First-Principles Studies on Effect of Functionalization and Adsorption of Various Gases on Two-Dimensional Nanostructures

By Dhanshree Pandey PHYS03201504002

Raja Ramanna Centre for Advanced Technology, Indore

A thesis submitted to the

Board of Studies in Physical Sciences

In partial fulfilment of requirements For the Degree of DOCTOR OF PHILOSOPHY

of

HOMI BHABHA NATIONAL INSTITUTE



June, 2021

Homi Bhabha National Institute¹

Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by Dhanshree Pandey entitled "First-Principles Studies on Effect of Functionalization and Adsorption of Various Gases on Two-Dimensional Nanostructures", and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

Chairman - Prof. Tarun Kumar Sharma	Date: 25/06/2021
Guide / Convener - Prof. Aparna Chakrabarti Aparna Chakrabarti	Date: 25/06/2021
Examiner - Prof. Manish Jain Manish L	Date: 25/06/2021
Member 1 - Prof. A. K. Sinha	Date: 25/06/2021
Member 2 - Prof. M. K. Chattopadhyay	Date: 25/06/2021
Member 3 - Prof. T. K. Ghanty Japan me Shanty	Date: 25/06/2021

Final approval and acceptance of this thesis is contingent upon the candidate's submission of the final copies of the thesis to HBNI.

I/We hereby certify that I/we have read this thesis prepared under my/our direction and recommend that it may be accepted as fulfilling the thesis requirement.

Date: 25/06/2021

Place: RRCAT, Indore

Aparna Chakrabarti

Signature Guide - Prof. Aparna Chakrabarti

¹ This page is to be included only for final submission after successful completion of viva voce.

STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at Homi Bhabha National Institute (HBNI) and is deposited in the Library to be made available to borrowers under rules of the HBNI.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgement of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the Competent Authority of HBNI when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

Shanshree

Dhanshree Pandey

DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

Shanshree

Dhanshree Pandey

List of Publications Arising From The Thesis

Journals

"First-principles study of adsorption of 3d and 4d transition metal atoms on aluminene",
 D. Pandey, C. Kamal, A. Chakrabarti
 Computational Condensed Matter, **2018**, 16, e00319.

2: "Intercalation of transition metals in aluminene bi-layers: An ab initio study", D. Pandey,
C. Kamal, A. Chakrabarti
The Journal of Chemical Physics, 2019, 150, 194702.

3: "Prediction of two-dimensional monochalcogenides: MoS and WS", **D. Pandey**, A. Chakrabarti

Physics Letters A, **2019**, 383, 2914.

4: "Stacking-dependent electronic properties of aluminene based multilayer van der Waals heterostructures", **D. Pandey**, A. Kumar, A. Chakrabarti, R. Pandey Computational Material Science, **2020**, 185, 109952.

5: "Improved Gas Adsorption on Functionalized Aluminene Surface: A First-Principles Study", D. Pandey, C. Kamal, R. Dutt, A. Chakrabarti Applied Surface Science, 2020, 531, 147364.

6: "Isoelectronically substituted group-III based monolayers: An ab initio study", C. Kamal, **D. Pandey**, A. Chakrabarti
Physical Review B, **2020**, 102, 085424.

Conferences

7: "Transition metal intercalated bilayer silicene", **D. Pandey**, C. Kamal, A. Chakrabarti AIP Conference Proceedings, **2018**, 1942, 050096.

8: "Strain Induced Magnetism and Half-Metallicity In Alkali Metal Substituted Aluminene",
D. Pandey, C. Kamal, A. Chakrabarti
AIP Conference Proceedings, 2019, 2115, 030351.

9: "Two dimensional monolayers of arsenides and silicides of Mo and W: A First Principles Study", **D. Pandey**, A. Chakrabarti AIP Conference Proceedings, **2020**, 2265, 030702.

Not included in the thesis

Journals

1: "Probing the possibility of coexistence of martensite transition and half-metallicity in Ni and Co-based full-Heusler alloys: An ab initio calculation", T. Roy, **D. Pandey**, A. Chakrabarti

Physical Review B, **2016**, 93, 184102.

2: "Unusual magnetic and electronic properties of Al-substituted Ga2MnNi: An ab initio study", A. Chakrabarti, J. Bhattacharya, R. Dutt, **D. Pandey** Journal of Magnetism and Magnetic Materials, **2019**, 490, 165521.

3: "Probing the Martensite Transition and Thermoelectric properties of CoxTaZ (Z = Si, Ge, Sn and x = 1, 2): A Study Based on Density Functional Theory", R. Dutt, **D. Pandey**, A. Chakrabarti

Journal of Physics: Condensed Matter, **2020**, 33, 045402.

4. "High-Performance Lithium-Ion Batteries Using Layered 2H-MoTe2 as Anode", M. R. Panda, R. Gangwar, D. Muthuraj, S. Sau, **D. Pandey**, A. Banerjee, A. Chakrabarti, A. Sagdeo, M. Weyland, M. Majumder, Q. Bao, S. Mitra Small, **2020**, 2002669.

5. "Electronic structure and morphology of thin surface alloy layers formed by deposition of Sn on Au(111)", P. Sadhukhan, **D. Pandey**, V. K. Singh, S. Sarkar, A. Rai, K. Bhattacharya, A. Chakrabarti and S. R. Barman Applied Surface Science, **2020**, 506, 144606.

6. "Ab Initio study of adsorption of fission gas atoms Xe and Kr on MoS2 monolayer functionalized with 3d transition metals", R. Gangwar, **D. Pandey**, S. Kancharlapalli, D. Raychaudhuri, A. Chakrabarti, A. Banerjee, T. Ghanty Accepted for publication in Journal of Physical Chemistry C, **2020**.

Shanshree

Dhanshree Pandey

To my extended family

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my supervisor, Prof. Aparna Chakrabarti, for her constant help, encouragement, and patience throughout my Ph.D. period. Her precious suggestions and constructive criticisms have always helped me communicate the scientific results in an efficient manner. She has always encouraged me to get involved in works other than my thesis project to enhance my skill and knowledge in other fields as well. I would also like to take the opportunity to express my sincere gratitude to Prof. Chakrabarti for her caring and motherly attitude towards me and for providing a homely environment here. I feel fortunate to have her as my thesis supervisor. I am also extremely thankful to Dr. C. Kamal for his rigorous mentoring, continuous support, and encouragement. He has always helped me a lot in improving my basic concepts and other academic skills. He has always motivated and guided me thoroughly in my Ph.D. work. Prof. Chakrabarti and Dr. C. Kamal have always shown immense faith and provided me a healthy environment to work and develop my skills in my own way. It would be impossible to count all the ways that they both have helped me in my career. I could not have imagined having a better advisor and mentor for my Ph.D. study, and I would be happy if I can adopt a few qualities from them.

I thank Prof. Arup Banerjee for fruitful discussions, which helped me a lot in the understanding of density functional theory. He gave constant support and also some valuable suggestions about my work. I would like to extend my sincere thanks to Prof. S. R. Barman for his valuable suggestions and support. I express my thanks to all the members of the doctoral committee. I thank Prof. T. K. Ghanty for his suggestions, specifically on the structure of the thesis. Prof. T. K. Sharma, Prof. A. K. Sinha, and Prof. M. K. Chattopadhyay are also thanked for their constant support and guidance. I am also thankful to Prof. S. R. Mishra, Prof. V. Kumar, Prof. A. Moorti, Prof. M. P. Singh, Prof. S. Bulusu, and Prof. H. Ghosh for their valuable suggestions. I thank Prof. A. Arya for his time for discussions.

I express my sincere gratitude to my collaborator Prof. Ravindra Pandey from Michigan

Technological University (MTU), for providing me an opportunity to work in his group, and develop additional skills. I thank him for all his support, constant mentoring and valuable suggestions in academic areas. Besides, I would also thank him for his non-academic support during my stay at MTU. I also thanks Prof Ashok Kumar from the Central University of Punjab, for his support and fruitful discussions.

Mr. P. Thander is thanked for all the help during the installation and running of the codes used in my Ph.D. work and computer division, RRCAT, is thanked for providing the computational facility. Director, RRCAT, group director and associate group director of Materials Science group board, and all the members of HRDS and SUS are thanked for their constant support and all the facilities. I would also like to thank Dr. C. P. Paul for his support throughout.

I thank my seniors Krishnakanta Mondal, Tufan Roy, and Smritijit Sen for their help and support in my initial period of Ph.D. They helped me in understanding various things related to computational simulations. I would like to thank all my seniors, especially Debashis da, Aditya Sir, Arijit Sir, Subhomoy sir, Rijul sir, Mangalika mam, Charu mam, and all my juniors, including Megha, Soumyadeep, Kiran, Sumit, Amit. I express my deepest thank you towards my juniors Rajeev and Joydipto and also Rashmi and Madhu mam. I am surely going to miss the time spent with them. I extend my thanks to my friends and batchmates, especially Azam, Preeti, Sabina, Lokesh, Jyoti, Shama, and Sushil, who always stood beside me in the different stages of my academic life. I also thank Geeta, Amreen, Cameron, and Sarvada, who made my stay in Michigan, USA, wonderful.

I would especially like to thank my sister, Sudha, for her constant support and for always being there for me. Above all, it would not have been possible for me to achieve this milestone in my research career without the encouragement and support from all my family members. I express my deepest gratitude for their endless sacrifice, support, and love.

> Hanshree Dhanshree Pandey

Contents

	SUMMARY	i
L	IST OF FIGURES	iv
L	IST OF TABLES	ix
1	Introduction 1.1 Introduction to Nanostructures 1.1.1 Uniqueness of Nanostructures 1.2 Materials at the Nanoscale 1.2.1 Carbon-based 2D Monolaver Graphene	$1 \\ 1 \\ 2 \\ 4 \\ 4$
	1.2.22D Nanostructures beyond Graphene1.2.2.1Motivation to study monoelemental 2D Aluminene1.2.2.2Motivation to study Binary 2D Monolayers	
	1.3Functionalization of 2D systems1.4van der Waals heterostructures of 2D systems1.52D systems as Gas Sensors1.6Outline of the Thesis	$13 \\ 16 \\ 18 \\ 19$
2	Computational Methodology	22
	2.1 Introduction 2.1.1 Schrödinger Equation 2.1.2 Born-Oppenheimer Approximation	$22 \\ 23 \\ 23$
	2.2 Density Functional Theory 2.2.1 2.2.1 The Hohenberg-Kohn Formulation Of Density Functional Theory 2.2.1.1 Hohenberg-Kohn First theorem 2.2.1.1	$25 \\ 26 \\ 26$
	2.2.1.2 Hohenberg-Kohn Second Theorem 2.2.2 Kohn-Sham Approach 2.2.3 Various Exchange-Correlation Functionals	$27 \\ 28 \\ 30$
	2.2.4Vienna Ab Initio Simulation Package (VASP)2.2.5Phonopy2.2.6Boltztrap:	31 33 33
3	Prediction of energetically stable β_{12} phase of Aluminene	34
	3.1 Introduction 3.2 Results and Discussion 3.2.1 Group III Atom Based Monolayers 3.2.1.1 Geometric Structure and Energetic Stability 3.2.1.2 Floatmania Dramatica	$ \begin{array}{r} 34 \\ 35 \\ 36 \\ 36 \\ 40 \end{array} $
	3.2.1.2 Electronic Properties 3.2.2 Effect of iso-electronic substitution 3.2.2.1 Geometric structure and energetic stability	$40 \\ 42 \\ 42 \\ 45 \\ 45$
	3.3 Summary	47
4	Functionalization of 2D Aluminene 4.1 Introduction 4.2 Results and Discussion 4.2.1 Transition Metal Adsorbed Aluminene 4.2.1.1 Analysis of Energetics and Geometry 4.2.1.2 Analysis of Charge Distribution and Charge Transfer 4.2.1.3 Electronic and Magnetic Properties	49 49 50 50 51 55 57

		4.2.2 Transition Metal Substituted Aluminene 60 4.2.2.1 Geometric and Energetic Stability 60 4.2.2.2 Charge Analysis 63
		4.2.2.3 Electronic and Magnetic Properties
		4.2.3 Intercalation of Transition Metals in Aluminene bilayers
	4.3	4.2.3.2 TM-intercalated bilayer aluminene
5	Alu:	minene based van der Waals heterostructures 81 Introduction 81
	5.2	Results and Discussion
		5.2.2 BN/Aluminene/BN Trilayer heterostructures
	5.3	Summary
6	Pre	diction of Two-Dimensional Binary Monolayers Based on Mo and W 95
	$6.1 \\ 6.2$	Introduction
		6.2.1.1 Structure and Energetics
		6.2.1.3 Electronic Structure
		6.2.1.5 Effect of Hybrid functional on the electronic band structure 107
		MoSi/WSi
	0.0	6.2.2.1 Energetics, Geometry and Charge Analysis
	6.3	Summary
7	Gas 7.1	Adsorption on 2D Surfaces 113 Introduction 113
	7.2	Results and Discussion
		7.2.1.1Adsorption of H_2 gas molecule1157.2.1.2Adsorption of CO gas molecule121
		7.2.1.3 Adsorption of NO gas molecule
		7.2.3 Gas adsorption on MoS and WS
		7.2.3.2 Adsorption of CO and NO gas molecule
	7.3	Summary

