First-Principles Study of Adsorption of Halogen Molecules on Graphene-MoS_2 Bilayer Hetero-system

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Abstract

We have performed density functional theory based first-principles calculations to study the stability, geometrical structures and electronic properties of pure 3×3 supercell of MoS_2, 4×4 supercell of graphene, graphene-MoS_2 bilayer hetero-system, F_2, Cl_2, Br_2 and I_2 molecules on hetero-system within the DFT- D_2 level of approximations. The preferable site and adsorption energy of halogen molecules are studied. The most stable geometries are considered to study their electronic band structure, Density of states and magnetic properties with reference to individual 2D components, graphene and MoS_2 .

1. Introduction

The strongest, thinnest and most stretchable material arranged in honeycomb lattice of thick sheet of sp^2-bonded carbon atoms termed as graphene is at focus of many research works worldwide due to its peculiar properties like observable quantum Hall effect at room temperature and existence of two-dimensional gas of massless Dirac fermions [1-5]. These nobel properties of graphene with its applications in the areas of spintronics, hydrogen storage, sensing [6-9] have attracted the most modern consent of researchers to predict other desirable properties.

On complementary to graphene, MoS_2 belonging to 2D transition metaldichalcogenide, well known as band gap semiconductor is becoming most studied material in the last 5 years [10-12]. MoS_2 is a layered transition metal dichalcogenide semiconductor with an indirect band gap in which Mo and S atoms are stacked together to give S-Mo-S sandwiches coordinated in a triangular prismatic arrangement [13]. In recent time, MoS_2 is attracting the attention of many researchers as it is excessively available in the form of a natural mineral, molybednite [14]. MoS_2 monolayer is widely used to produce transistors [15], integrated logic circuits, signal amplifiers [16], photodetectors and flexible optoelectronic devices. It is a promising material with highly potential applications in solar cells [17], photocatalysts, signal amplifiers and lubrication [18]. However, its properties are limited by band gap. The graphene-MoS_2 bilayer hetero-structure as shown in figure [1] offers the excellent mechanical flexibility, electronic properties, optical transparency, photoconductivity and favorable transport properties [19].

The association of two materials with their distinct electronic properties is believed to drag the desired properties in practical applications. Moreover, the adsorption of foreign atoms on hetrostructure is one of the promising approach to modify and exploit unwanted properties of any constituent. Combination of two materials standing for a brand new family with halogen, commonly known as reactive non metal and highly electronegative elements of periodic table is highly expected to start new direction towards mate-rials science research.Heterostructure may bee important to study the properties beyond the capacities of constituents as well as to eliminate the negative properties and drag desirable one.

Although the graphene-MoS_2 hetero-structure is used to study the adsorption of different metals on nano-scale channels [20], it has not been tested for the ability of heterostructure with reactive non-metals. Previous work for the adsorption of halogens on graphene layers opens very small gap (3-75 meV, highest in fluorine). Since MoS_2 is band gap material, we are interested to test halogens on graphene-MoS_2 bilayer to obtain high band gaps and particularly the role of fluorine to change the electronic structure. From both scientific and technological point of view, investigation of halogen adsorption on semiconducting surface is very important as halogen and its compounds are widely used in the etching technologies. To make comparison for the interaction of halogens and semiconductor surface is of prime importance. In this work, we consider adsorption of diatomic halogen molecules on graphene-MoS_2 bilayer hetero-system.

The remaining part of the paper is organized in the following way. In Sec. II, we discuss the computational details and the systems under our study. Sec. III gives a brief description of results of adsorption of F_2, Cl_2 , Br_2 and I_2 molecules on graphene-MoS_2 bilayer hetero-system. Here, we present the analysis of adsorption sites, binding energies, band structures and density of states. The last conclusion section summarizes the major findings and possible extensions of the ongoing research.

