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First-principles study of a molecular adsorption of fluorine on monolayer MoS_2

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Abstract

We have performed density functional theory (DFT) based first-principles calculations to study the stability, geometrical structures and electronic properties of pure monolayer Molybdenum disulphide (MoS_2) and Fluorine (F_2) adsorbed monolayer MoS_2 within the DFT-D2 level of approximations. Present study shows that a F_2 molecule adsorbed MoS_2 monolayer system is stable. From the geometry and information of adsorption energy of F_2 molecule on the different occupation sites of MoS_2 monolayer, it has been found that Fluorine prefers atomic adsorption above sulphur (S) atom. The binding energy per equivalent molecular Fluorine above the sulfur (S) atom is found to be 1.83 eV. The electronic structure calculations of MoS_2 and F_2 adsorbed MoS_2 monolayer shows that there is a band gap of 1.14 eV and 1.01 eV respectively, at the Fermi level. Further, the symmetry of total DOS for up and down spin calculations reveals that the F_2 adsorbed MoS_2 monolayer is non-magnetic as similar to that of pure MoS_2 monolayer. The projected density of states (PDOS) of a F_2 adsorbed MoS_2 monolayer is studied to understand the weighted contributions of different orbitals.

Keywords: Density functional theory; MoS_2 monolayer; band structure properties.

1. Introduction

After the discovery of graphene [1], atomic crystals of two-dimensional materials, consisting of single sheets, extracted from bulk materials are gaining considerable attention with a wide range of electronic properties and potential practical applications [2]. The study on low dimensional hexagonal structure based materials have become of great interest to many researchers for nanoscience and consequent nanotechnology. Molybdenum disulfide MoS_2, is a two dimensional transition metal dichalcogenide honeycomb structure with certain gap in its electronic bands, consistent with a semiconductor [3]. It is formed by weakly bonded three layers of sulphur, molybdenum and sulphur (S-Mo-S). It means that two planes of S atoms and an intercalated plane of Mo atoms are bound together in a trigonal prismatic arrangement [3, 4] of MoS_2. Currently, MoS_2 is attracting the most valuable researches because of its availability in the form of a natural mineral, molybdenite [5]. Adsorption of foreign atom/s and molecule/s on two-dimensional materials is a promising approach to suitably modify their properties [6]. The functionalization of MoS_2 has also occupied an important domain in the research activities to study electronic, magnetic and band structure properties [7]. A number of theoretical and experimental works have been carried out to study these important behaviors of different elements adsorbed MoS_2 monolayer, and have found to yield many interesting results [8].

In the Halogen group (VII), fluorine is the most electronegative and highly reactive element in our periodic table. The primary reason why we choose fluorine in our calculation is that the adsorption of fluorine molecule may have significant potential to modify the electronic properties of MoS_2 monolayer, which can be used in many desired electronic practical applications. Further, it may be a useful effort to synthesize chemically modified MoS_2 monolayer and present new directions in two dimensional materials. These purpose require the atomistic level of understanding, and in our best knowledge, it is yet to be understood for halogen adsorbed MoS_2.

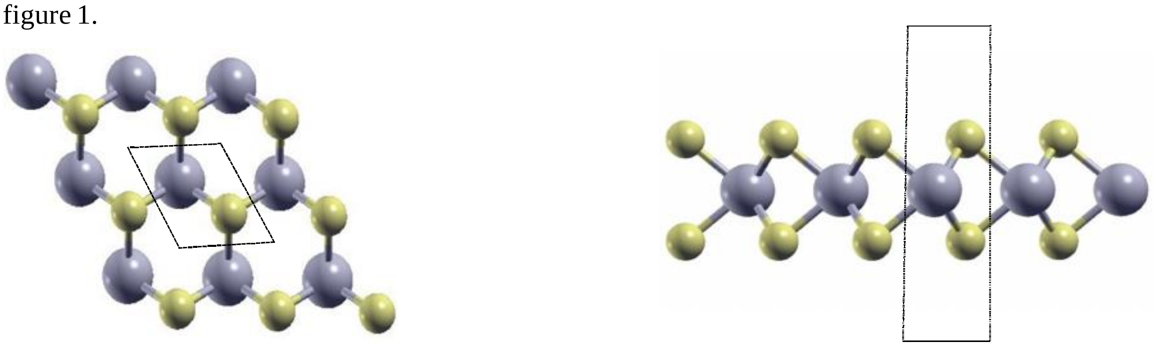
The remaining part of this work is organized in following way. We first discuss the computational details and the systems under our study. We then go into the results section and describe our findings for structural and binding properties of F2 adsorbed on MoS_2 monolayer. The section is followed by the discussion of adsorption properties of F2 on pure MoS_2 monolayer. The post-processing analysis, e.g. Density of states is incorporated in the section. The last section, conclusions, summarizes the major findings and possible extension of ongoing research work.