8 Summary and Conclusion

 $\mathbf{148}$

List of Figures

1.1	Schematic representation of bulk and quantum structures. L_X, L_Y, L_Z are the length of the material along the X, Y and Z directions and λ is the de-Broglie of the electron. Figure courtesy-Reference: [8]	3
1.2	Carbon based nanostructures like carbon nanotubes, fullerenes (buckyball), or bulk structure, graphite, by the different arrangement of a 2D nanostructure called graphene. Unit cell and the lattice unit vectors $(a_1 \text{ and } a_2)$ of graphene are also shown.	5
1.3	The electronic bands of graphene along $\Gamma - M - K - \Gamma$ direction.	6
1.4	Different allotropes of 2D aluminene	10
3.1	The geometric structure (top and side views) of the group III based monolayer in β_{12} structure in $2 \times 2 \times 1$ super cell configuration. The dashed rectangle represents the unit cell, with lattice constants a and b. A, B and C are the inequivalent atomic sites. d, θ and h represent the bond distances, bond angles and vertical heights	2.6
3.2	between the nearest neighbors, respectively. Spatial distribution of valence charge density for the group III based monolayers. 0 (blue) and 1 (red) in the bar scale represent the charge deficit and the charge rich region, respectively. Bader charges on symmetrically inequivalent atoms (1(2), 3(4) and 5, respectively, at the sites A, B and C) are shown.	30 39
3.3	The electronic band structures of the group III based monolayers in β_{12} configuration. The blue circles indicate the locations of linear band crossings (Dirac-like cones). The Fermi energy is set to 0 eV.	40
3.4	The binding energy of the group III based monolayers in β_{12} configuration as a function of iso-electronic substitution.	43
3.5	Variation of geometrical parameters with iso-electronic substitution for the group III based monolayers in β_{12} configuration.	44
3.6	Bader charges on atoms (shown in the inset) in the β_{12} structure. Negative charge signifies that the atom has gained electron and positive charge represents that the atom has lost electron	15
3.7	The electronic band structures of group III based monolayers in β_{12} configuration	40
	with iso-electronic substitution. The blue circles indicate the locations of linear band crossings (Dirac-like cones). The Fermi energy is set to 0 eV.	46
4.1	Aluminene (planar): (a) bare and with TM atoms adsorbed at different sites namely (b) Hollow (H) , (c) Top (T) and (d) Bridge (Br) ; top and side views are given in upper and lower panels respectively. Pink and blue balls represent aluminium and TM atoms, respectively. A and B represent two inequivalent Al atoms of the unit cell. (e),(f), (g) and (h) represent the same for bare silicene (arsenene) and TM adsorbed at different sites, respectively. Red and green balls represent silicon (arsenic) and TM atoms, respectively.	50
4.2	Binding energy per atom (in $eV/atom$) for 3d ((a), (c), (e)) and 4d ((b),(d),(f)) TM atoms adsorbed on different sites of planar aluminene as well as buckled silicene and arsenene as a function of atomic number (Z) of the TM atom. In the inset, plot is given for interaction energy (in eV) for adsorption at the site, which corresponds to the lowest energy configuration, as a function of Z of TM atoms.	52

4.3	Net charge on atoms using Bader method and electronegativity difference between TM and Al atoms as a function of Z is plotted for (a) 3d and (b) 4d TM atoms adsorbed on aluminene in the upper and lower panels, respectively for the T configuration for all systems except for Y (which favors H -site). (c) and (d) show the variation of electronegativity difference with Bader charges on 3d and 4d TM atoms. Dotted line is a guide to the eye. Charges on atom is obtained by taking the difference of the charge obtained from performing Bader analysis and the valence charge of the atom in the atomic limit (as defined in the atomic pseudopotential), i.e. positive	
4 4	charge on atom indicates electron denciency and negatively charged atom represents electron rich atom.	56
4.4	atom adsorbed aluminene at the three crystallographically inequivalent adsorption sites.	57
4.5	Spin-polarized (a) total density of states (TDOS) and (b), (c) and (d) partial density of states (PDOS) of 3d electronic orbitals for 3d TM atom adsorbed aluminene. The Fermi level has been set to zero and indicated by a vertical black dashed line. TDOS and PDOS are in the units of states/eV.	59
4.6	Comparison between the DOS of H and T -configuration for Co, Fe and Ti adsorbed	60
4.7	Schematic of top and side views of the optimized geometry of transition metal (TM = Sc-Cu) atom substituted 5×5 supercell of Aluminene. h is the height of the TM atom from the top layer of Aluminene. TM atom lies above and below the top layer of Aluminene lattice for (a) Sc, Ti and (b) V to Cu, respectively.	61
4.8	(a) Binding energy per atom (in units of eV/atom), (b) TM-Al bond distances and height of TM (in Å), (c) Bader charges on TM atoms (in units of e) and (d) magnetic moment (in units of μ_B) for 5×5 cell of TM-substituted Aluminene.	62
4.9	Total density of states (DOS) and partial density of states (PDOS) (in units of states/eV) for TM-substituted aluminene systems.	65
4.10	Top and side views of different starting configurations of pristine mono-layer buckled aluminene.	67
4.11	Different stacking configurations of pristine bilayer aluminene. (a)-(g) First and second panels from the top give the top and side views of the valence charge density distributions of the seven different configurations. (h)-(n) Third (bottom) panel exhibits the results of ELF calculations along (110) plane.	69
4.12	Electronic band structures for different configurations of pristine bilayer aluminene. Red (solid line) and blue (dashed line) colored bands represent bands without and with van der Waals dispersion correction, respectively. E_F is set to 0 eV.	71
4.13	Top and side views of initial geometries (schematic) of various possibilities of TM intercalation in different stacking configurations of pristine bilayer aluminene. Solid black line represents the unit cell.	72
4.14	(a) Optimized structure and (b) Formation energy (E_{form}) and binding energy per atom (E_B/atom) for TM intercalated bilayer aluminene. Blue balls represent Al atoms and different colored balls represent various TM atoms. Angle between a and b axes is 90° for Ti, Co and Ni cases.	73
4.15	Plot of (a) Bader charge versus electronegativity difference and (b) ELF for TM intercalated bilayer aluminene along (110) plane for minimum energy configurations.	75
4.16	Fermi surface for (a) Ti, (b) Co and (c) Ni intercalated bilayer aluminene. Red colored arrow shows the probable nesting vector. Momentum vectors corresponding to the first (leftmost) and the last (rightmost) bands crossing E_F are marked in this figure. k-vectors corresponding to bands crossing between the leftmost and rightmost bands are numbered in the ascending order, which are marked in the Fermi surface plot adjacent to the band structure. Due to lack of space, only the leftmost and rightmost k-points are marked in the left panels (band structures), and the numbers increase from left to right. In the right panels which depict the FS though, we mark almost all the k-point vectors.	77

5.1	Top and side views of aluminene/BN in AA, AB and AB' stacking configurations. E_B is the binding energy per atom and d is the interlayer distance. Green, grey and pink colored balls represent B, N and Al atoms, respectively.	83
5.2	Top and side views of the calculated valence charge density distribution (VCDD) for the aluminene/BN bilayers in different stacking configurations, with an isovalue of 0.03 e/A^3 . Yellow colored region depicts the electron rich region.	85
5.3	Orbital projected density of states and band structure for (a) pristine monolayer aluminene with intralayer Al-Al bond distance of 2.59 Å, (b) strained monolayer aluminene with intralayer Al-Al bond distance of 2.90 Å. Fermi energy (E_F) has been set to 0 eV.	86
5.4	Orbital projected band structures of AA, AB and AB' configurations of aluminene/BN. Fermi energy (E_F) is set to 0 eV. Insets represent the band dispersions for AA, AB and AB'-stacked configurations in the energy interval of -0.2 to 0.2 eV. Red, green, blue and orange colored bands represent the Al-s, Al-p, B-p and N-p orbitals, re- spectively (as shown in legend in the AA case).	87
5.5	Evolution of band structures of AB and AB' stacking configuration of aluminene/BN bilayers with a variation in the interlayer distance (d) in Å. Fermi energy (E_F) has been set to 0 eV.	88
5.6	Top and side views of BN/aluminene/BN stacked in AAA, ABA, AB'A and ABC configurations. R (Å) is the thickness of the heterostructure. E_B is the binding energy per atom. Green, grey and pink colored balls represents B, N and Al atoms,	20
5.7	Top and side views of the valence charge density distribution (VCDD) for the BN/aluminene/BN heterostructures in AAA, ABA, AB'A, and ABC stacking configurations, with the isovalue of 0.03 e/A ³ . Yellow colored region denotes the electron rich region.	89 90
5.8	Orbital projected band structures of (a) AAA, (b) ABA, (c) AB'A and (d) ABC stacked configurations of BN/aluminene/BN. Fermi energy (E_F) is set to 0 eV. Insets in (b), (c) and (d) represent the band dispersions for ABA, AB'A and ABC stacked configurations in the energy interval of -0.6 to 0.6 eV, respectively. Red, green, blue and orange colored bands represent the Al-s, Al-p, B-p and N-p orbitals, respectively (as shown in legend in (a)).	91
5.9	Calculated band structure for AAA stacked configuration of BN/aluminene/BN tri- layer with interlayer distance of 3.08 and 3.56 Å. Fermi energy (E_F) has been set to	0.9
5.10	Comparison of DOS for ABA configuration for BN/aluminene/BN case (lowest en- ergy configuration) with GGA-PBE and HSE06 hybrid functionals. Fermi energy (Ep) has been set to 0 eV	92
5.11	The I-V characteristics and density of states for AB stacked bilayer and ABA stacked trilayer heterostructures of aluminene and BN. Al/BN stands for aluminene/BN heterostructures.	92 93
6.1	Schematics of different possible configurations for XS ($X = Mo, W$): (a) planar, (b) buckled and (c) puckered configuration. The solid line indicates the unit-cell. Gray and red balls represent Mo/W and S atoms, respectively.	97
6.2	Valence charge density distribution (VCDD) for optimized geometry for (a) MoS- buckled, (b) WS-buckled, (c) MoS-puckered and (d) WS-puckered configurations. The solid line indicates the unit-cell. Gray and red balls represent Mo(W) and S atoms, respectively. Note that the yellow region indicates the electron rich re- gion, consequent to that, the gray color of Mo(W) is not clearly visible. (e), (f), (g) and (h) represent the phonon dispersion curves for MoS-buckled, WS-buckled, MoS-puckered and WS-puckered configurations, respectively. WS-puckered case (h) exhibits negative frequency with substantial values, near the Γ point	100

6.3	Band structure, partial density of states (PDOS) and bands with spin-orbit interac-	
	tion. (a)-(c) show the band structure plot, (d)-(f) represent the PDOS and (g)-(i) exhibit the band with the inclusion of spin-orbit coupling. X in the figure reperesents	
	Mo and W. MoS-buckled, WS-buckled and MoS-puckered cases are shown in left, middle and right papels respectively. (i) and (ii) in the inset of (b) and (c) respectively.	
	tively show the Brillouin zone for the buckled and the puckered system, respectively	101
64	Orbital projected density of states (DOS) for buckled monolayer of (a) MoS and (b)	101
0.1	WS DOS is in units of states /eV Inset shows partial charge densities corresponding	
	to band point CΓ shown in Fig.5(b.d).	102
6.5	Atom projected partial band structure for buckled monolaver of (a) MoS ₂ and (b)	
	MoS, (c) WS ₂ and (d) WS. X in the legend corresponds to Mo and W atoms. $C\Gamma$	
	and $V\Gamma$ represent the Γ -point in the conduction and valence band regimes, respectively	.103
6.6	Evolution of band structure due to bi-axial tensile and compressive strain on WS-	
	buckled system. Tensile strain causes opening of a bandgap	105
6.7	Orbital projected DOS (in units of states/eV) corresponding to +8% tensile strain for buckled (a) MoS and (b) WS. (c) Binding energy per atom (eV/atom) of monolayer	
6 9	buckled MoS and WS as a function of strain.	107
0.0	and HSE06 hybrid functionals. Fermi energy (E_{T}) has been set to 0 eV	107
6.0	(a) Optimized geometry for the Mo/W argenides and silicides in the (I) buckled	101
0.3	and (II) puckered configurations. Brown and blue colored balls represent Mo/W	
	and Si/As atoms, respectively. (b) Difference charge density (DCD) for (I) buckled	
	configuration and (II) puckered configuration, respectively. Yellow and cyan colors	
	denote the electron rich and deficit regions, respectively.	108
6.10	Band structures along the high symmetry directions for (I) buckled and (II) puckered	
	configuration respectively. Fermi energy (E_F) has been set to 0 eV	111
7.1	Schematic of optimized geometry (top and side view) of H_2 gas molecule adsorption	
	on Aluminene and IM-Aluminene (IM = II, Cr, Fe and Co). Blue, cream and group colored balls denote Al H and TM storms, respectively.	117
7 2	(a) Difference charge density (DCD) for H ₂ adsorbed Aluminene and TM Aluminene	111
1.2	(TM=Ti Cr. Fe and Co) systems. Red and green colored regions show electron rich	
	and electron deficit regions respectively. The DCD are plotted with 0.002 e/A^3 for	
	Aluminene and TM-Aluminene, respectively, for all the cases of gas adsorption. (b)	
	and (c) represent total density of states (DOS) and partial density of states (PDOS)	
	of H_2 gas adsorbed systems. The Fermi level has been set to zero and indicated by	
	a vertical black dashed line. The brown-shaded area in (b) corresponds to the DOS	
	of H_2 adsorbed systems with red colored boundary	120
7.3	Schematics of optimized geometry (top and side view) of adsorption of CO gas	
	balls denote Al C O and TM atoms respectively	122
74	(a) Difference charge density (DCD) for CO adsorbed Aluminene and TM-Aluminene	122
1.1	(TM=Ti, Cr. Fe and Co). Red and green colored regions show electron rich and	
	electron deficit regions, respectively, for all the cases of gas adsorption. (b) and	
	(c) represent total density of states (DOS) and partial density of states (PDOS) of	
	CO gas adsorbed systems. The Fermi level has been set to zero and indicated by a	
	vertical black dashed line. The brown-shaded area in (b) corresponds to the DOS of	
	CO adsorbed systems with red colored boundary.	124
7.5	Partial density of states (PDOS) of TM (=Ti, Cr, Fe and Co) atoms (d_{z^2} or d_{σ}	
	and a_{π} or $a_{xz,yz}$) and molecular orbitals (5 σ and 2 π) for the comparison of CO	
	gas molecule before and after adsorption. FDO5 for each 1 M atom has sub-figures (from upper to lower panel) corresponding to $CO.5\sigma$ (2π) orbitals in isolated and	
	in adsorbed cases and $TM-d_{\pi}$ (d_) states with and without gas adsorbtion. Note	
	that the DOS corresponding to the CO-adsorbed case is the sum of the C and O	
	contributions	125