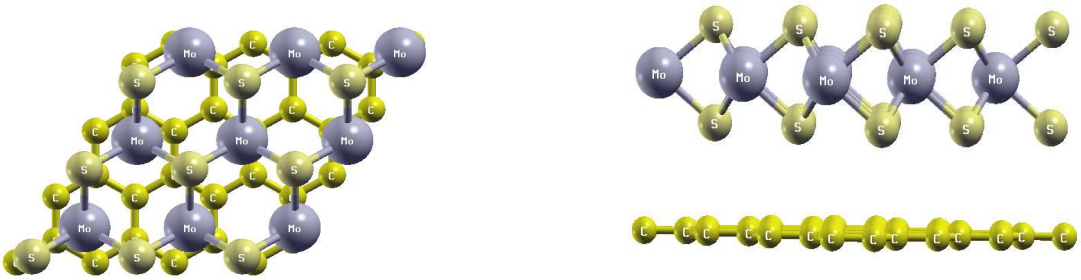

Figure 1: 3×3 supercell of MoS_2 Monolayer and 4×4 super cell of graphene to form a MoS_2 -graphene bilayer hetero-system, (a) Top-view and (b) Side-view respectively

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2. Computational Details

In the present work, we have incorporated Density Functional Theory (DFT) [21, 22] implemented in the Quantum Espresso (QE) [23] code to study the geometrical and structural properties of 3×3 supercell of MoS_2 , 4×4 supercell of graphene, graphene-MoS_2 bilayer hetero-structure and halogen molecules adsorbed graphene- MoS_2 bilayer hetero-structure. The Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) [24] with van Der Waals interaction via Grimme's model [25, 26] is used to treat inter electron interaction. The bfgs algorithm with Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) model of ultrasoft pseudopotential is used to account the interaction between the ion cores and valence electrons. The unit cell is optimized with respect to lattice parameter 'a', kinetic energy cut-off (E_{cut}) for plane wave and the number of k-points along x- and y-axes respectively. Based on these convergence tests, we obtained the lattice constant 'a' for the unit cell of MoS_2 as 3.176 $^\circ$A which agrees with the previous results [13, 14].
For the 3×3 supercell of MoS_2 the lattice constant is three times that of the unit cell. Further, the plot of the total energy verses the number of k-points reveals that the energy of the unit cell of monolayer MoS_2 is almost constant after n_{kx} equal to 10. Hence a mesh of 10×10×1 k-points, in case of unit cell,

could be used for the Brillouin-zone integration. The mesh was reduced to 4×4×1 for 3×3 as per relations of direct and reciprocal lattice geometries, which helps to minimize the computational cost. A plane wave basis set with energy cut-off values of 476 eV (35 Ry) for the wave-function and 4760 eV (350 Ry) for the charge density is used for the expansion of the ground state electronic wave functions.

3. Results and Discussion

3.1 Adsorption of halogen molecules on Graphene-MoS_2 bilayer hetero-structure:

The MoS_2/graphene heterostructures is made using 3 × 3 supercell of MoS_2 and 4 × 4 supercell of graphene by considering the lattice mismatch. There are two possibilities for the construction of the heterostructures accounting the difference in lattice parameters between 18.006 Bohrs of MoS 2 and 18.600 Bohrs of graphene. If lattice constant of MoS_2 is used (i.e MoS_2 is taken reference and graphene is modelled on it), there will be compressive strain of 3.3 % on graphene sheet. If lattice constant of graphene is used i.e graphene as reference and MoS_2 is modelled on it, there will be 3.2 % tensile strain to MoS_2 . In this study, Both cases are taken with the different stacking and configurations to find the minimum energy state for the calculations of the electronic structurs of the heterostructures. Vaccum length is made greater than 20 ˚A along z- axis to avoid the interactions between the adjacent supercells. We have considered six different occupation sites of high symmetry : the hollow site, at the center of hexagonal plane of MoS_2 , top of molybdenum atom (Mo-Top), top of sulphur atom (S-Top) from MoS_2 side and hollow site at the center of hexagon of graphene (C-Hollow), bridge between two carbon atoms (C-Bridge) and top of carbon atom (C-Top) from graphene side as shown in figure [2]. The adsorbates (halogens) were kept in two different orientations before optimization, viz. Parallel and Perpendicular to the graphene and MoS 2 sheets. Reverse to the order of bond dissociation energy in halogen molecules (Cl_2 >Br_2 >F_2 >I_2), the B.E. of halogens on MoS_2 sheet is found in the order Cl_2 <Br_2 <F_2 <I_2 . The reason is obvious, the halogen molecule with the stronger intra-atomic bonding gain its inert state and becomes less reactive towards MoS_2 monolayer.