2. Computational Details

In the present work, we study the geometrical and electronic properties of monolayer MoS_2 and fluorine molecule adsorbed monolayer MoS_2. To perform the calculations, we have used Density Functional Theory (DFT) [9, 10] implemented in the Quantum ESPRESSO [11] code. The Perdew-Burke-Ernzerhof (PBE) variant of the generalized gradient approximation (GGA) [12], incorporating van der Walls interaction via Grimme's model [13, 14] is used to treat electron-electron interaction. The algorithm has used Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) model of ultra- soft pseudo-potentials to account the interaction between the ion cores and valence electrons. The plane wave expansion with kinetic energy cut-off values of magnitudes 35 Ry, and 350 Ry, respectively, are used for wave-function and charge density. A mesh of 10×10×1 k-points is used for unit cell of MoS_2 monolayer for Brillouin-zone integration and a mesh of 4×4×1 k-points is taken for 3×3 supercell of monolayer MoS_2. Further, in order to minimize the interactions between two adjacent MoS2 layers, a vaccum distance of 12 Å is maintained in the calculations. All the structures are optimized using the BFGS (Broyden-Fletcher-Goldfarb-Shanno) [15] scheme until the total energy change is less than 10^{-4} Ry between two consecutive scf steps and force acting is less than 10^{-3} *Ry/Bohrs*. The 'Marzarri-vanderbilt' [16] smearing or cold smearing with a small broadening width of 0.001 Ry is used. Furthermore, diagonalization method is chosen as 'david', with mixing factor 0.6 for self-consistency. Spin polarized calculations are accommodated to study the magnetic properties of the systems. For the density of states (DOS) calculations of pure monolayer $MoS2$ and $F2$ adsorbed monolayer $MoS2$ systems, we have used 3×3 supercell of monolayer $MoS2$ with a denser mesh of (8×8×1) k-points.

3. Results and Discussion

A hexagonal unit cell of monolayer MoS_2 with the basis of three (1-Mo and 2-S) atoms in honeycomb lattice structure is initially constructed by using experimental value [17]. It is build up by single layers of S-Mo-S atoms as shown in figure 1. It consists of two planes of Sulphur (S) atoms and an intercalated plane of Molybdenum (Mo) atoms bound with the sulphur atoms in a trigonal prismatic arrangement. Each Mo atom is surrounded by six first-nearest neighbouring S atoms, while each S atom is connected to three first-nearest neighbouring Mo atoms [3, 5] as shown in figure 1.