7.6	Variation of E_{ads} and d-band centre (dbc with respect to Fermi level (0 eV)) as a function of TM atoms for the CO adsorbed systems.	127
7.7	(a) Difference charge density (DCD) for NO adsorbed Aluminene and TM-Aluminene	
	(TM=Ti, Cr, Fe and Co). Red and green colored regions show electron rich and	
	electron deficit regions, respectively, for all the cases of gas adsorption. (b) and	
	(c) represent total density of states (DOS) and partial density of states (PDOS) of	
	NO gas adsorbed systems. The Fermi level has been set to zero and indicated by a	
	vertical black dashed line. The brown-shaded area in (b) corresponds to the DOS of	
	NO adsorbed systems with red colored boundary.	130
7.8	Top and side views of the optimized geometry for the H_2 adsorbed MoS/WS system.	136
7.9	(a) 3D and 2D (slice) plots for difference charge density (DCD). Red and green (blue	
	for 2D slice) region show the charge accumulated and depleted regions, respectively.	
	(b) Total density of states (DOS) for the H_2 adsorbed MoS/WS system for the lowest	105
7 10	energy configuration.	137
1.10	10p (and side) views of the optimized geometry for the CO/NO adsorbed MoS/WS	190
7 1 1	(a) Difference charge density (DCD). Bud and groop region show the charge accu	199
1.11	mulated and depleted regions respectively. (b) Total density of states (DOS) for the	
	CO adsorbed MoS/WS system for the lowest energy configuration (c) represents the	
	partial DOS corresponding to the CO molecule in the isolated (blue dashed line) and	
	adsorbed (red colored) phase. Note that the DOS corresponding to the CO-adsorbed	
	case is the sum of the C and O contributions	142
7.12	(a) Difference charge density (DCD). Red and green region show the charge accu-	
	mulated and depleted regions, respectively. (b) Total density of states (DOS) for the	
	NO adsorbed MoS/WS system for the lowest energy configuration. (c) represents the	
	partial DOS corresponding to the NO molecule in the isolated (blue dashed line) and	
	adsorbed (red colored) phase. Note that the DOS corresponding to the NO-adsorbed	
7 1 9	case is the sum of the N and O contributions.	143
(.13	Molecular LUMO and HOMO levels and Fermi-level (E_F) of the pristine MoS and WS monolevers. The error represents the direction of transfer of charge from the	
	sheet to the LUMO of the molecule	144
	sheet to the DOMO OF the molecule	1.4.4

List of Tables

3.1	Binding energies and geometrical parameters for the group III element based mono- layers in β_{12} configuration.	37
4.1	Geometric and energetic data for different configurations (case I through case VII) of pristine bilayer aluminene. d_1 and d_2 represent intra and interlayer (vertical) Al-Al distances, respectively. Values in parentheses are results from calculations performed with van der Waals interaction. The values of lattice constants a and b are same, $\alpha=\beta=90$ and $\gamma=120$ degrees. Values of a , d_1 and d_2 are in Angstrom. E _B /atom is binding energy per atom in units of eV/atom. E_{form} is the formation energy in units of kJ/mol	68
	$\operatorname{Im}_{\mathcal{B}}^{\mathcal{B}} \operatorname{Im}_{\mathcal{B}}^{\mathcal{B}} Im$	
5.1	Geometric, energetic and electronic properties of aluminene/BN heterostructures calculated at the DFT-D2 level of theory.	84
6.1	Binding energy per atom (E_B/atom) in units of eV/atom for different configurations	
6.26.3	for MoS and WS monolayers. Geometric and energetic data for the buckled and puckered configurations of MoS and WS monochalcogenide. E_B /atom and a represent the binding energy per atom (in eV/atom) and the lattice constants, respectively. Δ is the buckling parameter, d_1 and d_2 represent X-S and X-X bond distances, respectively. Values of a , Δ , d_1 and d_2 are in Angstrom. α and β represent the bond angles (in degrees) S-X-X and S-X-S, respectively, where X = Mo and W. ΔQ shows the amount of Bader charge transfer between the X and S atoms in the units of e. Lattice constant (a), buckling parameter (Δ), W-S bond distance (d_1), W-S-W bond	98 99
	angle (α) and the bandgap (E_g) are tabulated for different tensile bi-axial strain. a ,	106
6.4	Structural parameters and energetic data for different configurations of MoY and WY (Y = Si, As) binary systems. $E_B/atom$ and a, b represent the binding energy per atom (in eV/atom) and the lattice constants, respectively. Δ is the buckling parameter, d ₁ , d ₂ represent the Mo/W-Y bond distances. Values of a, b, Δ, d_1 , d ₂ are in units of Å. $\alpha, \beta, \gamma, \delta$ (in deg) represent the angles shown in Figure 6.9. Last column indicates whether the structure is dynamically stable from the phonon dispersion calculation or not.	110
7.1	E_{ads} is the adsorption energy, Δq is the Bader charge on H ₂ gas molecule. H-H is the distance between the two H atoms in H ₂ molecule after adsorption. D is the molecule-surface distance after optimization. Negative value of Δq indicates that the gas molecule has gained electron from the 2D surface.	116

7.2	E_{ads} is the the adsorption energy, Δq is the Bader charge on CO gas molecule. C-O is the distance between C and O atoms in CO molecule after adsorption. D is the	
	molecule-sheet distance after optimization.	123
7.3	E_{ads} is the adsorption energy, Δq is the Bader charge on NO gas molecule. N-O is	
	the distance between N and O atoms in the NO molecule after adsorption. D is the	
	molecule-sheet distance after optimization.	128
7.4	Percentage change (%) in the quantity σ' for the H ₂ , CO and NO gas adsorbed	
	systems in the lowest energy configurations calculated using Eq. 7.1.	133
7.5	E_{ads} is the adsorption energy. Δq is the Bader charge on H ₂ gas molecule. d_{H-H} is	
	the distance between the two H atoms in the H ₂ molecule after adsorption. Δh is	
7.0	the vertical distance between the sheet and the molecule.	136
7.6	E_{ads} is the adsorption energy. Δq is the Bader charge on CO gas molecule. d_{C-O} is	
	the distance between C and O atoms in the CO molecule after adsorption. Δn is the	
	vertical distance between the sneet and the molecule (atom of the molecule facing	1.40
	the sheet).	140
1.1	E_{ads} is the adsorption energy. Δq is the Bader charge on NO gas molecule. d_{N-O}	
	is the distance between N and O atoms in the NO molecule after adsorption. Δh	
	is the vertical distance between the sheet and the molecule (atom of the molecule	1.10
	facing the sheet).	140
7.8	Comparison of the listed adsorption energy values (E_{ads} in eV) for H ₂ , CO and NO	
	gas adsorption on different 2D nanostructures from literature, and studies carried	1 4 -
	out in this thesis.	145

Chapter 8

Summary and Conclusion

As discussed in the Introduction (Chapter 1) of this thesis, it is well-known that the study of two-dimensional (2D) materials is an active area of research because of the various fascinating properties and applications associated with this class of materials. The 2D materials have received enormous attention from researchers after the discovery of monoelemental 2D monolayer of carbon, namely, graphene. Due to the recent developments and exciting applications in the field of gas sensing, catalysis, and magnetic recordings, etc., metallic nanomaterials have appeared to be important in the emerging field of 2D materials, which makes them an appealing topic of research. Hence, in this thesis we focus our research primarily on 2D metallic systems, composed of aluminium atom.

Aluminium, a group III element, is the most abundant metal in the Earth's crust and the third most abundant element generally. It is lightweight, strong, and highly recyclable. These facts serve as a motivation to study various structural manifestations of aluminium at the nanoscale and their possible applications. Hence, the systems studied in this thesis include different allotropes of aluminene as well as van der Waals heterostructures of 2D planar aluminene. Moreover, the effect of functionalization (through adsorption, substitution and intercalation), specifically on the geometric and the electronic properties of various 2D allotropes of aluminene, has been studied. We also study few 2D monolayers beyond the monoelemental monolayer and compare various physical properties of the same with aluminene systems. In this direction, our focus is on few binary 2D monolayers based on transition metal atoms Mo and W. Finally, the ability of the 2D surfaces (pristine and functionalized aluminene and binary monolayers based on Mo/W) to serve as a suitable substrate for gas adsorption has also been discussed.

In this regard, firstly, we have performed density functional theory (DFT) based electronic structure calculations (discussed in Chapter 2) to analyze the geometric, electronic and magnetic properties of aluminium monolayer, named aluminene, and its allotropic modifications. Theoretical studies on various structures of aluminene in the literature include planar (P6/mmm), buckled (P3m1), 8-Pmmn, and a buckled triangular lattice (D2h-13 Pmnm). Because of the metallic bonding exhibited by the group-III elements, they exhibit several allotropes with interesting electronic properties, as was also observed for another group-III element, boron (2D monolayers of this atom is termed as borophene). The existence of a low-temperature β_{12} phase of borophene with the presence of low-energy fermionic excitations (Dirac cone), particularly near the E_F and the quest for new 2D Dirac materials have motivated us to study the hitherto unexplored β_{12} configuration made of aluminium atom. Hence, in Chapter 3 of this thesis, we have probed the possibility of stabilizing 2D aluminium monolayers in this particular configuration. For comparison, we also explore the possibility of finding another group-III element - gallium (referred to as gallenene), in this configuration. The results indicate that all the probed monolayers are energetically stable and possess metallic nature. Like borophene, the two monolayers also exhibit linear band crossings but these are lying much closer to the Fermi level compared to borophene. Besides, the Fermi velocities corresponding to the Dirac dispersions in aluminene and gallenene are found to be comparable to graphene. Thus, the observed location of the Dirac cones and the appreciable values of the Fermi velocity suggest that these 2D elemental monolayers may show exciting transport properties. Further, to tune the positions of the linear crossing observed in the pristine cases, we have also studied the influence of substitution of iso-electronic (B, Al, Ga, In and Tl) elements at the inequivalent C-site of β_{12} monolayers (borophene, aluminene, and gallinene). Interestingly, we find that when compared with the pristine cases, the positions of Dirac dispersion in many substituted systems lie closer to the Fermi level. Hence, iso-electronic substitution in the β_{12} configuration has been found to serve as a potential way to alter the electronic structure of group III based monolayers probed in this thesis.

In Chapter 4, we study the functionalization of planar as well as buckled aluminene by different means like adsorption, substitution, and the intercalation of transition metal (TM) and alkali metal (AM) atoms. Along this direction, we study the adsorption of first (3d (Sc-Cu)) and second (4d (Y-Ag)) row TM atoms on planar aluminene at different in-equivalent crystallographic sites (hollow, top and bridge). It is found that the TM atoms prefer to reside at the top site and that the optimized structure of TM-adsorbed planar aluminene exhibits a buckled geometry. A comparative study reveals that the adsorption of TM atom yields higher interaction energy in case of aluminene when compared with silicene and arsenene systems. Among all the 3d and 4d TM atoms adsorbed on aluminene, composite systems with Ti, V, Fe, Co, Ni (among 3d) and Tc, Ru, Rh (among 4d) are found to possess high interaction energy. Induced magnetism is also observed in some of the composite systems. Further, from the charge analysis, we observe that the amount of charge transfer (between TM and aluminene), and even the polarity can be tuned by varying the TM atom, which can be useful for the sensing of environmentally important gases. Alike the case of 3d TM adsorption on the aluminene, a similar trend of energetics, charge transfer, and magnetism has been observed for 3d TM-substituted aluminene. Compared to the TM-substituted aluminene, the substitution of AM atom (Li, Na and K) leads to a non-magnetic metallic electronic structure. However, the strain application on AM-substituted planar aluminene induces magnetism in the cases of substitution of Na and K, and half-metallicity is observed for 15% bi-axial tensile strain. In Chapter 4, we have also studied the intercalation of TM atoms (Ti, Cr, Mn, Fe, Co, and Ni) in bilayer aluminene systems. Interestingly, for Ti, Co, and Ni-intercalated systems, after full geometry optimization, the starting trigonal symmetry has been seen to change to a tetragonal symmetry. In addition, presence of parallel surfaces in the Fermi surface for Co and Ni intercalated systems indicate the presence of Fermi surface nesting and consequently, the possibility of the presence of charge density wave in these systems. Overall, the above studies based on functionalizing 2D non-magnetic monoelemental aluminene exhibit interesting geometric, electronic, and magnetic properties and may have important implications in the field of magnetism, spintronics, as well as for the sensing of environmentally important gases.

In Chapter 5, we explore the possibility of opening of bandgap in aluminene and providing a theoretical pathway towards a potential bandgap material. In this direction, using van der Waals (vdW) dispersion corrected DFT, we investigated the stability, structural and electronic properties of heterostructures of aluminene and BN monolayers, which are found to be stabilized by the vdW interaction. We have observed a strong dependence of the electronic structure on the stacking arrangements as well as on the number of layers in the heterostructure. The case of trilayers comprising aluminene and BN monolayer are predicted to be metallic except the case of ABA-stacked BN/aluminene/BN, which is found to be semiconducting in nature. Our present results suggest that unlike the graphene/BN heterostructures, where inequivalence of the carbon lattice leads to the bandgap, in the aluminene/BN heterostructures, opening up of the gap in the system is facilitated by the interaction of Al atoms with the N atoms.

Because of the increasing research interest in "post-graphene" structures, due to the possible application of these 2D materials in the areas of semiconductors, optoelectronics, photoelectronics, etc., probing the possibility of new 2D binary monolayers also has become an interesting topic of recent research. In this direction, in Chapter 6, we predict the stability of monolayered 2D monosulfides, arsenides, and silicides of Mo and W based systems. The buckled and the puckered structures are the two most stable configurations, as is evident from the results of binding energy calculations. For all the three binary systems, MX and WX (X = S, As, and Si), the puckered structure is found to be energetically the most

favorable structure. Non-magnetic metallic nature has been observed for both the MoS and WS-puckered structures. On the contrary, an indirect semimetallic nature with nonmagnetic behavior is observed for the WS-buckled system. An effect of strain application has been probed for MoS-buckled and WS-buckled configurations. An electronic transition from semimetal to an indirect bandgap semiconductor is found for the WS-buckled system upon applying tensile strain. Interestingly, we observe Dirac-like features close to E_F for MoSi and WSi in puckered (lowest energy) configurations, which may play an important role in the transport properties. Hence, from this study, we conclude that the silicides and sulfides of Mo/W can prove to be significant in the field of semiconductor physics and may also exhibit interesting transport properties.

