Cu, respectively, when both are adsorbed in H site. Although we made spin-polarized calculations, the DOS in the majority and minority spin channel look the same and we report only one of the two. We compare the total density of states of the adatom-graphene (red line) with that of pure graphene (green line). Of course, since we have a different number of electrons, the Fermi energies are different with or without adsorbed atoms, but for the sake of comparison we align the occupied bands of pure graphene and we set as zero the Fermi energy of pure graphene. The Fermi energy of K on graphene is about 1 eV above the zero and the Fermi energy of Cu on graphene is only few MeV above. We see from Fig. 5 that K changes the DOS above the Fermi energy of pure graphene, whereas it is very clear a peak related to Cu at about 2 eV below the Fermi energy of pure graphene in case of Cu in H site.

For Cu, we then consider also the most favored case, i.e., adsorption on T site. The main features, i.e., a pronounced peak close to and below E_F, is similar to the H case. Other details are also a bit different. The spin polarized calculations show the same huge peak in majority and minority spin channels, but a difference immediately above E_F, as it is visible in Fig. 4. A good agreement for our calculated DOS and the results from the literature (Ref. [11]) is also found for Cu (Fig. 5).

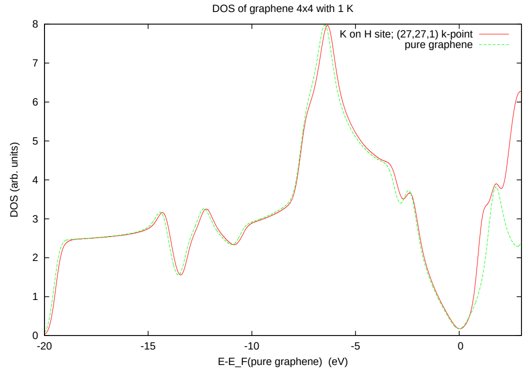

FIG. 4: Density of states of K adsorbed in H site on graphene (red curve) compared with that of pure graphene (green line). For the sake of comparison, the occupied bands of pure graphene are aligned in the two cases and the Fermi energy of K on graphene is about 1 eV above the zero. Spin polarized calculations, but with fractional occupation are allowed (DOS of majority and minority spin channel are similar).

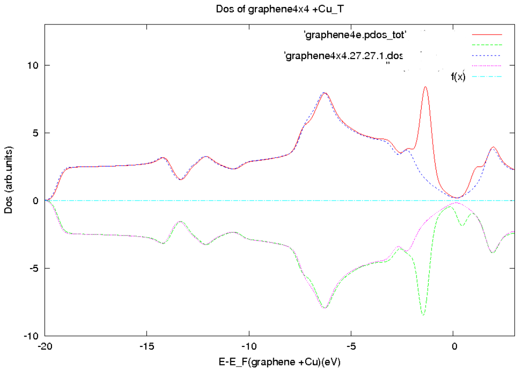

FIG. 5: Density of states of Cu adsorbed in T site on graphene (red curve: majority; green curve: minority). Spin polarized calculations but with fractional occupation are allowed.

3.3. Lateral interactions between adatoms

In this work we define the lateral interaction as

$$\begin{aligned} E_{lat} &= E_{2adatomsongraphene} - E_{graphene} \\ &\quad -2(E_{isolatedatom} - E_{ads.singleatom}) \quad (2) \end{aligned}$$

Where, $E_{2\ adatoms\ on\ graphene}$ is the total energy per two adatom of the supercell 4x4 graphene layer, $E_{graphene}$ is the energy of the clean 4x4 supercell graphene, $E_{isolatedatom}$ is the energy of the isolated adatom, and $E_{ads.\ single\ atom}$ is the adsorption energy of a single adatom. We study the lateral interaction of two kind of atoms, Copper (Cu) and potassium (K), initially adsorbed at different sites and distances on the clean graphene. We allow the atoms to relax and we obtain a final configuration given by Figs. 6 and 7.

Our calculations show that K atoms tend to repel each other (Fig. 6), whereas two Cu atoms initially placed at top site and at a finite distance (Fig. 7) tend to diffuse on graphene and aggregate in order to form a σ bond at a finite distance.

We make a summary of our results in Table II.

TABLE II: Lateral interaction energy and the adatom-adatom distance.

Atom	*sites*	$E_{lat}(eV)$	$d_{adatom-adatom}(\mathring{A})$(initial)	$d_{adatom-adatom}(\mathring{A})$(final)
K	H-H	0.50	4.3	4.98
Cu	B-B	-1.66	4.53	2.26

4. Conclusion

In this work, we investigated the interaction of single atoms and dimers with grapheme, i.e., a single layer of graphite, using of density functional theory calculations (DFT). After some tests, we decided to use the generalized gradient approximation (GGA). We found that a single adsorbed K prefers to occupy the hollow (H) site and transfer to graphene about 0.84 electrons, thus establishing a rather ionic type of bonding. Instead, the Cu adatom prefers to occupy top (T) or bridge (B) sites (the adsorption energies are very similar) and gives to graphene less electrons (about 0.20), thus establishing with graphene a more covalent binding.

Our results are in good agreement with those available in literature.

The most original part is related to the adsorption of dimers. Starting from K and Cu dimers, we obtained different results. At variance with K, for Cu, we observe a trend towards aggregation. Differences in the charge transfer to graphene between the cases of K and Cu dimers are also found.

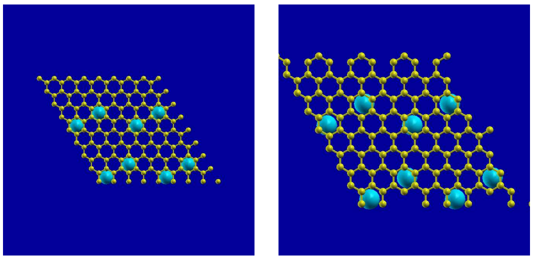

FIG. 6: Initial (left) and final (right) images of the stick-and-ball model of 4x4 repeated supercells describing a K pair of adatoms in H sites (H0-H2 configuration).
Distance between the K of the pair: initial 4.3 Å, final 4.98 Å.
The final distance is bigger than the initial one.
Lateral interaction energy: 0.50 eV (aggregation is NOT favored).

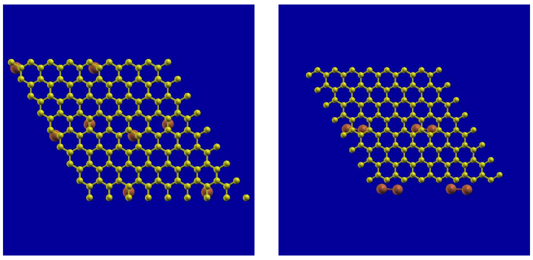

FIG. 7: Initial (left) and final (right) images of the stick-and-ball model of 4x4 repeated supercells describing a Cu pair of adatoms in B sites (B0-B2 configuration).
Distance between the Cu of the pair: initial 4.53 Å, final 2.26 Å.
The two Cu atoms tend to diffuse and to aggregate. The dimer has a final distance that is almost the same independent on the initial configuration.
Lateral interaction energy: −1.66 eV (aggregation is favored).

We conclude that our results seem to indicate the same trend reported in Ref. [12], although that paper used a completely different approach.

Aknowledgments

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