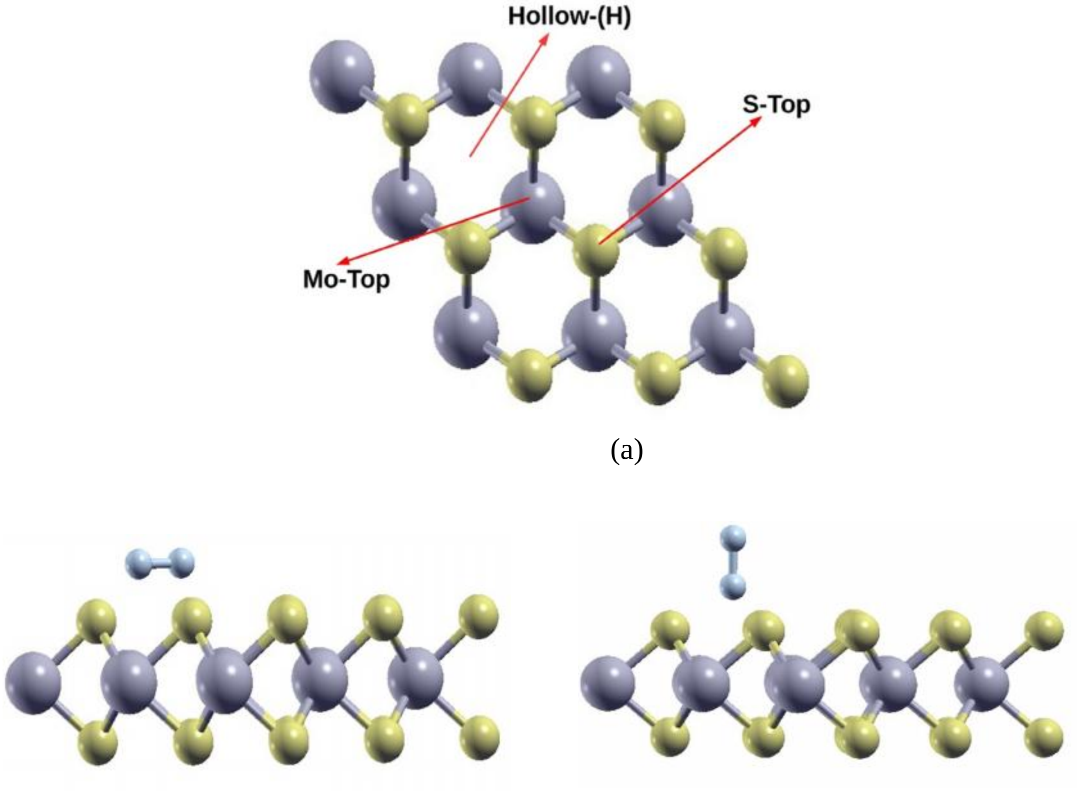


(a) (b)

Fig. 1: Unit cell of monolayer MoS_2 (shown by dotted parallelogram), (a) Top-view and (b) Side-view. The unit-cell consists of a single Mo atom intercalated between two S atoms at a bond length of 2.42 Å and S-MO-S angle of 80.80^o. Propagation of MoS_2 unit-cell along x- and y-directions to form 3×3 supercell of monolayer MoS_2. Single Mo-atom is covalently bonded with 6 S-atoms to form hexagonal honey-comb structure.

After the construction of the unit-cell, the structure is optimized with respect to latticeparameter '*a*', kinetic energy cutoff ($E_{cut-off}$) for plane wave and the number of k-points along x- and y-axes respectively. Based on these convergence tests, we obtained that the lattice constant '*a*' for the unit cell of monolayer MoS_2 is 3.18 Å, which agrees with the previous results [3, 5]. For the 3×3 supercell of monolayer 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 shows that the energy of the unitcell of monolayer MoS_2 is almost constant when the number of k points ($n_{k\,x} = n_{k\,y}$) crosses 10. A a mesh of 10×10×1 k-points is, therefore, used for Brillouin-zone integration of unit cells and a mesh of 4×4×1 k-points are taken for 3×3 supercell. A plane wave basis set with energy cutoff values of

35 Ry for the wave-function and 350 Ry for the charge density is used for the expansion of the ground state electronic wave functions.