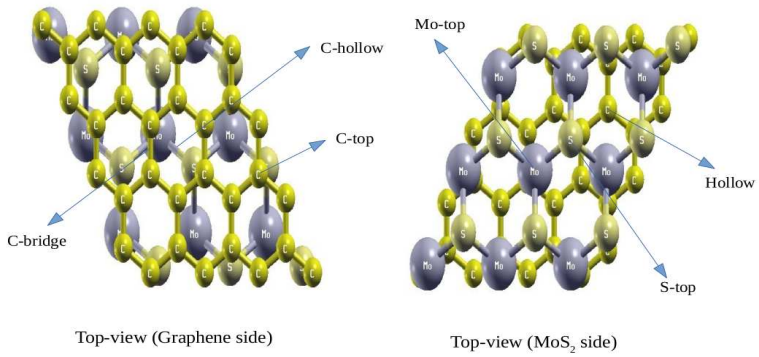


Figure 2: Different possible adsorption sites for the adsorption of halogen molecules on graphene-MoS_2 bilayer hetero-structure.

The binding energy (adsorption energy) of a halogen molecule on graphene-MoS_2 bilayer hetero-system is calculated by using the relation

$$\Delta E = E_{hal} + E_{graphene-MoS2} - E_{hal-graphene-MoS2} \quad (1)$$

where E_{hal} is ground state energy of a fully relaxed halogen molecule, $E_{graphene-MoS2}$ is the ground state energy of graphene-MoS_2 bilayer hetero-structure and $E_{hal-graphene-MoS2}$ is the ground state energy of halogen adsorbed graphene-MoS_2 bilayer hetero-structure. The positive binding energy reflects the stability of the system. The total energy of a halogen molecule adsorbed graphene- MoS_2 bilayer hetero-structure is calculated in 3×3 supercell of MoS_2 and 4×4 supercell of graphene. Out of the six adsorption sites, the site with the largest binding energy is indicated as the most favourable site for adsorption of the halogen molecule. The different parameters obtained from our calcula-tions are shown in tables below.

Table 1: Table for Binding Energy (E), perpendicular distance of centre of adsorbed molecule from sulphur plane of MoS_2 (h_1), reference (h_1)*[27], distortion on MoS_2 sheet (d_{MoS2}) and observed bond length of adsorbed halogen molecule (d) along graphene side of graphene- MoS_2 bilayer heterostructure

Halogen	Orientation	C-hollow					C-bridge					C-top				
		ΔE (eV)	h_1 (Å)	h_1^* (Å)	d_{MoS2} (Å)	d (Å)	ΔE (eV)	h_1 (Å)	h_1^* (Å)	d_{MoS2} (Å)	d (Å)	ΔE (eV)	h_1 (Å)	h_1^* (Å)	d_{MoS2} (Å)	d (Å)
F_2	Parallel perpendicular	1.882 0.284	3.560 3.900	3.230 3.700	0.119 0.001	2.823 2.610	0.417 0.234	3.700 3.380	3.170 3.470	0.011 0.008	3.010 3.088	1.012 0.437	3.720 3.390	3.230 3.460	0.014 0.003	1.650 1.640
Cl_2	Parallel perpendicular	0.163 0.153	3.580 4.170	3.580 4.340	0.035 0.007	1.900 2.000	0.189 0.188	3.590 4.110	3.630 4.210	0.040 0.005	2.000 2.010	0.182 0.194	3.540 4.180	3.640 4.210	0.041 0.006	2.000 2.020
Br_2	Parallel perpendicular	0.239 0.225	3.610 4.510	3.770 4.670	0.020 0.002	2.310 2.320	0.267 0.273	3.690 4.320	3.740 4.510	0.013 0.005	2.310 2.330	0.258 0.281	3.660 4.200	3.770 4.450	0.030 0.005	2.310 2.340
I_2	Parallel perpendicular	0.365 0.315	3.590 4.600	3.850 4.730	0.019 0.019	2.699 2.699	0.389 0.352	3.520 4.698	3.800 4.740	0.002 0.017	2.695 2.709	0.383 0.359	3.650 4.750	3.830 4.850	0.001 0.020	2.694 2.709