Finally, in Chapter 7, we have probed the efficacy and suitability of some of the abovestudied systems, i.e., pristine and TM (Ti, Cr, Fe, and Co) functionalized aluminene and pristine Mo/W based monosulfides (MoS/WS), as gas sensors for the adsorption of H_2 , CO, and NO gases using, vdW dispersion corrected DFT. Interestingly, enhanced adsorption of all the gases for TM-substituted aluminene has been observed when compared to the pristine case. It has been found that the Kubas interaction plays an important role in stabilizing the H₂ adsorption on TM-substituted systems. CO and NO adsorption on TMaluminene surfaces have been successfully explained from the Blyholder model of the bonding of molecule to the TM atom through the frontier orbitals of the molecules. Moreover, the reactivity trend of TM-aluminene surfaces for CO/NO adsorption has been discussed based on the position of the TM d-band centre with respect to E_F and the spread of the TM d-bands. Analysis of recovery time and the percentage change in electrical conductivity for all the systems in their preferred lowest energy configurations indicate that aluminene and the TM-substituted aluminene (for H_2 and CO gases) may hold promises for the reusable gas sensor as well as gas storage. Further, a comparative analysis of gas adsorption on binary 2D monosulfides, MoS, and WS has also been performed. The study predicts that the adsorption of gases on these two surfaces is likely to be more significant in comparison to that of pristine and TM-substituted aluminene. Further, a comparative analysis of gas adsorption reveals that, in comparison with the pristine 2D systems studied in the literature, the 2D surfaces probed in this thesis, namely pristine and TM-substituted aluminene, and chalcogenides (S being the chalcogen) of Mo/W may fare better in terms of adsorption and sensing of these gas molecules.

In conclusion, this thesis attempts to predict new and novel 2D materials (monoelemental and binary) and their suitable functionalization in pursuit of potential applications. In this regard, successful predictions have been made about the possibility of (i) group-III-based aluminene 2D monolayers, with interesting Dirac cones lying close to the Fermi level with Fermi velocity comparable to that in graphene, and (ii) new transition metal monochalcogenides with bandgaps. Such systems may hold promises as new members of "Dirac materials", and "2D bandgap materials", respectively, which suggests potential future applications in nanoelectronics, and energy materials. Further, exciting properties like emergence and tuning of magnetic moments and the charge polarities, signature of Fermi surface nesting have been observed from the studies of functionalization of 2D aluminene lattice. Besides, these pristine and functionalized 2D systems have been employed to leverage their modified properties for various applications, like gas sensing behavior of these 2D materials. Thus, in this thesis, we have made an attempt to shed light into the fundamental aspects and also shown the potential future application of few novel pristine and functionalized 2D systems theoretically.

Future work: Although this thesis deals with the basic electronic and gas sensing properties of 2D systems, it is essential to explore other different properties that may be relevant from the viewpoint of possible application.

The increased energy needs, and the potential to efficiently discover, extract, and use energy is essential to make a revolution in the energy paradigm. One such progressive attempt is already continuing in the field of energy science, based on 2D materials. As already discussed in this thesis, the 2D monolayer systems have shown great promises for nextgeneration energy materials, especially batteries, and thermoelectric materials [323–325]. Hence, as part of the future work and continuation of this thesis, we aim to probe the 2D surfaces (in particular, the monochalcogenides) studied in this thesis for thermoelectric and battery applications. The motivation to choose 2D binary chalcogenides is because of the fact that the chalcogenides have received immense attention in the literature, specifically as efficient thermoelectric materials [326]. Moreover, it has been shown that narrow bandgap semiconductors prove efficient thermoelectric materials with a high figure of merit [327]. Since the 2D monolayers of monochalcogenides of Mo and W predicted in this thesis possess a narrow bandgap in their electronic structure, we will investigate the thermoelectric properties of these 2D binary surfaces and also probe them for ion storage (Li or Na) for the application in batteries, as part of the future work.

SUMMARY

Due to the large surface-to-volume ratio and quantum confinements of charge carriers, low-dimensional materials exhibit many novel properties that are distinctly different from the properties of their bulk counterparts. Among these materials, atomically thin twodimensional (2D) materials have received enormous attention from researchers after the discovery of graphene. The rich properties exhibited by the 2D systems are primarily due to specific atomic arrangements leading to a variety of electronic properties, covering from metals to insulators. Such systems, with a large surface area, are appealing for their wide applicability in the fields of gas sensing, and storage, catalysis, magnetism, etc. The distinctive properties of 2D systems, including electronic, mechanical, magnetic, and optical, are exploited to develop devices that find applications in numerous fields.

Theoretical predictions from first-principles calculations based on density functional theory (DFT) play a crucial role in the quest for new materials with tailored properties or novel functionalities, and these provide results comparable to experiments. The central topic of this thesis is primarily focused on the studies of probing new and novel 2D materials (monoelemental and binary), followed by their suitable functionalization in pursuit of potential applications. In this regard, firstly, we have predicted that a new Dirac material. We have shown that the 2D monoelemental aluminene system exhibit a stable β_{12} phase (similar to borophene), which is, however, not its lowest energy state. Its electronic structure reveals interesting Dirac cones lying quite close to the Fermi level with Fermi velocity comparable to that in graphene. Further, we have investigated the conventional approaches of tuning the properties of materials, such as adsorption, substitution, and intercalation of foreign atoms in different allotropes of 2D aluminene lattice. Exciting properties like emergence and tuning of magnetic moments and the charge polarities, signature of Fermi surface nesting have been observed as a result of functionalization of these allotropes. Moreover, bandgap in metallic planar aluminene has been successfully induced via the formation of the van der Waals trilayer heterostructures of aluminene with BN monolayers. In this thesis, we also predict the structural and energetic stability of novel binary 2D monolayers of Mo and W monosulphides, monoarsenides, and monosilicides. Some of these materials show interesting electronic properties like semiconducting bandgaps, while some show Dirac cone-like features close to the Fermi level.

Further, different 2D nanostructures studied in this thesis, namely pristine and TM substituted aluminene, and chalcogenides (S being the chalcogen) of Mo/W, have also been probed for sensing of gas molecules (H₂, CO, and NO). A comparative analysis reveals that in comparison with the pristine 2D systems studied in the literature so far, the 2D surfaces (pristine and TM functionalized aluminene and pristine monochalcogenides) probed in this thesis serve better for adsorption and sensing of H₂, CO, and NO gas molecules. Thus, in this thesis, we have predicted a few novel 2D systems, attempted to shed light on the fundamentally important aspects of physics of these materials, and shown the potential future application of some of these novel pristine and functionalized 2D systems theoretically.

Chapter 1

Introduction

1.1 Introduction to Nanostructures

Nanostructures comprise of (material) structures involving a length scale in the range of 1-100 nm. A nanometer indicates almost ten times the atomic size (10^{-10} m) . The branch of science which deals with the study of nanostructures is called nanoscience. When we come to the nanoscale, we reach the dimensions of molecules and atoms. So, for the nanostructured materials, quantum mechanics plays a vital role rather than classical mechanics, and atomic or molecular interactions play important role in the stability and the arrangement of the nanostructures. In a lecture entitled "There's Plenty of Room at the Bottom" [1] in 1959, Richard Feynman stressed the importance of the reduced-sized matter. Feynman talked about incredible viewpoints on the possibility and growth of materials at the nanoscale level. According to him, it should even be feasible to design an apparatus to handle materials at the nanoscale to "arrange the atoms the way we want." Following this, there has been expeditious progress made in the areas of nanomaterials due to the existence of sophisticated techniques for the fabrication and characterization of the materials at the nanoscale [2–4]. The basic two approaches to reach the nanoscale regime includes (i) top-down and (ii) bottom-up approach. In the top-down approach, we go from bulk to nano-sized material, while in the second one,

we start from an atomic or molecular scale to reach the nanoscale region.

There exist an enormous number of reasons to study nanostructures and nanotechnology. To list a few, in biology, the parts of cells (the smallest forms of life) have sizes of the order of nanometers. Nanostructure-based technology proves to be economical, the true evidence of which is provided by the semiconductor industry. A chip is a technology that shows the efficiency of reducing the sizes of the devices. Because of the growth in the nanotechnology field, microscopes possessing ability to resolve significant characteristics even below the wavelength of light have also been manufactured. Therefore, now, it is possible to have a clear image of even a single atom.

1.1.1 Uniqueness of Nanostructures

Nanoscience draws tremendous interest, especially in view of the increasing usefulness and interesting properties present in the nanomaterials but nonexistent in their corresponding bulk analogue. For example, bulk gold is an inert material; however, at the nanoscale regime, gold nanoparticles are highly reactive. Moreover, bulk gold appears yellow while the color of gold nanoparticles depends on the shape and size of the nanoparticle [5]. Similarly, carbon at nanoscale exhibits various exciting properties (electronic, mechanical, optical, etc.) in the form of, for instance, two-dimensional (2D) graphene, one-dimensional (1D) carbon nanotubes (CNT), and zero-dimensional (0D) fullerenes [6]. We wish to mention that graphite, a three-dimensional (3D) allotrope of carbon, is a soft material. However, in the nanoscale regime, the single layer counterpart of graphite, namely graphene, is harder than diamond, along with excellent stretchability and flexibility. Further, carbon nanotubes are around 100 times stronger than steel, very flexible, and have unique electrical properties [2]. So nanostructured materials have a long list of interesting properties which the corresponding bulk materials do not exhibit.

The major reasons for the modifications in the properties of materials at the nanoscale are the following. First, these have larger surface to volume ratio. As we reduce the dimension of the material, the number of atoms at the surface becomes appreciable, compared to the bulk, and consequently, many of the properties change from bulk. The modifications in the properties include enhanced chemical reactivity at the nanoscale. Some materials change from semimetal to metal or semiconductor [2]. Melting point of a material are also seen to be lower at the nanoscale [7].

Secondly, quantum confinement is caused by the reduction of dimensionality. This phenomenon is observed when the dimension of the material is too small to be comparable with the de-Broglie wavelength of the particle (i.e., electron). As the name itself suggests, this phenomenon causes confinement of the motion of the particles in some specific direction and hence leads to the discretization and alteration in the energy levels of electrons leading to materials with novel properties. The classification of nanostructured materials in



Figure 1.1: Schematic representation of bulk and quantum structures. L_X, L_Y, L_Z are the length of the material along the X, Y and Z directions and λ is the de-Broglie of the electron. Figure courtesy-Reference: [8]

different nanoscale regimes depends on the number of dimensions the particles are allowed to move in (Figure 1.1). 0D nanostructures (e.g., nanoclusters, quantum dots, fullerene, etc.) constitute a class in which the dimension of the material in all the three directions is in the nanometer range. One of the well-known examples belonging to such a family is gold nanoparticles. The quantum-sized gold nanoparticles and their doped variants possess distinctive electronic, magnetic, optical, and fluorescent properties due to the confinement effect [9, 10]. 1D nanostructures (e.g., nanofibre, quantum wires, nanotubes, etc.) include the class of materials, where the electrons are allowed to freely move in one direction and confined in the other two dimensions. The study on the influence of quantum confinement of nanotubes and nanowires of zinc oxide with varying diameters demonstrated that the energy gap tends to increase due to the reduced diameter, and they can be useful in the field of nanoscale optoelectronics [11]. In the case of 2D nanostructures (e.g., films with nanometer thickness, graphene, quantum well, etc.), the electrons are confined in only one dimension. A representative example is a 2D quantum well, which is a hybrid system of a thin layer of semiconductor material sandwiched between two layers of a different material, both materials having different bandgaps [12].

1.2 Materials at the Nanoscale

Studies of materials at the nanoscale have been extensively studied since last few decades. However, this field has seen an enormous surge of interest in the researchers since the discovery of carbon based 2D monolayer graphene [13].

1.2.1 Carbon-based 2D Monolayer Graphene

Carbon-based nanomaterials, notably 2D graphene, 1D carbon nanotubes, and 0D fullerene, have received considerable interest following their inventions and have served as potential candidates in nanoscience and nanotechnology these days [6]. However, among these lowdimensional materials, 2D graphene receives enormous attention from researchers [13, 14], since it is considered as the 'mother' of all graphitic carbon-based nanostructures, or bulk structure (i.e. graphite). It constitutes an essential key element for 0D fullerene, 1D carbon nanotubes, and 3D bulk graphite by its different arrangement (Figure 1.2). Graphene, the first-ever discovered 2D structure, is a single atom thick layer of sp² hybridized carbon atoms arranged in a hexagonal honeycomb lattice structure. The presence of the delocalized π -electrons contributes to the fascinating electronic and transport properties of graphene. Graphene was theoretically studied by P. R. Wallace back in 1947 [15]. But, in 2004, Andre K. Geim and Konstantin S. Novoselov, from the University of Manchester, UK, succeeded in isolating graphene from graphite using a simple scotch tape by the process called mechanical exfoliation [13]. They received a "Nobel prize in Physics in 2010 for the groundbreaking discovery of graphene".



Figure 1.2: Carbon based nanostructures like carbon nanotubes, fullerenes (buckyball), or bulk structure, graphite, by the different arrangement of a 2D nanostructure called graphene. Unit cell and the lattice unit vectors $(a_1 \text{ and } a_2)$ of graphene are also shown.

The electronic band structure (Figure 1.3) shows that graphene is a zero bandgap semiconductor or semimetal. We see that at the high symmetry K point, there is a crossing of π valence and π^* conduction bands (at a single momentum vector) in the Brillouin zone exactly at the Fermi level, and both the bands are linear to a good approximation. The dispersion relation for graphene near the K point follows the following equation:

$$E_{\pm}(\vec{k}) = \pm \gamma_o \frac{\sqrt{3}}{2} a |\vec{k} - K$$

Such points, around which the energy dispersion shows linear behavior are called the Dirac points. Due to the presence of this linear dispersion near the Fermi level, the charge carriers in graphene behave like massless Dirac Fermions (i.e., behave like relativistic particles). Such behavior leads graphene to exhibit many novel and exciting properties such as Klein tunneling and anomalous half-integer quantum Hall effect [14,16]. Its carrier mobility is extremely high (in the range of 2000-5000 cm⁻²/V s), and it also possesses a high thermal conductivity (5000 W m⁻¹ K⁻¹) [17]. Consequently, graphene finds potential applications in the field of high-speed nanoelectronics, photovoltaic cells, electrochemical sensing, super-capacitors, and data storage devices, etc. [17, 18]. Hence, the discovery of graphene This marked a turning point in the field of research and further exploration of new exotic 2D materials with a variety of applications.