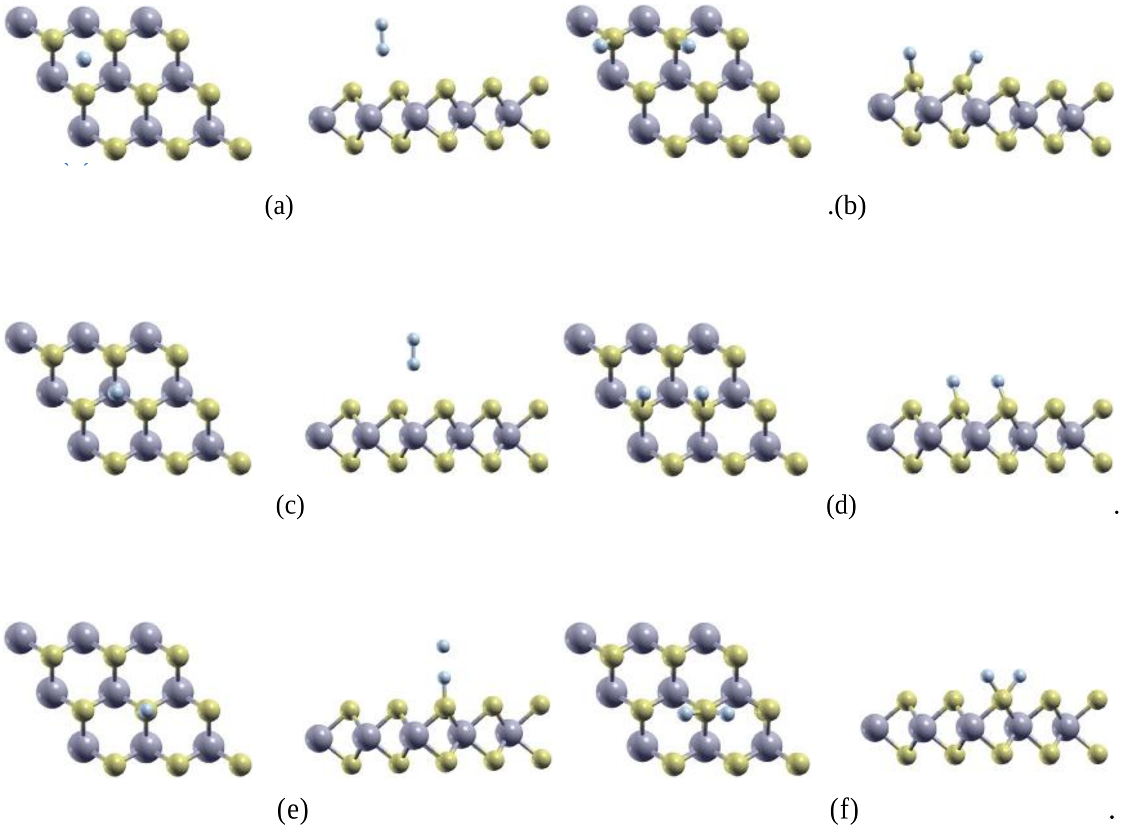
(a)

(b)

(c)

Fig. 2: Initial structures of MoS_2 and F_2 added MoS_2. (a) Different possible adsorption sites, (b) horizontal (parallel) configuration of molecular F_2 and (c) vertical (perpendicular) configuration of molecular F_2 for the adsorption of molecular F_2 on monolayer MoS_2.

A molecular fluorine (F_2) is adsorbed on monolayer MoS_2 of size 3×3 supercell. The adsorption is carried out at different possible sites of MoS_2 (figure 2(a)), with different orientations/configurations of F2 molecule. We have taken three different occupation sites for the adsorption, which are: the Hollow (H) site at the center of the hexagonal ring, the top of the Mo atom (Mo-Top) site, and the top of the S atom (S-Top). Further, two configurations of molecular F_2 for its adsorption, i.e., the vertical (perpendicular) to the MoS_2 plane and the horizontal (parallel) to the MoS_2 plane, are considered. All together we have studied six different possible ways for its adsorption. For each of the sites and the configurations, the total energy and hence the binding energy (B.E) of the adsorbed molecule is calculated. The most suitable site with the suitable configuration is determined by using the information of total energy (minimum) or the binding energy (maximum).



(a) .(b)

(c) (d) .

(e) (f) .