Table 2: Table for Binding Energy (E), perpendicular distance of centre of adsorbed molecule from sulphur plane of MoS_2 (h_1), distortion on MoS_2 sheet (d_{MoS2}) and observed bond length of adsorbed halogen molecule (d) along MoS_2 side of graphene-MoS_2 bilayer heterostructure

Halogen	Orientation	hollow				Mo-top				S-top			
		ΔE (eV)	h_1 (Å)	d_{MoS2} (Å)	d (Å)	ΔE (eV)	h_1 (Å)	d_{MoS2} (Å)	d (Å)	ΔE (eV)	h_1 (Å)	d_{MoS2} (Å)	d (Å)
F_2	Parallel perpendicular	0.291 0.261	3.002 3.600	0.001 0.021	1.527 1.538	0.229 0.284	3.990 3.475	0.001 0.000	1.526 1.532	0.199 0.732	3.800 3.200	0.001 0.079	1.527 1.798
Cl_2	Parallel perpendicular	0.158 0.159	3.400 4.040	0.060 0.004	1.990 2.010	0.162 0.150	3.370 4.060	0.065 0.054	1.995 2.010	0.156 0.247	3.430 3.980	0.070 0.008	2.000 2.060
Br_2	Parallel perpendicular	0.238 0.244	3.390 4.200	0.040 0.003	2.310 2.330	0.239 0.226	3.400 4.220	0.040 0.050	2.310 2.320	0.239 0.404	3.250 4.020	0.070 0.001	2.310 2.330
I_2	Parallel perpendicular	0.387 0.344	3.398 4.445	0.003 0.014	2.695 2.712	0.385 0.325	3.394 4.550	0.004 0.011	2.695 2.706	0.379 0.489	3.459 4.150	0.003 0.024	2.694 2.764

Tables 1 & 2 show the binding energy values of different structures at different occupation sites. The perpendicular distance of centre of adsorbed molecule from sulphur plane of MoS_2 (h_1) is found to agree well with the reference values of (h_1) [27]. The bond length of adsorbed molecule on graphene-MoS_2 bilayer hetero-structure is not obtained to be significantly changed during adsorption process because the obtained molecule-surface interaction is much weaker than the intra molecular bonding in halogens. Here, we consider the system with the highest B.E. or the least total energy is most stable one. The fluorine adsorbed graphene- MoS_2 bilayer hetero-structure is most stable at the hollow site (C-Hollow) at the center of hexagon of the graphene sheet in the parallel configuration. But all the remaining halogen molecules adsorbed hetero-structures are obtained to be most stable while they are perpendicular to the sheet and above the sulphur atom of MoS_2 sheet (S-Top). The highest value of B.E. are 1.882 eV, 0.247 eV, 0.404 eV and 0.489 eV respectively for fluorine atom, Cl_2, Br_2 , and I_2 molecules adsorbed hetero-structures. The geometrical structures with the highest B.E. are considered to draw the various properties of the respective systems. In addition, the distance between two F-atoms increases when it is bound more strongly to MoS_2 sheet of graphene- MoS_2 bilayer hetero-structure. This result indicates that the bonding of F or F_2 with the substrate happens on the cost of weakening of F-F interaction. The adsorption geometries of molecular halogens (i.e. perpendicular and parallel orientations) above the graphene side of hetero-structure is shown in figure [3], while the optimized structures of different halogens on hetero-structure at the most stable occupation site are shown in figure [4].