Figure 1.3: The electronic bands of graphene along $\Gamma - M - K - \Gamma$ direction.

1.2.2 2D Nanostructures beyond Graphene

Since the discovery of graphene [14, 16] (atom from group IV), interest in atom-thin 2D structures, based on atoms from group III (borophene, aluminene, gallenene) [19–21], group

IV (silicene, germanene, stanene) [14, 16, 22–27] and group V (phosphorene, arsenene, antimonene, bismuthene) [28–32] has increased manifold. It is worth to mention that the 2D materials cover the usual classes of electronic materials. While the 2D materials based on atoms from group IV are, in general, zero bandgap materials, systems based on group III, are predicted to be a metal. On the contrary, 2D structures based on atoms from group V show different electronic properties, exhibiting direct and indirect bandgaps. The prediction and discovery of new materials in the class of 2D materials as well as studies of their novel properties have led to an enormous amount of research as is seen in the literature [14, 16, 19, 20, 22–27, 29, 30, 33, 34]. These materials can be useful in providing solution to large-scale production of low-cost, flexible sensors, actuators, and nano-devices for several applications [35, 36].

Over the past few decades, the research interest in "post-graphene" structures has also led to the exploration and subsequent addition of many new members to the family of 2D materials made of more than one element. For instance, systems like hexagonal boron nitrides (h-BN), transition-metal dichalcogenides (e.g. MS₂, WS₂,), MXenes (e.g. Ti₃AlC₂), metal oxides (e.g. MoO₃, WO₃, SnO₂), metal - organic frameworks (e.g. UiO-67) reveal interesting new physics and are also found to serve as potential candidates for future applications in diverse fields, ranging from electronics to catalysts [37, 38]. Specifically, in recent times, extensive research has been carried out on 2D binary monolayers as seen in the literature. Some of the materials of recent importance consist of group III-VI (like GaS, GaSe) [39], group IV-VI (like SnS, CSe, SiTe) [34, 40], group III-V (like BN, AlN, GaN) [41] and several other type of binary monolayer systems [42]. These materials have been seen to generate increasingly expanding interest due to their possible application in the areas of semiconductors, optoelectronics, photoelectronics, etc.

The 2D monoelemental structures have a preference over other 2D materials due to the ease in the process of purification and productivity, which contribute to high-quality monoelemental materials [33]. Hitherto, among all the predicted 2D structures, graphene, silicene, germanene, stanene, phosphorene and borophene [19,22,27,43,44] have already been synthesized. Also, the growth of a few layers of arsenene, antimonene and bismuthene have also been reported in the literature [45,46]. Besides, a large number of experiments are found in the literature related to the potential applications of such materials [26,47–49]. Recently, it has been experimentally demonstrated that silicene can act as a field-effect transistor (FET) at room temperature [49]. Germanene has been shown to exhibit quantum spin Hall effect at experimentally accessible temperatures [26]. Both silicene and germanene [22,50–52] offer the possibility to have a bandgap opening when an external electrical field is applied and also with the adsorption of foreign atoms. This opening up of the bandgap provides a possibility to use germanene-based materials as field-effect devices [26]. Hence, from both fundamental and practical points of view, the field of 2D monoelemental materials is a topic of interest for experimentalists and theoreticians alike.

1.2.2.1 Motivation to study monoelemental 2D Aluminene

It is well known that the arrangement of atoms in a solid is closely related to the bonding nature existing in the solid and hence governs its associated physical properties. For instance, carbon is known to exist in different forms of allotropes: graphite and diamond, both of which have entirely different structures and hence corresponding properties. Graphite, in the 3D bulk form, has a layered hexagonal structure (layers connected via weak vdW forces) with strong in-plane covalent bonding. Similar to graphite, several 3D bulk materials exist in nature that are built of 2D atomic layers and that the layers are bonded to each other via weak vdW forces. This facilitates easy exfoliation of the layers into 2D atomic sheets [53]. Contrary to this, structures with metallic bonding favor close-packed arrangement due to the non-directional feature of the metallic bonds. Hence, it is challenging to achieve 2D materials with metallic bonding in the free-standing form through delamination (a top-down approach). This constitutes a major reason that the metallic 2D systems are less explored in comparison to the covalently bonded 2D systems [54, 55]. Nevertheless, because of the availability of various bottom-up approaches, it is possible to attain significant progress in the synthesis of ultrathin 2D metals with controllable size and thickness [55]. In this regard, there exist some studies on 2D metals supported on substrates employing various deposition techniques to design and fabricate metallic thin films [54–60]. As a consequence of recent developments and exciting and useful applications in the field of gas sensing, catalysis, and magnetic recordings, etc., metallic nanomaterials indeed appear to be important in the emerging field of 2D material, which makes them an appealing topic of research [55–58].

As stated above, the family of 2D monoelemental nanostructures, including elements from groups III, IV, V, and VI, is experiencing rapid growth through both experimental and theoretical studies. Among group III, successful theoretical and experimental studies demonstrate the existence of an atomically thin sheet of metallic group-III Ga based atom, namely "gallenene" on a Si substrate [21]. The study reveals the possibility of two distinct layers of bulk α -Ga having orientation along [100] and [010] direction, leading to planar and buckled structures, respectively. The metallic behavior of gallenene ascertains that it behaves as a "2D metallic layer" [21]. Since boron is isoelectronic to gallium, we wish to highlight recent advances in 2D materials made of boron atoms. Recently, borophene - atom thin monolayer of boron atom has been successfully grown on Ag (111) and several other surfaces, namely, Cu(111), Al(111), Au(111) and Ir(111) surfaces [19,61–65]. Borophene has been found to be a metal with highly anisotropic electronic properties [19].

It has been shown that because of the deficiency of electron, borophene is not stable in a graphene-like planar structure, and hence requires an additional electron for stabilization in honeycomb lattice [66]. The study on the growth of borophene reveals that its geometry is stabilized in the hexagonal honeycomb lattice, with one extra boron atom lying above the plane of the atoms which form the hexagonal lattice [67–69]. Another possible way of stabilizing the system is by introducing hexagonal holes in the system. Recently, two phases of borophene, namely, β_{12} and χ_3 with different arrangements of hexagonal holes in a triangular lattice have been identified from scanning tunneling microscopy [61]. The former
phase has been found to be the low-temperature structure (minimum energy structure). Interestingly, in β_{12} phase of borophene, a signature of the crossing of two linear bands (Dirac-like cones) is observed, which lie at about 2 eV and 0.5 eV above the Fermi level (E_F) [61]. The presence of both boron and gallium atom based atomic thin 2D systems in the literature establish the importance of in-depth studying of the 2D metallic monolayers made up of group-III atoms.



Figure 1.4: Different allotropes of 2D aluminene

Recalling the motivation of studying 2D metallic nanostructures, in this thesis, we study the 2D structure of group-III based element, aluminium (Al), which is named as "aluminene". Bulk aluminium is the most abundant metal in the Earth's crust and the third most abundant element. It is lightweight, strong, and highly recyclable. These practical facts serve as a motivation to probe the possibility of existence of different structural manifestations of aluminium at the nanoscale. The bulk structure of aluminium does not possess a layered structure. But as mentioned above, thin films are easily achievable through various bottom-up approaches. Thus, with this anticipation, first-principles based electronic structure calculations have been performed for different allotropes of monolayer of 2D aluminene system [20,70–72] (Figure 1.4). The first theoretical prediction is made by Kamal *et al.* [20]. The study suggests the possibility of aluminene to be stable in a graphene-like planar honeycomb structure (with P6/mmm space group). Its electronic structure reveals that it is a metal and possesses Dirac-like points located 1.6 eV above the Fermi level (E_F). Hence, it has been argued that this 2D system can be regarded as a highly hole-doped graphene system. Being a metal, it has been seen to possess an interesting Fermi surface (FS), with features corresponding to free-electron-like and hexagonal warped surfaces, which may play an important role in governing its transport properties. Apart from the planar honeycomb structure, theoretical studies on various other structures of aluminene have also been reported, which include buckled (P3m1), 8-Pmmn [70], and a buckled triangular lattice (D2h-13 Pmnm) [71]. Yeoh et al. reported the structural stability of aluminene with D2h-13 Pmnm space group up to 7% tensile strain. Moreover, the analysis of coupling between electron and phonon suggests the superconducting behavior of aluminene, with a critical temperature (T_c) of 6.5 K, which is further enhanced upon tensile strain [71]. Additionally, planar aluminene has been predicted to be suitable for charge storing nano-capacitors [73]. Based on the recent theoretical investigations available in the literature, the planar and buckled aluminene have recently been predicted to be stable on Cu(111) and graphene substrates due to the strain effect [74]. Such exciting structural and electronic properties with a possibility of experimental synthesis motivate us to explore further the unfathomed properties exhibited by 2D aluminene from both the fundamental and application perspectives. Hence, we study this system in this thesis.

1.2.2.2 Motivation to study Binary 2D Monolayers

Many 2D honeycomb lattices of binary compounds from group III-V and II-VI, motivated by the significant theoretical and experimental studies on graphene [41] have been probed. In this direction, the h-BN honeycomb sheet was reported as a stable 2D monolayer, which possesses a planar structure similar to graphene [75]. However, contrary to the semimetallic nature of graphene, because of the ionic nature of bonding between B and N atoms, h-BN has been seen to reveal a large bandgap of 4.61 eV (from LDA exchange potential) [41]. Similar binary compounds from group III-V constitute planar or buckled 2D honeycomb lattice with semiconducting gaps [41]. Further, ZnO monolayer is reported as a group II-

VI binary metal-oxide and is an analogue of hexagonal graphene and h-BN [76]. Another group-IV binary combination exhibiting remarkable properties is a planar 2D SiC honeycomb sheet with a bandgap of 2.53 eV [77]. In contrast to the planar honeycomb structures of the above mentioned binary systems, many group IV-VI binary materials (like SnS, CSe, SiSe, etc.) [34] have been found to be stable in the puckered structure, similar to black phosphorene, with direct as well as indirect bandgaps in their electronic structures. The systems like GeS, SnS, GeSe, and SnSe have been reported as ferroelastic materials because of their remarkable anisotropic puckered structure [78]. First-principles studies have been performed to investigate binary materials from elements belonging to groups IV and V (IV) = C, Si, Ge, Sn, Pb and V = N, P, As, Sb, Bi). Results of electronic structures with large bandgaps, relative band positions, and the signature of quadratic band-edges lead to anticipation of such materials to qualify as efficient candidates in the field of optoelectronics, water splitting, and thermoelectrics [79]. A recent review on 2D binary materials of group V-V, with puckered and buckled structures, are predicted to have a direct bandgap and high carrier mobility, which assist these materials in serving as a potential candidate for the applications in next-generation solar cell devices and nanoelectronics [80].

We note that much of the literature studies are focused on the 2D binary monolayers consisting of chalcogens bonding with sp-electron elements. We wish to mention here that these chalcogens form bonds with the transition metal atoms (having d electrons, for example, Mo, W) as well, as has been observed in cases of transition metal dichalcogenides (TMDCs). Among numerous interesting studies based on TMDCs, the most studied systems are Mo and W disulfides. However, the absence of any Mo/W monochalcogenides (or monosulfides) prompt us to probe the existence of monolayer monochalcogen (= sulfur) of Mo and/or W in this thesis. We would like to explore whether this stoichiometry leads to stable structures or not, both from the energetic and dynamic point of view; and if MoS and WS do have stable structures. For comparison, we also explore the possibility of formation of 2D binary monolayers of monosilicides (group IV) and monoarsenides (group V) with TM atoms Mo and W.

1.3 Functionalization of 2D systems

The electronic structures and hence, the properties of 2D materials exhibit a strong and direct dependence on the arrangement of atoms in the crystal structures. Because of the large surface to volume ratio, 2D surfaces are susceptible to foreign atoms or molecules and are expected to show significant alteration in their surface structures and the associated properties in the presence of such impurities.

In this respect, various approaches towards surface modification or functionalization of 2D materials have been employed in literature to modulate different properties, like structural, electronic, magnetic, etc., to enhance their functionalities, improve their limitations, and also to probe their potential from the viewpoint of various applications. To this end, some of the extensively used methods include the adsorption of foreign atoms (magnetic or non-magnetic) or molecules, substitutional doping of different atoms [81–97], strain application [30,98–102], intercalation of impurity atoms [103–109] application of electric field, etc., [98,110–113].

It has been well established that the semimetallic nature severely limits the application of graphene in the areas of nanoelectronics, regardless of its extraordinarily high electric and thermal conductivity and also remarkable mechanical properties [13,114]. Nevertheless, via successful modification, it becomes plausible to significantly change the properties of graphene [115,116]. For instance, graphene oxide reveals insulating behavior; substitutional doping with N and B atoms, and hydrogenation of graphene exhibit an opening of sizable bandgap [115–117]. Such tuning of electronic properties of graphene proves to be efficient to find potential applications in batteries, sensors, catalysis, etc. [118]. Functionalization has also led to the enhancement in the stability of 2D black phosphorous, a group-V member, against deterioration in the presence of ambient conditions [116, 119]. Honari *et al.* have studied the functionalization of borophene, a group-III member, with H, Cl, and F atoms in three experimentally synthesized boron structures, i.e., stripped, β_{12} and the χ_3 structures. They reported that the full-hydrogenation in stripped case results in a transformation from metallic to Dirac-type band structure. Further, H-functionalized χ_3 structure shows a sizable bandgap of 0.88 eV [120]. 2D tellurium nanostructure, a group-VI member, functionalized with atomic cobalt atoms is reported to act as an effective co-catalyst for enhancing the production of photocatalytic H₂ and CO₂ reduction reactions [121].