Fig. 3: Optimized geometries of F_2 molecule adsorbed monolayer MoS_2 with top- and side-view respectively, (a) F_2 molecule perpendicular to MoS_2 plane at H-site (H- perpendicular), (b) $F2$ molecule parallel to MoS_2 plane at H site (H-parallel), (c) F_2 molecule perpendicular to MoS_2 plane at Mo-T site (Mo-T-perpendicular), (d) F_2 molecule parallel to MoS_2 plane at Mo-T site (Mo-T-parallel), (e) F_2 molecule perpendicular to MoS_2 plane at S-T site (S-T-perpendicular) and (f) F_2 molecule parallel to MoS_2 plane at S-T site (S-T-parallel)

The Binding Energy (B.E)/adsorption energy (ΔE) of a molecular fluorine on monolayer MoS_2 is calculated using the relation,

$$\Delta E = E_{F_2} + E_{MoS_2} - E_{MoS_2+F_2} \qquad (1)$$

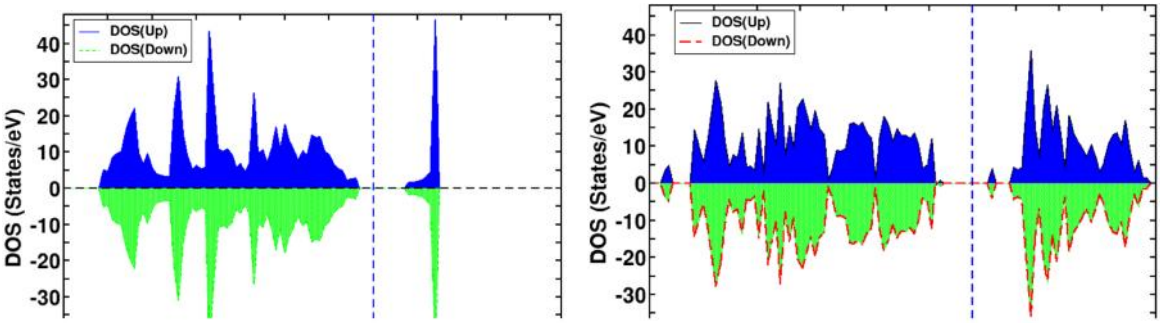
where, E_{F_2} , E_{MoS_2} and $E_{MoS_2+F_2}$ are the total energies of the isolated F2 molecule, mono- layer MoS_2, and the F_2 adsorbed monolayer MoS_2 system respectively. Of the three ad- sorption sites (H, Mo-T and S-T), with two possible configurations taken, the site with the largest adsorption energy is referred as the suitable site for adsorption. The optimized structures of F_2 adsorbed monolayer MoS_2 systems are shown in the figure 3.

Table 1: The table lists the adsorption energy of molecular Fluorine (ΔE), it's height from the average of upper sulphur plane (h), optimized F-F distance in F_2 molecule (d_{F-F}) after adsorption, the distance of the atomic F from it's nearest S-atom (d_{S-F}) and the distortion observed in 3 × 3 supercell of monolayer MoS_2 (d_{MoS2}) due to adsorption of F_2.

Adsorption site	Configuration of F2	ΔE (eV)	h (Å)	d_{F-F} (Å)	d_{S-F} (Å)	d_{MoS_2} (10^{-1}Å)
Hollow (H)	Perpendicular	0.1788	3.187	1.486	3.031	-0.823
	Parallel	1.4661	1.634	4.487	1.791	-0.139
Mo-Top	Perpendicular	0.1455	3.358	1.464	3.191	-0.943
	Parallel	0.9916	1.582	2.979	1.764	-0.135
S-Top	Perpendicular	0.6327	2.657	1.827	1.827	-0.039
	Parallel	1.8304	1.396	2.159	1.729	0.366