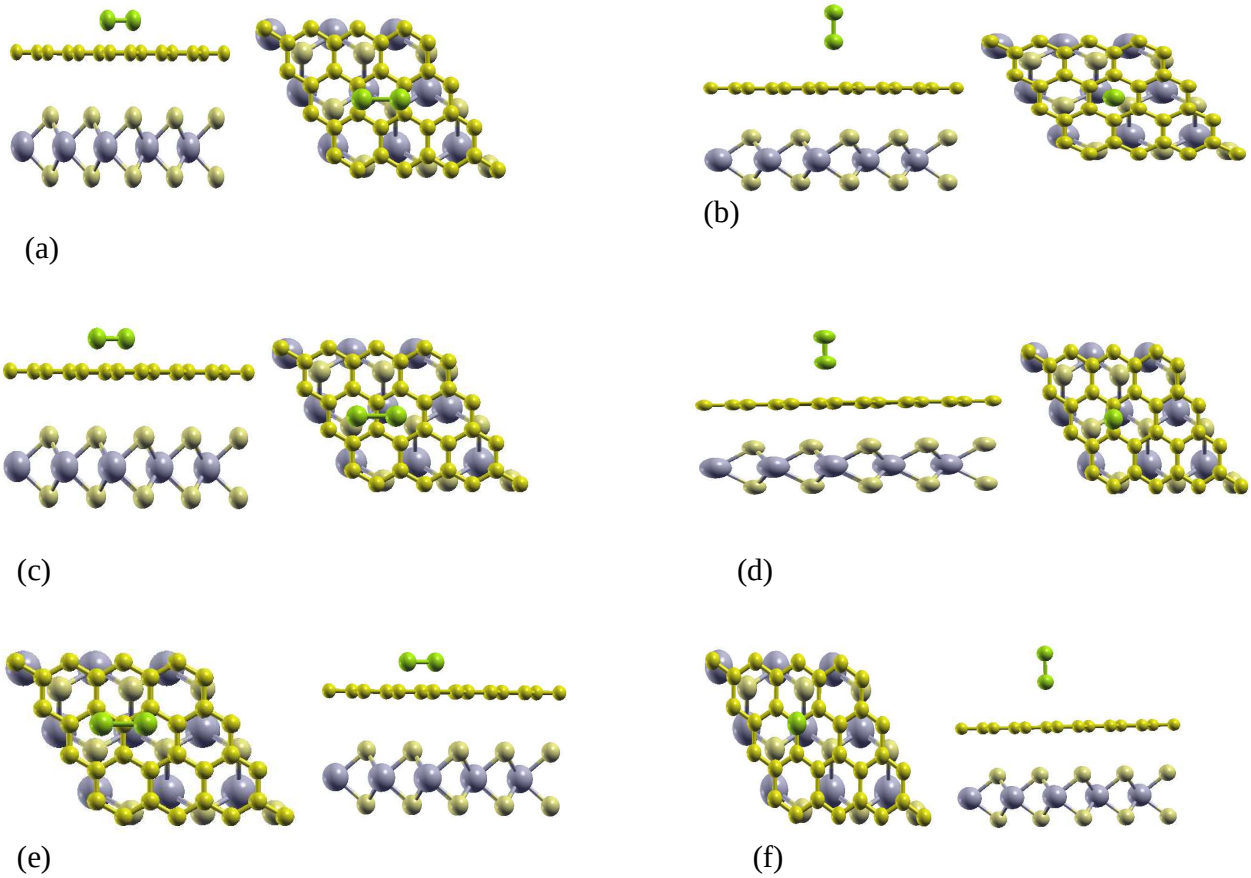
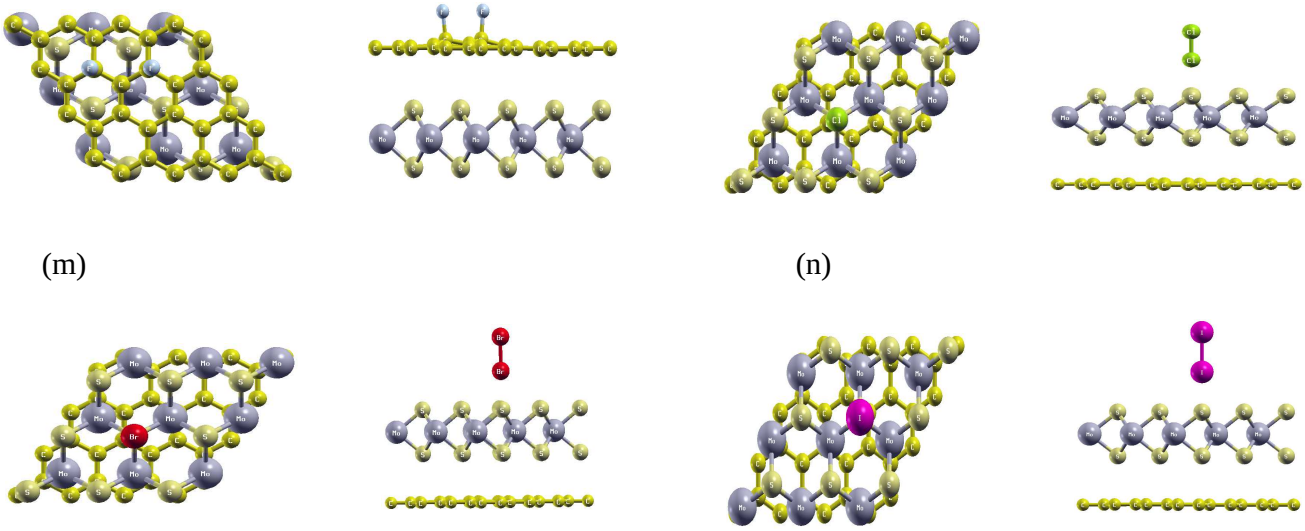