It has been shown in the literature that most of the 2D structures in their ground state pristine form carry no net magnetic moment [16, 20, 22, 25–27, 29, 30, 70, 71, 81]. Thus, many in-depth research studies have been carried out towards modulating the spin characteristic of 2D materials, via adsorption of or substitution by transition metal (TM) atoms. This is further accompanied by the modification in the electronic structures of 2D materials as well |81-97, 122-124|. Mao *et al.* |93| reported that after adsorption of Mn, Fe and Co at the hollow (H) site of graphene, the magnetic moment for Fe and Co atoms is reduced whereas it increases for the case of Mn atom (by 0.56 μ_B) in comparison with their atomic moment [93]. Hashmi et al. [123] have reported TM doped phosphorene as dilute magnetic semiconductor (DMS) material, though phosphorene is non-magnetic in its pristine form. Further, Du et al. [92] have shown that a ferromagnetic coupling exists between the magnetic moments induced by Ti, V, Mn, and Fe atoms, and an anti-ferromagnetic coupling is induced by Cr atom, when 3d TM atoms are doped on arsenene systems. Kaloni [88] has found that V-adsorbed germanene can exhibit the quantum anomalous Hall effect. In the case of borophene, it is observed that [81] the adsorption of some of the TM atoms like Ti, V, Cr, Mn, and Fe on borophene make the composite system ferromagnetic.

Application of strain also provides an efficient way to tune and engineer the electronic and magnetic properties of 2D materials [30,99–102]. Huang *et al.* have discussed the tuning of magnetism in graphene decorated by (TM) atoms by controlling the strain [99]. Zheng *et al.* have reported about tunable magnetism in Cr and Fe doped silicene under tensile strain [100]. Tao *et al.* have showed that strain induces magnetism in single-layer MoS₂ with atomic single vacancies [101].

Alongside embedding (substitution) or adsorption of foreign species, intercalation has also been shown in the literature to manipulate electronic and magnetic properties, carrier concentration, superconductivity, etc., [125]. Such a functionalization approach is a key component of a plethora of energy storage devices, spanning from batteries to supercapacitors. Besides, interesting periodic distortions of the host lattice and the possibility of exotic charge density waves also contribute to the key signature of intercalation into the layered materials [126–130]. Another interesting advantage of intercalation lies in the fact that it enables to synthesize unique heterostructures through the generation of a secondary layer of the intercalating ions or molecules into a host material. For instance, Koski *et al.* [128] and Chen *et al.* [129] demonstrated the formation of layered heterostructures by intercalating zerovalent metal atoms into the interlayer space of 2D-layered chalcogenide material.

We wish to mention here that the insertion of TM atoms and/or their complexes is of surmounting interest because of the magnetism associated with them. In this regard, magnetism has been extensively probed in the 2D composite systems like TM-intercalated graphitic materials, [106, 131], silicene [108] and borophene [109]. Using different TM atoms in the case of bilayer graphene, it has been shown that a Dirac point can be tuned or shifted and further one can create new 2D Dirac materials [132]. Mykhailenko *et al.* [108] have reported about a difference in symmetry in cases of Co and Fe-intercalated silicene. In this work, the authors show that Co-intercalated silicene forms a stable hexagonal lattice. However, at a higher temperature (625 K), the hexagonal lattice changes to a cubic lattice. On the other hand, the Fe-composite system is found to be stable in the cubic lattice structure. 100% spin polarization has been reported for V/Mn intercalated bilayer phosphorene, which could be used for spintronics as plausible spin-filter materials [133]. Evidence of Cr-intercalated hetero-bilayer of different allotropes of borophene [134] and signature of Dirac semimetal with antiferromagnetism in the ground state for Ti-intercalated borophene heterolayers [135] have also been reported in the literature. All these studies on the functionalization of 2D materials, with novel and intriguing properties, provide a new avenue for probing and further fabricating new materials with interesting properties, that may find application in various fields, including the area of magnetic semimetal/semiconductor as well as electronic and and nanoscale magnetic memory devices. Keeping all these studies in mind, we study various approaches of functionalization of 2D aluminene in this thesis.

1.4 van der Waals heterostructures of 2D systems

Looking beyond the field of research of 2D single atomic layers, there exists a possibility to assemble or integrate the distinct 2D isolated atomic layers into designer heterostructures via the lateral combination of two or more atomically thin layered materials with different electronic structures in a precisely chosen sequence. For decades, the fabrication of new materials by stacking monolayers that belongs to the same or two different materials via the epitaxial growth has been the focus of intensive research [136]. A. Geim and I. Grigorieva discussed the concept of van der Waals (vdW) heterostructures [137] by stacking two or more 2D atomic layers (with strong in-plane covalent bonding) that adhere primarily through noncovalent interactions [138, 139], as the stacking layers interact via the vdW forces. Because of the increasingly sophisticated devices and the availability of the fabricating technology to many research groups, such heterostructures have attracted immense attention of the researchers, with the possibility of artificial manupulation of periodic superstructures with interesting band structures. This is possible also due to the availability of so many 2D systems as well as possible sequences to consider.

Because of vdW interactions between the layers, the requirement of lattice matching between the stacked hetero layers is relaxed. Combinedly, such heterostructures enable to leverage the properties of the constituent layers and also facilitate in optimizing the performance of a device [140]. In the recent years, vertical vdW heterostructures of 2D materials have been studied which exhibit properties ideal for their applications in the fields of nanoelectronics [141,142] and optoelectronics [143–145]. To mention a few examples, FET has been fabricated employing heterostructure of graphene (a semimetal), h-BN (an insulator) and MoS₂ (a semiconductor) layers. In this, graphene acts as both source or drain and gate electrodes, h-BN as the high-k dielectric, and MoS₂ as the channel [146]. Li intercalation in Gr-HfS₂, an anode material with ultrafast charging/discharging rates, is attractive for rechargeable ion battery applications as it overcomes the volume expansion problem faced by many electrode materials [147]. 2D heterostructures, for instance, ZnO/WX₂ (X = S, and Se), have been theoretically reported as efficient water-splitting photocatalysts [148].

It has been established in the literature that due to the semimetallic nature of graphene, it fails to be of importance in the field of electronic devices [14, 16]. The electronic structure of monolayer graphene possesses linearly dispersing bands, which are degenerate at the point of crossing ("Dirac points") at the Fermi level. This degeneracy is preserved due to two equivalent sublattices, A and B, which constitute the unit cell of graphene. Only via introducing inequivalence into these sublattices, thereby breaking the symmetry, it is possible to turn graphene into a semiconductor [149]. In this regard, several experimental and theoretical approaches were proposed [150-159]. The growth of graphene on Si-terminated SiC substrate has been shown to result in a gap of 0.26 eV [151]. In the case of graphene deposited on oxygen-terminated SiO_2 [152], a gap of 0.35 eV has been produced. Besides, it is reported in the literature that through the fabrication of heterostructures of graphene and h-BN, it is possible to induce a gap in graphene [150] due to the non-equivalent carbon sublattices [156]. In trilayer BN/graphene/BN structure as well, a stacking-dependent bandgap was observed [157]. Therefore, altering the number of layers in a given 2D material may lead to bandgap engineering. Because of the close resemblance of graphene with planar aluminene (a system like highly-hole-doped graphene [20]) from the geometric and electronic structure viewpoint, in this thesis, we attempt to alter the electronic structure of metallic 2D planar aluminene via considering different heterostructures of aluminene and BN monolayers. We compare the results with those of heterostructures between aluminene and graphene as well as between graphene and BN.

1.5 2D systems as Gas Sensors

In the literature, many practical possible applications of 2D systems have been discussed. The sensing of environmentally important gas molecules has been one of the most well-studied and relevant amongst these, due to the large surface-to-volume ratio of the 2D materials [160]. Therefore, a large number of studies have been carried out on probing 2D materials as a potential candidate for sensing and detection of gas molecules [161] for the last few decades. For instance, graphene is the first elemental 2D system to be synthesized, and sensing of hazardous gases like CO, NO, etc. using this system has been extensively studied [162, 163]. Silicene and phosphorene have been studied for gas detection application as well [164–166]. For pristine graphene, it is observed that the adsorbed gas molecules are primarily physisorbed [167, 168], because of its chemical stability. On the other hand, for pristine silicene, Feng *et al.* have shown [164] that adsorption of gases like NO, NH₃, NO₂, O₂, SO₂, etc. leads to moderate to strong adsorption energies, which results in chemisorption of these gas molecules on this surface.

It has also been established in the literature that functionalization of various 2D surfaces (be it through adsorption of and substitution by suitable foreign atoms or by introducing vacancies) improves the adsorption properties of these systems [169–179]. With the introduction of defects and doping, graphene has been shown to be a good sensor for NO and NO₂ gas molecules [169]. Chen *et al.* have found enhanced interaction between H₂CO molecule and graphene when doped with elements like Ti and V [170]. Further, Al-doped graphene has been probed as a sensor material for CO gas [171]. Li and Na metal atom doped silicene systems are found to be efficient for high-capacity storage of hydrogen [175]. Further, Aghaei *et al.* have observed the physisorption of CO₂ molecule on pristine germanene. However, interestingly, with Li functionalized germanene, the authors find a significant enhancement of the adsorption energy of CO₂ molecule [176]. Recently, borophene has been predicted to be a better candidate for gas sensing [180]. In this work, Shukla *et al.* have established that the prospect of borophene as a gas sensor for various environmentally relevant gases is better compared to other 2D systems like graphene, silicene, phosphorene and MoS₂. Very recently, Nagarajan *et al.* [181] have studied gas (CO and NO) adsorption on buckled aluminene surface and discussed about the sensitivity of aluminene surface towards the detection of NO and CO gas molecules. However, the literature lacks any study on the adsorption of gas molecules on TM-functionalized aluminene surface. Hence, in this thesis, we explore this possibility. Further, a similar analysis of gas adsorption on binary 2D monochalcogenides, MoS, and WS has also been carried out to investigate the ease of adsorption and explore the possibility of these surfaces for prospect of efficient gas sensing.

1.6 Outline of the Thesis

Reminiscence of the importance of 2D materials, their functionalization, and further their applicability as potential candidates in different fields like 2D nanoelectronics, magnetic materials, gas sensing, etc. as stated above, the work carried out in this thesis primarily focus on probing the possibility of new and novel 2D materials (monoelemental and binary), followed by their suitable functionalization in pursuit of potential applications. In this regard, investigation of various methods of functionalizing different allotropes of 2D aluminene has been carried out. Further, we study some of these functionalized aluminene surfaces and the 2D binary systems (MoS and WS), predicted in this thesis for gas sensing application.

In Chapter 2, we describe the methodology used for the electronic structure calculations which are carried out for the thesis work.

In Chapter 3, a theoretical prediction of a 2D aluminene system in β_{12} configuration similar to 2D borophene has been made in pursuit of a new 2D "Dirac material" with linear dispersion in the electronic structure. For comparison, the possibility of another group-III element - gallium (referred to as gallenene), in this configuration has also been investigated. Further, the effect of iso-electronic substitution in these 2D monolayers has also been studied, by exploring the possibility of changes in the position and dispersion of the possible linear bands in the energy-momentum space.

Chapter 4 deals with the aspects of absence of magnetism in aluminene, using approaches like (i) deliberately introducing a foreign impurity into the aluminene sheet via adsorption, substitution, and intercalation, and (ii) strain application. In this direction, various methods of functionalizing different allotropes of aluminene and its effect on geometric and electronic structures and magnetism in the system have been analyzed in detail. The adsorption and substitution of transition metal (TM) atoms in buckled and planar aluminene have been probed. Besides, the influence of substitution of alkali metal (AM) atoms in the aluminene lattice has also been investigated. Additionally, intercalation of some TM atoms (Ti, Cr, Mn, Fe, Co, and Ni) in bilayer aluminene has also been probed. For this, first, the probing of various possible stacking arrangements of bilayer aluminene has been carried out, followed by the TM atom intercalation in unique bilayer aluminene systems. We also explore the possibility of the nesting of the Fermi surface in these composite systems.

In Chapter 5, the possibility of opening of bandgap in aluminene has been presented in an attempt to provide a theoretical pathway towards a potential bandgap material. Because of the similarity between 2D planar aluminene and graphene from the geometric and electronic structure viewpoint, and the existing literature on bi- and trilayer heterostructures of graphene/BN, heterostructures consisting of aluminene/BN and BN/aluminene/BN have been probed, anticipating that such heterostructures may exhibit interesting geometric and electronic properties, including opening up of a bandgap.

Due to the increasing research interest in "post-graphene" structures, the possibility of a few new 2D binary monolayers has also been probed in Chapter 6. Theoretical prediction of novel 2D binary monolayers of Mo and W monosulfides, monoarsenides, and monosilicides, in different geometric structures have been carried out. Analysis of results of energetic and dynamical stability has been presented in detail. The effect of different exchange-correlation potentials and the influence of the application of strain on the electronic structure is also explored to predict the suitability of the newly predicted binary systems in the field of 2D semiconductors.

As mentioned above, it is reported in the literature that the 2D nanostructures have also gained significant interest in the field of gas sensing applications due to their high surface-to-volume ratio and specific chemi- or physisorption capabilities. Further, studies on the embedding of TM atoms in 2D systems have been found to enhance the sensitivity of gas molecules to a large extent. Hence, in Chapter 7, we explore the possibility of 2D monoelemental, aluminene and binary monochalcogenides, MoS/WS surfaces, to serve as an efficient gas sensor. To analyze the sensing ability of these 2D surfaces, we study the environmentally important gas molecules (H_2 , CO, and NO). Further, a comparative analysis of gas adsorption with the pristine 2D systems studied in literature has been probed to shed light on the potential ability of the 2D surfaces, examined in this thesis, in terms of adsorption and sensing of gas molecules.

At last, in Chapter 8, we summarize all the studies carried out in this thesis and conclude the work with a discussion on the importance of the thesis, which is followed by a brief note on the potential future scope.