Table 1 represents the adsorption/binding energy values (ΔE), the relaxed distance ofcenter of mass of molecular F2 from S-plane of monolayer MoS_2 (h), the separation be- tween the two F atoms in F_2 (d_{F-F}), the distance of a F atom from nearest S-atom (d_{S-F}) and the distortion observed in 3 × 3 supercell of monolayer MoS_2 (d_{MoS2}) due to adsorption of F_2. The table shows that a F_2 molecule is bound to all the adsorption sites considered and the parallel configuration on the top of the S atom is the most stable one among them. There is a large variation in the binding energy values of molecular fluorine, which is due the different configurations of F_2 molecule towards the varying sites of substrate. During the optimization of the adsorbed system it is found that the molecular fluorine, in some of the cases, breaks it's bond and each of the isolated F atom gets bonded with the nearest S atom. The geometries with the atomic adsorption of F are seen more stable (see table 1). The table also reveals that the system having maximum B.E has the minimum planer distance from the S-plane. In addition, the distance between two F atoms increases when it is bound more strongly to monolayer MoS_2. The results imply that the boding of F/F_2 with the substrate happens on the cost of weakening of F-F interaction.

The Density of States (DOS) of up and down spin for pure and F_2 adsorbed MoS_2, with reference to Fermi level (represented by vertical dotted line), are shown in the figures 4(a) and 4(b). Present calculations show that the Fermi energy for the pure and F_2 adsorbedmonolayer MoS_2 are 0.5647 eV and -0.0461 eV, respectively. The values (of Fermi energy) imply that there is a shift in Fermi level by 0.6108 eV after the adsorption of F_2. The density of states for pure monolayer MoS_2 can also reveal that there is a gap (between valence and conduction bands) of about 1.14 eV near in the Fermi level. Since the PBE type GGA calculations underestimate the band gap near by the Fermi level [18, 19], the value of the band gap obtained from the present calculations is smaller than the previously reported values [3, 4]. However, the electronic band structure (figure is not shown) reveals that the material is direct band gap semiconductor, which is consistent with the core concept of the band structure reported in the references. Further, the symmetry in the up- and down-DOS supports the fact that the monolayer MoS_2 is non-magnetic material.



(a)   (b)

Fig. 4: Density of states (DOS) of (a) monolayer MoS_2, and (b) F_2 adsorbed monolayer MoS_2.

On the other hand, the band gap near the Fermi level of F_2 adsorbed monolayer MoS_2 is found to be 1.01 eV. It means that the band gap has decreased by 0.13 eV due to adsorption of F_2. It may be due to the fact that fluorine is highly reactive and most electronegative element in the nature, and certain bands at valence/conduction band are occupied by the addition of F_2 electrons. The high peaks which are seen in total DOS of pure monolayer MoS_2 are found to be decreasing after the adsorption of F_2. The symmetry of DOS (for up- and down-DOS) of F_2 adsorbed monolayer MoS_2 shows that the system remains non-magnetic after the adsorption of F_2 as well.

To get the better understanding of the sharp energy bands on total DOS of the F_2 molecule adsorbed monolayer MoS_2, we have performed the partial DOS analysis (PDOS). The contributions of different orbitals of Mo, S and F atoms on the F_2 molecule adsorbed MoS_2 are presented in the figures 5, 6 and 7. In the figures the Fermi energy is taken as reference, and represented by the vertical dotted line. The figures reveal that 4d, 3p and 2p orbitals of Mo, S and F atoms respectively, are the dominant contributions on the sharp energy bands of total DOS.