Figure 3: Top and Side view respectively for the adsorption of halogen molecules with different orientations of adsorbates in the direction parallel ((a), (c), (e)) and perpendicular (fig. (b), (d), (f)) to the graphene sheet. Figures (a) and (b) show the adsorption in C-Hollow (H) region, (c) and (d) at C-Bridge and (e) and (f) at C-Top, respectively.
Similarly, the adsorption of halogen molecules with different orientations of adsorbates in the parallel and perpendicular direction to the Mo $_2$ sheet are tested to know the most occupation site.



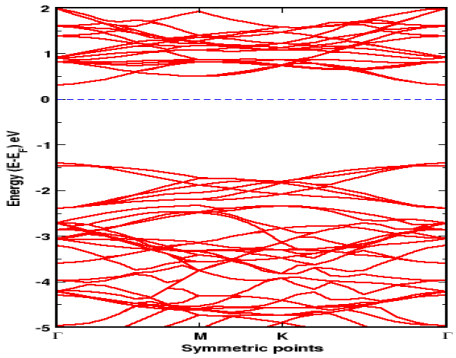
(m) (n)

(o) (p)

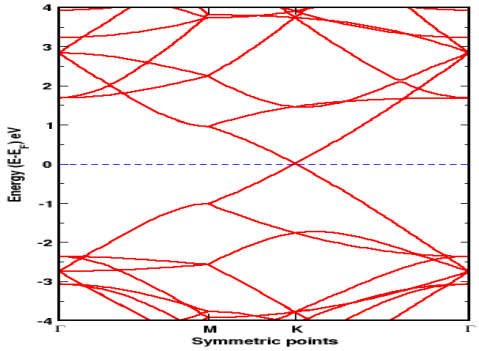
Figure 4: Optimized geometries of a halogen molecule adsorbed graphene-MoS_2 bilayer hetero-structure with top and side-view respectively. The figures, (m) fluorine atoms parallel to graphene plane at Hollow-site (C- hollow), (n) Cl_2 molecule perpendicular to MoS_2 plane at S-Top site (o) Br_2 molecule perpendicular to MoS_2 plane at S-Top site, (p) I_2 molecule perpendicular to MoS_2 plane at S-Top site.

3.2. Electronic structure calculations:

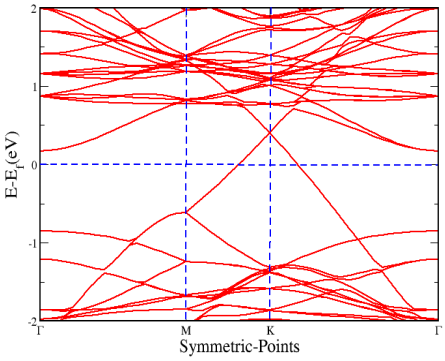
In order to understand the impact of adsorption of halogen molecules, we first need to understand the electronic properties of 3×3 sheet of MoS_2 monolayer as shown in figure [5(a)], 4×4 sheet of graphene as in figure [5(b)] and graphene-MoS_2 bilayer hetero-structure as in figure [5(c)]. Figure [5(a)] shows the band structure of 3×3 sheet of MoS_2 monolayer. Since, the conduction band minimum and valence band maximum lie at the same symmetric point, it is a direct band gap semiconductor with band gap of 1.65 eV. In case of 4×4 sheet of graphene, there is no band gap as conduction band and valence band coincides at Fermi level indicating that the graphene is a zero band gap semiconductor. Figure [5(c)] shows the band structure of graphene-MoS_2 bilayer hetero-structure. Here, the Dirac point shifts about 0.40 eV above the Fermi level which shows that the graphene-MoS_2 bilayer hetero-structure is metallic in nature. Afterwards, we have studied the effect of adsorption of halogen molecules on the hetero-structure along graphene plane and MoS_2 plane. The band structures of different systems are shown in figures [5(d)], [5(e)], [5(f)], and [(5(g).