Chapter 2

Computational Methodology

2.1 Introduction

The electronic structure of matter, having electrons as the constituent particles, involves studying the motions of electrons and the interactions between different particles like with other electrons and nuclei. By the electronic structure calculation, one can estimate the energy, geometry, nature of bonding, etc., of a physical systems. These calculations use quantum mechanics to analyze a given system and calculate the electronic states by solving the Schrödinger's equation. Further, the state of an electron is determined by a wavefunction ψ which can be obtained using Schrödinger's equation. The wave-function contains all the information about a given system. If the system includes many electrons and nuclei, it becomes very complicated to solve the Schrödinger equation. The Density Functional Theory (DFT) plays an important role here. DFT uses the electron density as a basic variable instead of the wave-function of the particles. Hence, in this chapter, we will discuss the basics of DFT used to solve an electronic structure problem.

2.1.1 Schrödinger Equation

In quantum mechanics, the ground state properties of many-particle systems containing electrons and nuclei are described by the time-independent Schrödinger equation, and their solutions are stationary eigen states of the time-independent Schrödinger equation. We will discuss here only the time-independent Schrödinger equation, as we do not require the time dependence of the Hamiltonian in calculating the properties studied in the present thesis. The time-independent Schrödinger equation for the system having many electrons moving under the nuclear potentials is as given below:

$$\mathbf{H}\Psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_{N_I}) = E\Psi(r_1, r_2, \dots, r_N, R_1, R_2, \dots, R_{N_I})$$
(2.1)

where $\dot{\mathbf{H}}$ is the Hamiltonian and E is the total energy of the system. Ψ is the many-body wave-function. The Hamiltonian operator for a many body system is given as (in the atomic units):

$$\hat{\mathbf{H}} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \frac{1}{2} \sum_{I=1}^{N_{I}} \frac{\nabla_{I}^{2}}{M_{I}} + \sum_{i< j=1}^{N} \frac{1}{|r_{i} - r_{j}|} + \sum_{I< J=1}^{N_{I}} \frac{Z_{I}Z_{J}}{|R_{I} - R_{J}|} - \sum_{i=1}^{N} \sum_{I=1}^{N_{I}} \frac{Z_{I}}{|r_{i} - R_{I}|}$$
(2.2)

 M_I is the ratio of the mass of nucleus I to the mass of an electron at R_I and r_i is the position vector of the i^{th} electron. Z_I corresponds to the atomic number of nucleus I. These terms represent the operator corresponding to the following respective order: (i) kinetic energy of electrons, (ii) kinetic energy of nuclei, (iii) interaction between electrons themselves, (iv) interaction between nuclei themselves, and (v) interaction between electrons and nuclei.

2.1.2 Born-Oppenheimer Approximation

Solving the Schrödinger equation (SE) (Eq 2.1) corresponding to the Hamiltonian given by Eq 2.2 is a challenging problem. Apparently, the wave-function (solution of SE) is the func-

tion of $3(N + N_I)$ spatial coordinates (coordinates of both electrons and nuclei), and the motion of electrons and nuclei are coupled. This approximation enables us to separate the motion of the electrons and nuclei. Since the nucleus is much heavier than the electron, the electron's motion is much faster than the nucleus. According to Born-Oppenheimer (BO) approximation, the motion of the nuclei is considered negligible with respect to the electron's motion. Additionally, in this approximation, nuclear motion is not accompanied by changes in the electronic state of the system. Further, the nuclear-nuclear interaction term is independent of the coordinates of electrons. So this term is considered constant for a fixed set of nuclei. Moreover, the nuclei are stationary at different nuclear position coordinates, although they are considered to be at rest with respect to the electrons. Thus, the wave function Ψ can be decoupled into electronic and nuclear wave-functions and can be written as $\Psi(r_1, r_2, \dots r_N, R_1, R_2, \dots R_{N_I}) = \psi(r_1, r_2, \dots r_N)\phi_n(R_1, R_2, \dots R_{N_I})$

So, as a result of this approximation, the above Hamiltonian reduces to the electronic Hamiltonian, which is given by:

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i< j=1}^N \frac{1}{|r_i - r_j|} - \sum_{i=1}^N \sum_{I=1}^{N_I} \frac{Z_I}{|r_i - R_I|}$$
(2.3)

As we can see from the Hamiltonian expression, it still contains the electron-electron interaction term, which hinders us to solve the many-electron Schrödinger equation exactly. Hence, in order to solve the many-electron Schrödinger equation, there exist various wave function based approximate methods. One of the well-known methods is the Hartree-Fock (HF) method which is based on the variational principle. This method includes the fermionic nature of an electron in its wave-function, and a result of this, a term known as the exchange term (a non-local characteristic) is observed in the HF equation. The exchange term helps lower the total energy, and because of this term, the HF method does not contain any selfinteraction. Although the HF includes the exchange term, the solution of the Hartree-Fock equations does not correspond to the actual ground state. The main reason is: this method does not take into account the effect of electron-electron correlation. Therefore, the difference between the Hartree-Fock energy and the exact ground state energy is the electron-electron correlation energy. Many other wave function-based methods, categorized as post HF methods, have also been developed to consider the effect of this correlation. These include the configuration interaction (CI) theory, the coupled-cluster (CC) theory, and the many-body perturbation theory (MBPT) [182]. We wish to mention here that although these wave function based theories take into account the correlation effect, it becomes very complicated and time consuming to solve the Schrödinger equation if the system includes many electrons and nuclei. The density functional theory plays an important role here, and is discussed in the next section.

2.2 Density Functional Theory

The quantum mechanics uses wave function ψ as a tool to know a given system. But the problem with a wave-function is that it depends upon 3N spatial and N spin coordinates for a given many-body system having N number of electrons. So when N is large, the wave-function based approach like the Hartree-Fock method becomes difficult to handle. On the other hand, density functional theory is a theory where the dimensionality of the problem gets reduced. Instead of the complicated N-electron wave function $\psi(q_1, q_2, ..., q_N)$ (where coordinate includes space and spin coordinates both), the Schrödinger-like equation can be written in terms of the electron density $\rho(r)$ that depends only on the three spatial coordinates. Thus working with DFT reduces the 3N dimensional problem to a 3-dimensional problem in space.

In 1927, the very first initiative was taken by Thomas and Fermi [183, 184] to introduce the concept of density. Thomas and Fermi used a semi-classical approach. They have used a statistical consideration to express the kinetic energy as a functional of density and treated the particles classically so that one can write the potential energy in terms of density as well. In this model, there were no exchange and correlation terms. Despite an attempt to employ density as a basic variable, this theory has major drawbacks: (i) it could not explain the shell structure of atoms and (ii) it could not explain the stability of the molecules. This non-bonding theorem was originally asserted by Teller, which states that "in Thomas-Fermi theory, no molecular system is stable," i.e., the binding energy of the molecule formed is greater than the energy of the isolated atoms from which it is formed [185]. This problem does not arise in another density based theory given in the year 1964, which is described in details in the next subsection.

2.2.1 The Hohenberg-Kohn Formulation Of Density Functional Theory

A landmark theory for electronic structure calculations based on density was given by Hohenberg and Kohn in 1964 [186]. It primarily consists of two theorems discussed below.

2.2.1.1 Hohenberg-Kohn First theorem

Hohenberg and Kohn used the density of electrons as the basic variable to describe the ground state properties of a system. The theorem states [187]

"There is a one to one correspondence between the ground state density $\rho(r)$ and the external potential (the potential due to Coulomb interaction between electron and nucleus) for any interacting system under an external potential $v_{ext}(r)$. An immediate consequence is that the expectation value of any observable is a unique functional of the exact ground-state electron density."

Since knowing $\rho(r)$ determines uniquely the external potential and consequently the Hamiltonian and in principle the wave-function of a given system, thus as a consequence of first Hohenberg-Kohn theorem, it is clear that it should be possible to write the electronic energy as a functional of density.

$$E_{v}[\rho(r)] = T[\rho(r)] + E_{ne}[\rho(r)] + E_{ee}[\rho(r)]$$

= $F_{HK}[\rho(r)] + \int \rho(r)v_{ext}(r)dr$ (2.4)

where

$$F_{HK}[\rho(r)] = T[\rho(r)] + E_{ee}[\rho(r)]$$
(2.5)

and it is called **Hohenberg Kohn energy functional** which is a **universal functional** of the ground state density in the sense that it does not depend on the external potential of the system. $E_v[\rho(r)]$ is the total energy functional under the external potential v_{ext} . $E_{ne}[\rho(r)]$ is the energy corresponding to the attractive potential between the electrons and the nucleus and is the energy corresponding to the external potential. $E_{ee}[\rho(r)]$ is the energy due to the repulsive potential between the electrons.

2.2.1.2 Hohenberg-Kohn Second Theorem

The first Hohenberg-Kohn theorem tells us if we have the ground state density, then in principle, we can obtain all the properties of interest for any given system. But given some density $\rho(r)$, how do we ensure that it is the ground state density? This question is answered by the second Hohenberg-Kohn theorem. It is a variational theorem for density analogous to the variational theorem for the wave-function. This theorem states that [185]

"For a given trial density $\tilde{\rho}(r)$, such that $\tilde{\rho}(r) \ge 0$ and $\int \tilde{\rho}(r) dr = N$,

$$E_o \leq E_v[\tilde{\rho}]$$

where $E_v[\tilde{\rho}]$ is the energy functional of eq (2.4). In other words, if $E_v[\tilde{\rho}]$ for a given external potential (v_{ext}) is evaluated for some density that is not the ground state density of the system under that potential, one can never find the energy that is below the true ground state energy. We stress here that the Hohenberg-Kohn theorems are the mathematical foundations to DFT. This gives an exact picture of how to determine the ground-state properties for any given system. But this theory does not give the functional form of $F_{HK}[\rho]$. However, the key step towards such a problem, taken by Kohn and Sham, in 1965 [188], came to the rescue, which we will discuss now. They provided a way for the practical implementation of the two theorems and hence DFT to study the many-body systems.

2.2.2 Kohn-Sham Approach

The Kohn-Sham approach maps a given N-particle interacting system, which is of our interest, having the real potential onto a non-interacting (fictitious) system under some potential, provided that **both the systems have the same density**. The advantage of this approach is that it helps to evaluate or determine the major part of the kinetic energy (which corresponds to N non-interacting particles) and the residual (small) amount of kinetic energy (corresponding to the interaction of the actual interacting system of N electrons) can be calculated using some approximations.

Consider a non-interacting particle system with Hamiltonian \hat{H}_s under an external potential v_s having ground state density ρ_s with N number of electrons in the system. The ground state wave function is a Slater determinant of single-particle orbitals ϕ_i [185]

$$\psi_s = \frac{1}{\sqrt{N!}} \det[\phi_1 \phi_2 \dots \phi_N]$$

where ϕ_i s satisfy the equation $\left[-\frac{1}{2}\nabla^2 + v_s\right]\phi_i(r) = \epsilon_i\phi_i(r)$

And the ground state density for the non- interacting system is given by $\rho_s(r) = \sum_i^N |\phi_i(r)|^2$. Applying the Hohenberg-Kohn theorem to this non-interacting system, we can get at most one external potential which generates the density ρ_s . Therefore, knowing ρ_s , all the properties of the system are determined like the kinetic energy and the total energy which are given as

$$T_{s}[\rho_{s}] = \left\langle \psi_{s} | \sum_{i}^{N} (-\frac{1}{2} \nabla_{i}^{2}) | \psi_{s} \right\rangle$$
$$= \sum_{i}^{N} \left\langle \phi_{i} | (-\frac{1}{2} \nabla_{i}^{2}) | \phi_{i} \right\rangle$$
(2.6)

Now we consider our real interacting system with an external potential $v_{ext}(r)$ which has an electronic density $\rho(r)$ (which is equal to $\rho_s(r)$). The energy for this system is given by

$$E_{v}[\rho] = F_{HK}[\rho] + \int \rho(r) v_{ext} dr$$

$$= T[\rho] + E_{ee}[\rho] + E_{ext}[\rho]$$

$$= T_{s}[\rho] + T[\rho] - T_{s}[\rho] + J[\rho] + E_{ee}[\rho] - J[\rho] + E_{ext}[\rho]$$

$$= T_{s}[\rho] + J[\rho] + E_{ext}[\rho] + E_{xc}[\rho]$$

(2.7)

where $E_{xc}[\rho] = T[\rho] - T_s[\rho] + E_{ee}[\rho] - J[\rho]$ is the exchange-correlation energy. $E_{xc}[\rho]$ is functional of density by virtue of the HK theorem for the interacting system and $T_s[\rho]$ is functional of density by virtue of the HK theorem for the non-interacting system. The density dependence of $E_{ext}[\rho]$ and $J[\rho]$ are known. It is clear from the above that, through the introduction of orbitals, the major part of the kinetic energy, which is the kinetic energy for the non-interacting system, $T_s[\rho]$, is determined by Eq 2.6. But the form of the $E_{xc}[\rho]$ is not known. So various approximations to $E_{xc}[\rho]$ are made in the literature so that the exact density and the energy of the given interacting N-electron system can be obtained. Corresponding to the Kohn-Sham scheme for any ground state density $\rho(r)$ of an interacting system there exists a non-interacting system with the same ground state density. Hence, the equation (2.7) can be written as

$$E[\rho] = \sum_{i} \int \phi_{i}^{*}(r) (\frac{-1}{2} \nabla^{2}) \phi_{i}(r) dr + J[\rho] + E_{xc}[\rho] + \int v_{ext} \rho(r) dr$$

Minimization of $E[\rho]$ under the constraint from orthogonality condition, gives us the famous Kohn-Sham equations to solve the ground state density of the interacting system

$$\left[-\frac{1}{2}\nabla^2 + v_s(r)\right]\Phi_i(r) = \epsilon_i \Phi_i(r)$$
(2.8)

where $v_s(r) = v_{ext}(r) + v_H(r) + v_{xc}([\rho], r)$ and $v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}$. The Kohn-Sham single-particle equations are exact and are easy to solve. However, the unknown exchange-correlation energy must be approximated. Some of the approximations of exchange-correlation energy will be described in the next section.

2.2.3 Various Exchange-Correlation Functionals

In this thesis, various exchange-correlation functionals have been used. These are described below.