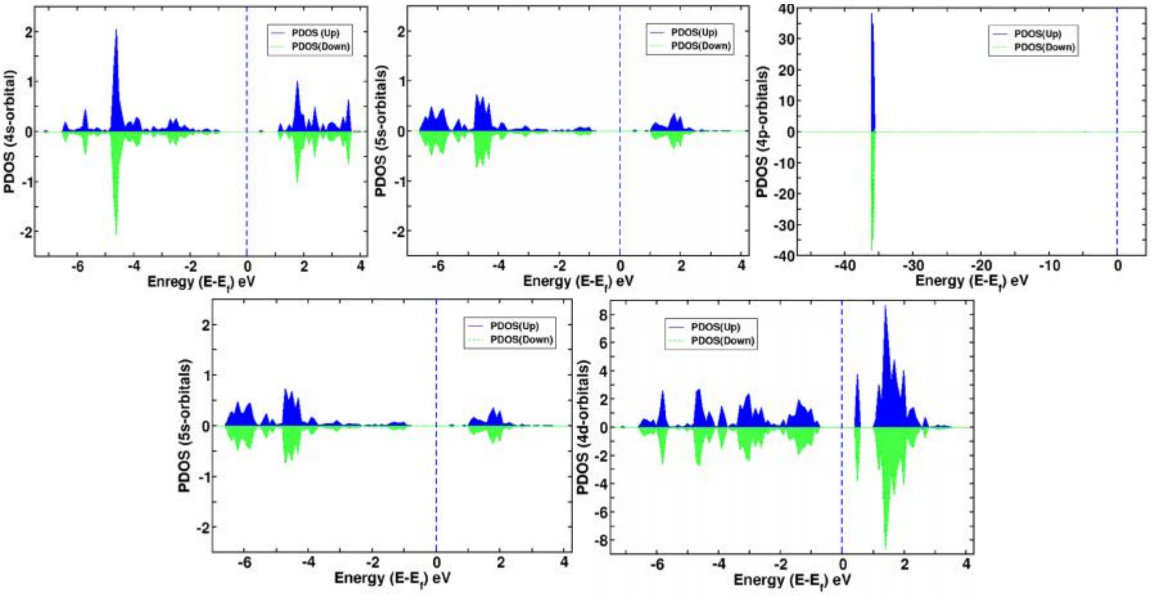


Fig. 5: PDOS of 4s, 5s, 4p, 5p and 4d orbitals of Mo atom respectively. PDOS due to 4d-orbitals is seen dominant over the others.

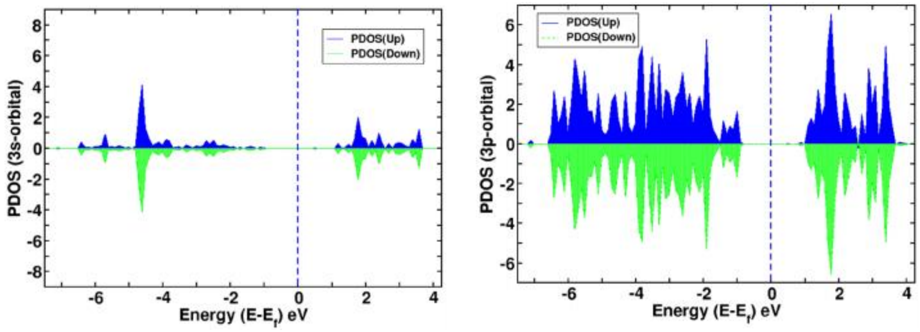


Fig. 6: PDOS of 3s and 3p orbitals of S atom, respectively. PDOS due to 3p-orbitals, poisoned nearby Fermi level, is seen dominant.

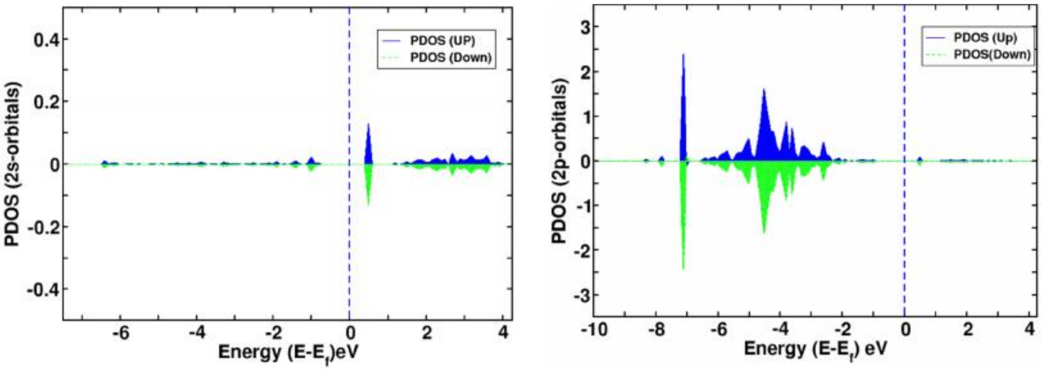


Fig. 7: PDOS of 2s and 2p orbitals of F atoms respectively. The PDOS due to 2p-orbitals is seen dominant over the 2s-orbitals.