Energy (E-E$_F$) eV
Γ
M
K
Γ
Symmetric points

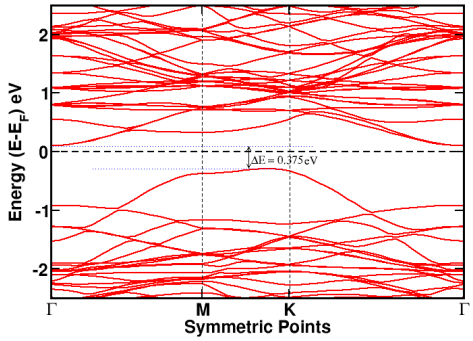
(a)


Energy (E-E$_F$) eV
Γ
M
K
Γ
Symmetric points

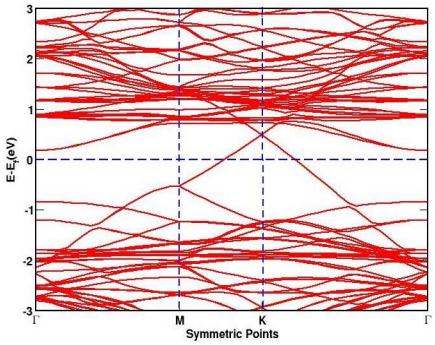
(b)


E-E$_f$ (eV)
Γ
M
K
Γ
Symmetric-Points

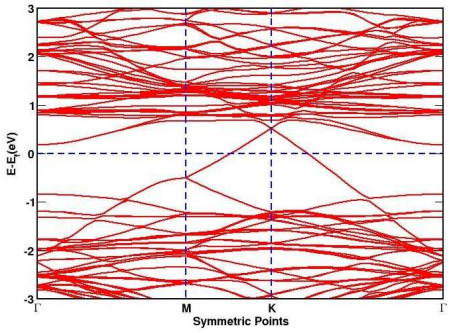
(c)


Energy (E-E$_F$) eV
ΔE = 0.375 eV
Γ
M
K
Γ
Symmetric Points

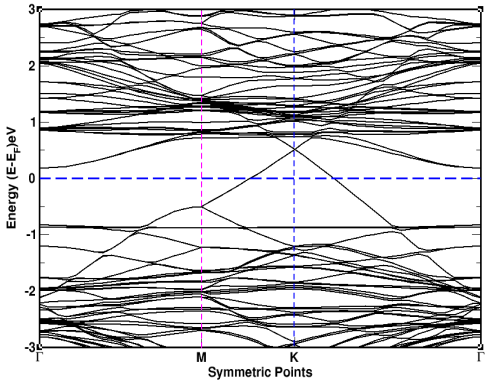
(d)


E-E$_f$(eV)
Γ
M
K
Γ
Symmetric Points

(e)


E-E$_f$(eV)
Γ
M
K
Γ
Symmetric Points

(f)



(g)

Figure 5: Band structures of (a) 3×3 sheet of MoS_2 monolayer (b) 4×4 sheet of graphene (c) graphene-MoS_2 bilayer (d) fluorine atoms (e) Cl_2 (f) Br_2 (g) I_2 molecule adsorbed graphene-MoS_2 bilayer hetero-structure.

The modifications in band structures is illustrated in table [3]:

Table 3: Electronic properties of halogen adsorbed Graphene/MoS2 system.

Optimized structure	Band Gap (eV)	Fermi Energy (eV)	Dirac Point(eV)	Dirac Shift (eV)
Graphene-MoS_2 bilayer	-	1.819	0.400	-
F_2-graphene MoS_2	0.375	1.174	-	-
Cl_2-graphene MoS_2	-	1.868	0.480	0.080
Br_2-graphene MoS_2	-	1.870	0.500	0.100
I_2-graphene MoS_2	-	1.996	0.520	0.120

From table [3], it is clearly seen that the band gap of 0.375 eV is found in the case of fluorine atoms adsorbed graphene-MoS_2 bilayer but in other halogen adsorbed bilayer, Dirac point shifted above the Fermi level. The formation of band gap in fluorine adsorbed system is due to the bonding and anti-bonding states of the electrons in the orbitals ans also due to band folding property of electrons in the orbitals. The band structures of other halogen adsorbed systems resembles the band structure of graphene-MoS_2 bilayer. The shift of Dirac point increases from Cl_2 to I_2 adsorbed graphene-MoS_2 bilayer. Also the Fermi energy is seen to be in the increasing order from Cl_2 to I_2 adsorbed graphene-MoS_2 bilayer. Since fluorine atom has the highest electronegative value among halogens, it could easily go for interaction in presence of other reacting species. This could be seen at the B.E. values in table [1]. Our results strongly show the favourable condition to absorb halogens particularly fluorine molecule in excited mode as done to store hydrogen molecule/s on metal decorated graphene [28]. Similarly, the magnetic properties of our system are studied with the help of information displayed by density of states (DOS) as shown in figure [6]

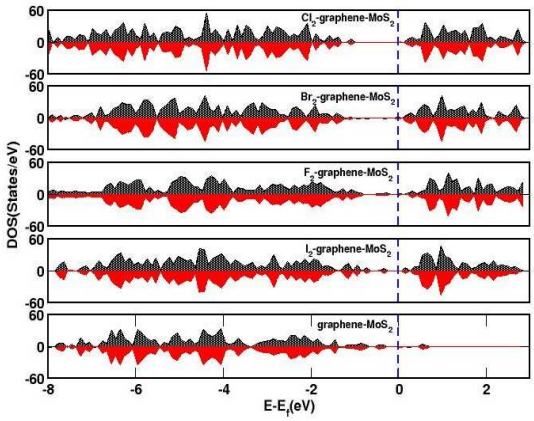


Figure 6: DOS of graphene- MoS_2 bilayer hetero-structure and halogen adsorbed graphene- MoS_2 bilayer hetero-structure. The curve above zero x-axis in each plot represents up-DOS, and that below the axis represents down-DOS.

The plot of DOS shows that both up-DOS and down-DOS are symmetrical about the axis in graphene-MoS_2 bilayer hetero-system as well as halogen molecules adsorbed bilayer hetero-structures. This means, the non magnetic nature of graphene-MoS_2 bilayer hetero-structure is still preserved with adsorption of halogens on it. From figure [6], it is clear that the DOS shift above the Fermi level due to adsorption of halogen molecules on hetero-structure.

4. Conclusions:

We have studied a first-principles study of geometrical and electronic properties of graphene-MoS_2 bilayer hetero-structure and halogen molecules adsorbed hetero-structures. The adsorption sites and orientations are tested to draw the most stable configurations. The fluorine atoms adsorbed system is stable at hollow site of hexagonal plane of graphene (C-Hollow) in parallel configuration with the binding energy 1.882 eV. The Cl_2 , B_2 and I_2 adsorbed hetero-structures all are most stable in the perpendicular configuration above the sulphur atoms of MoS_2 plane (S-Top) with binding energies 0.247 eV, 0.404 eV and 0.489 eV respectively. Band structure unalters in case of Cl_2 , B_2 and I_2 adsorbed graphene-MoS_2 bilayer hetero-structure but Dirac point shifts above the Fermi level. The band gap of 0.375 eV is found in fluorine atoms adsorbed hetero-structure. Our work suggests a way to tune the electronic properties of heterostructure with adsorption of halogens. We then analyzed DOS of respective systems and concluded that monolayer MoS_2 and halogen adsorbed system are non magnetic.

5. Acknowledgements:

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