4. Conclusions

The structural and electronic properties of pure and F2 adsorbed monolayer MoS2 systems are studied. The binding energy values of F2 at different sites suggest that F2 can be adsorbed on monolayer MoS2 and the parallel configuration of F2 above sulphur (S) atom is found to be the most stable with the binding energy of 1.83 eV. The geometry reveals that the molecular F2 dissociates and each atom of F is adsorbed to nearby S in the structure. The DOS calculations of the pure monolayer MoS2 find a band gap of 1.14 eV and reiterates that the system is non-magnetic. In case of F2 adsorbed monolayer MoS2, the band gap decreases to 1.03 eV. Up- and down-DOS are again symmetrical, and indicate that the F2 adsorbed monolayer MoS2 is also non-magnetic.

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References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Nature, 438 (2005) 197.
http://dx.doi.org/10.1038/nature04233

[2] E. L. Wolf, Application of Graphene, Springer, Brooklyn, USA, 2014.
http://dx.doi.org/10.1007/978-3-319-03946-6

[3] E.S.Kadantsev, P.Hawryla, Sol. St. Comm., 152 (2012) 909-913.
http://dx.doi.org/10.1016/j.ssc.2012.02.005

[4] S. Lebegue and O. Eriksson, Phy. Rev. B, 79 (2009) 115409.
http://dx.doi.org/10.1103/PhysRevB.79.115409

[5] D. Lembke, S. Bertolazzi, A. Kis, Acc. Chem. Res., 1(2015) 48.
http://dx.doi.org/10.1021/ar500274q

[6] T. P. Kaloni, R. P. Joshi, N. P. Adhikari and U. Schwingenschlogl, Appl. Phys. Lett., 104 (2014) 073116 .
http://dx.doi.org/10.1063/1.4866383

[7] Q. Yue, S. Chang, S. Qin and J. Li Phy. Lett. A., 377 (2013) 1362-1367.
http://dx.doi.org/10.1038/ncomms7298

[8] Y. Wang, B. Wang, R. Huang, B. Gao, F. Kong and Q. Zhang Physica E., 63 (2014) 276-282.
http://dx.doi.org/10.1063/1.4922419

[9] P. Hohenberg and W. Kohn, Phys. Rev. B, 136 (1964) 864.
http://dx.doi.org/10.1103/PhysRev.136.B864

[10] W. Kohn and L. J. Sahm, Phys. Rev. , 140(1965) 1133.
http://dx.doi.org/10.1103/PhysRev.140.A1133

[11] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, et al., J. Phys., Condens. Matter, 21 (2009)395502.
http://dx.doi.org/10.1088/0953-8984/21/39/

[12] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 77 (1996) 566.
http://dx.doi.org/10.1103/PhysRevLett.77.3865

[13] S. Grimme, J. Comput. Chem., 25 (2004) 1463.
http://dx.doi.org/10.1002/jcc.20078

[14] S. Grimme, J. Comput. Chem. 27 (2006)1787.
http://dx.doi.org/10.1002/jcc.20495

[15]B. G. Pfrommer, M. Cote, S. G. Louie, M. L. Cohen, J. Comput. Phys., 131 (1997) 233.
http://dx.doi.org/10.1103/PhysRevB.80.235418

[16] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, Phys. Rev. lett., 82 (1999) 3296 .
http://dx.doi.org/10.1103/PhysRevLett.82.3296

[17] K. Novoselov, D. Jiang, F. Schedin, T.Booth, V.Khotkevich, S.Morozov and A. Geim, Proc. Natl. Acad. Sci. U.S.A., 102 (2005) 1045.
http://dx.doi.org/10.1073/pnas.0502848102

[18] F. Karlicky, R.Zboril and M. Otypka , J. Chem. Phys., 137 (2012) 034709.
http://dx.doi.org/10.1063/1.4736998

[19] X. Li, S. Wu, S. Zhou and Z. Zhu, Nano. Res. Let., 9 (2014) 110.
http://dx.doi.org/10.1186/1556-276X-9-110