Generalised Gradient Approximation: As we know that Local Density Approximation (LDA) does not take into account the gradient of density. To take into consideration the inhomogeneity of the true electron density, a further improvement was made by the inclusion of spatial variation of density in the Generalised Gradient Approximation (GGA). The GGA exchange-correlation energy functional form is given as

$$E_{xc}^{GGA}[\rho] = \int f(\rho(r), \nabla \rho(r)) dr$$

The most popular GGA exchange-correlation functional form is given by Perdew, Burke, and Ernzerhof (PBE) [189, 190], and in this thesis, we have primarily used this functional only for the estimation of ground-state electronic structures of the studied systems.

Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional: Although the most commonly used approximations of the exchange-correlation functionals, such as LDA and GGA, are proven to be extremely successful for providing an accurate prediction of the electronic and structural ground-state properties, these systematically fail to predict the accurate bandgap in the electronic structure of the system [191, 192], due to the presence of a spurious self-interaction [193]. Heyd, Scuseria, and Ernzerhof (HSE) [194, 195] proposed an efficient and accurate screened hybrid functional in which the a fraction of the HF exchange energy is mixed with conventional GGA exchange-correlation functional given by the following expression

$$E_X^{HSE} = \frac{1}{4} E_X^{HF,s.r}(w) + \frac{3}{4} E_X^{PBE,s.r}(w) + E_X^{PBE,l.r}(w) + E_c^{PBE}$$

In this thesis, we have used this HSE functional to predict the accurate bandgap of any semiconducting system studied in this thesis. In what follows, we provide a brief introduction to the codes and softwares used to carry the electronic structure calculations in this thesis.

2.2.4 Vienna Ab Initio Simulation Package (VASP)

The equilibrium lattice constants and fractional coordinates of the systems have been optimized by density functional theory (DFT) based electronic structure calculations as implemented in Vienna Ab Initio Simulation Package (VASP) [196, 197]. We use the projector augmented wave (PAW) method [198]. Convergence tests have been performed for energy cut-off, k mesh, and vacuum distance. We use an energy cut-off of 400-500 eV for the planewaves. For the simulation of the 2D structures, we use a vacuum length of about 18 Å in the z-direction (direction perpendicular to the plane of 2D surface) to avoid the interaction between two adjacent unit cells along z-direction in the periodic arrangement. The energy and the force tolerance for our calculations are 1 μ eV and 10 meV/Å, respectively. For obtaining the electronic properties of the optimized structures, the Brillouin zone integration has been carried out using the tetrahedron method implemented in VASP [196, 197]. In order to account for weak dispersion force, if any present in the system, we have also probed the effect of long-range van der Waals (vdW) interaction by using the DFT-D2 [199] and DFT-D3 [200, 201] methods as implemented in VASP [196, 197]. The geometric structures, valence charge density distributions, and electronic localization function are plotted using the VESTA software [202].

Energetic stability: For probing the energetic stability of 2D materials studied in this thesis, we calculate different energies as discussed below:

1: Firstly, to check whether these materials form bound systems (means energetically stable) or not, we have used the standard definition of binding energy (given below), which is defined as the amount of energy released when we bring the constituent atoms from infinity to form the system. The binding energy is given by, $E_B = E_{tot} - \sum_i n_i E_i^{atom}$, where *i* denotes different types of atoms present in the unit cell of the material, E_{tot} and E_i^{atom} are the energy of the system and corresponding atom *i*, respectively and n_i represents the number of same type (*i*) of atoms present in the system.

2: Further, sometimes it is useful to calculate the amount of energy liberated when a composite system is formed of some particular fragments (for example adsorbates and surfaces, instead of the individual atoms). We calculate the interaction energy/adsorption energy to understand the relative ease of adsorption of various adsorbates on different inequivalent sites on the different 2D substrates. The interaction energy, E_{int} , of the composite system is defined as $E_{int} = E_{total} - E_{2D} - E_{adsorbate}$, where E_{total} , E_{2D} and $E_{adsorbate}$ are the energies of the optimized composite system, bare 2D surface and the adsorbate, respectively.

3: The formation energies (E_{form}) have also been calculated with the aim to explore the possibility of preparing the material experimentally, as $E_{form} = E_{tot} - \sum_i n_i E_i^{bulk}$, where E_{tot} , i, n_i denote the same parameters as explained above. E_i^{bulk} is the energy of the corresponding atom i in its bulk form.

Strain calculations: In this thesis, we have also probed the influence of the application of biaxial strain (tensile or compressive) to analyze the modification in the geometry and the electronic structures. The applied strain, δ , is defined as $\delta = ((a-a_0)/a_0) \times 100\%$, where a and a_0 are the lattice constants of strained and unstrained systems, respectively. For each value of bi-axial strain, all atoms are relaxed with the fixed lattice constant. In the case of applying the bi-axial strain, we deform the in-plane lattice parameters a and b by an equal amount.

2.2.5 Phonopy

To calculate the phonon spectra of a given system, first-principles phonon calculations have been performed employing the finite displacement method [203] as implemented in PHONOPY packages [204,205], which is an open-source code. We wish to mention here that a supercell (typically of 6×6 mesh size for the 2D systems studied in this thesis) is chosen for the calculation of phonon dispersion.

2.2.6 Boltztrap:

The calculation of electrical conductivity is carried out using the software BoltzTraP [206]. BoltzTraP predicts the transport properties based on a semi-classical theory under relaxation time approximation. The following equations [206–208] are used to calculate electrical conductivity (σ) under the relaxation-time approximation

$$\frac{\sigma_{\alpha\beta}(T,\mu)}{\tau} = \frac{1}{V} \int e^2 \nu_{\alpha}(i,\mathbf{k}) \nu_{\beta}(i,\mathbf{k}) \Big[\frac{-\partial f_{\mu}(T,\epsilon)}{\partial \epsilon} \Big]$$

where the group velocity, ν_{α} , of electrons in α direction is given by $\nu_{\alpha}(i, \mathbf{k}) = \frac{1}{\hbar} \frac{\partial \epsilon_{i,\mathbf{k}}}{\partial k_{\alpha}}$

 τ is the relaxation time. ϵ , **k** are energy and reciprocal vector, respectively. μ , T are chemical potential and temperature of the system, respectively. α , β represent the x,y,z directions and i, **k** represent the band-index and k-points, respectively. $f_{\mu} = \frac{1}{1+e^{\beta(\epsilon-\mu)}}$ is the Fermi-Dirac distribution function. τ is considered as isotropic in nature nad independent of the ϵ and k.

Chapter 3

Prediction of energetically stable β_{12} phase of Aluminene

3.1 Introduction

As stated in the introduction, 2D materials have received enormous attention of researchers after the discovery of graphene. Following the discovery of graphene, the atomically thin layer of materials composed of single atomic variants of other elements of group IV, and also group VI and V elements have been pursued and these are found to display many exciting properties [209]. Further, a 2D elemental monolayer system based on group III element boron, named as borophene, has recently been predicted. It has been found to be stable in many different allotropes and has successfully been grown on silver substrate and the results of studies of electronic structure indicate its metallic behavior [19, 61–65]. Besides borophene, another elemental 2D material, made of group III element gallium, namely, gallenene, has also been experimentally realized by Kochat *et al.* via exfoliation technique to isolate atomically thin gallium layer [21]. This 2D material exhibits a buckled structure.

In the literature, the β_{12} configuration [61] has been reported as the low temperature phase of borophene. It has been found to be a metal with highly anisotropic electronic properties. Further, the β_{12} phase of borophene exhibits linear band dispersion (Dirac cone), particularly near the Fermi energy (E_F), which is well known to give rise to many fascinating properties, including an extremely high mobility of the carriers [210, 211].

As already discussed in Chapter 1, the 2D monoelemental monolayer made of Al atom, namely aluminene, has been theoretically predicted [20, 70, 71] to be stable in only a few configurations, e.g., planar, buckled, 8-Pmmn, and D2h-13 Pmnm space-group [20,70,71]. However, so far, stability of aluminene in the β_{12} configuration has not been explored. The possibility of stabilizing 2D aluminium monolayers in this particular configuration may, therefore, be worth investigating, and we probe the same in this chapter^{**}. For comparison, we also probe the possibility of finding another group III element - gallium, in this configuration. Besides, we also probe, whether stable 2D monolayers of a luminium and gallium in β_{12} configuration exhibit a signature of linear dispersion, close to the Fermi level, like borophene [61] (as mentioned above) and we indeed find the signature of linear bands (Dirac-like features) in these systems. In this chapter, we also explore the effect of iso-electronic substitution by B, Al, Ga, In, and Tl atoms in these 2D monolayers and examine the possibility of variation in the position and dispersion of the linear bands in the energy-momentum (E-k) dispersion. The motivation behind such a substitution is to probe if the Dirac points present in the pristine cases shifts closer to the Fermi level, and to predict materials with interesting transport properties.

3.2 Results and Discussion

In what follows, we first discuss the results of geometric, energetic, and electronic properties of Al and Ga based monolayers in β_{12} configuration. For the sake of comparison and completeness, we also present the results of B atom based monolayers. Further, in the end, the results of iso-electronic substitution of the above-mentioned group III element based

^{**}This work is published by the author of this thesis and others in the year 2020 in Physical Review B belonging to APS Publishing group. https://journals.aps.org/prb/abstract/10.1103/PhysRevB.102.085424

monolayers will also be presented.

3.2.1 Group III Atom Based Monolayers

3.2.1.1 Geometric Structure and Energetic Stability

Figure 3.1 represents the geometric structure of β_{12} phase, containing five atoms in the unit cell. Among them, four atoms (gray colored balls) are located at the atomic sites, A and B, forming a honeycomb lattice as observed in the case of honeycomb lattice of graphene. The fifth atom (golden colored balls), which is expected to donate electron to the honeycomb structure, makes the system more stable. This atom is positioned at the hollow site and is slightly above the plane of the honeycomb lattice. This site is named as the C-site. As is observed in Figure 3.1, in the β_{12} configuration, only half of the hollow sites are occupied by the extra atoms.



Figure 3.1: The geometric structure (top and side views) of the group III based monolayer in β_{12} structure in $2 \times 2 \times 1$ super cell configuration. The dashed rectangle represents the unit cell, with lattice constants a and b. A, B and C are the inequivalent atomic sites. d, θ and h represent the bond distances, bond angles and vertical heights between the nearest neighbors, respectively.

Table 3.1 summarizes the results of the optimized geometrical parameters and binding energies for monolayers of B, Al, and Ga in β_{12} configuration. First, we present our results on the geometric properties of borophene, which exhibits a planar structure. The calculated values for the lattice constants exhibit excellent matching with the experimental ones [61]. The bond angles, θ_1 and θ_2 , are found to be very close to 120°, and the values for θ_3 and θ_4 are near 60° (Table 3.1). These observed results indicate that borophene favors a sp²like hybridization. To quantify the buckling present in the β_{12} structure, three vertical heights $(h_1, h_2 \text{ and } h_3, \text{ as indicated in Figure 3.1})$ between the neighboring atoms have been identified. h_1 refers to the vertical distance between atoms A and B; the same between the atom at the C-site and its neighbor A (B) atom is represented by h_2 (h_3). All the three heights are zero for borophene in the β_{12} phase indicating the planarity of the structure. Table 3.1 also lists the nearest neighbor bond distances $(d_i, \text{ with } i = 1-4)$, and we observe finite differences between the bond distances. The values of d_1 and d_4 are significantly lower than those of d_2 and d_3 with a maximum deviation of around 4 % between them. Further, the ratio, b/a, is quite close to $\sqrt{3}$ as that of the honeycomb lattice. The minor variations in bond lengths and angles mean that there is no effect of the extra atom at the C-site on the geometry.

Binding Energy Lattice Constant (Å) Bond Angle ($^{\circ}$) Height (Å) System Bond Length (Å) $(\theta_1, \theta_2, \theta_3, \theta_4)$ (eV/atom) \mathbf{a} b (d_1, d_2, d_3, d_4) (h_1, h_2, h_3) В -5.9072.9295.071.65, 1.71, 119.7, 120.5,

1.70, 1.69

2.55, 2.69,

2.71, 2.60

2.48, 2.72,

2.77, 2.55

(5.07 [212],

5.00 [61]

7.88

7.73

60.6, 59.1

121.5, 105.5

, 60.8, 57.8

121.9, 109.6,

61.3, 55.2

0.80.

1.15, 0.35

0.59,

1.32, 0.73

(-6.147 [212],)

-6.230 [61])

-2.680

-2.220

Al

Ga

(2.93 [212],)

3.00[61])

4.14

4.16

Table 3.1:	Binding	energies	and	geometrical	parameters	for	the	group	Ш	element	based
monolayers	in β_{12} co	onfigurati	lon.								

Now we discuss the results of the structural properties of aluminene	and gallenene.	For
these structures, the lattice constants have increased greatly compared to a	those of boroph	ene.

This is because of the large enhancement in the ionic radii: from B to Al and Ga (B: 0.41, Al: 0.67 and Ga: 0.76 Å) [213]. It is apparent from the results presented in Table 3.1 that the β_{12} structure is non-planar for each of these two monolayers. The non-zero values of h_1 , h_2 , and h_3 reveal that the structures are buckled. An important finding from Table 3.1 is that the ratio b/a for both aluminene (1.90) and gallenene (1.86) significantly deviate from the value of $\sqrt{3}$. It is observed that the β_{12} phase of aluminene has lower buckling compared to the buckled aluminene (2.45 Å) [70]. Because of the presence of buckling, deviation in the bond angle θ_2 from 120° has been observed. On the contrary, the variations of the other three bond angles compared to borophene are relatively smaller, with a maximum change of about 5%. We note that the variation in the angle θ_2 (θ_4) is related to the change in the h_1 (h_3) distance and vice versa.

Table 3.1 reveals that the highest deviation of θ_2 from 120° to 105.5° is observed for aluminene in the β_{12} -configuration. This leads to the largest buckling height h_1 (0.80Å) for the aluminene case. Contrary to this, θ_4 exhibits the least deviation from 60° (value being 57.8°), and hence, h_3 is minimum for aluminene. For gallenene, a similar trend has been observed for bond distances and angles. Interestingly, θ_2 is 109.6° for gallenene, which is close to 109.5° and suggests that sp³-like hybridization is favored by the atom A in this case. It is worth noting here that the buckling in the geometry strongly governs the hybridization present in the system. In cases of both aluminene and gallenene, the changes in the geometric structures because of buckling suggest that the hybridization will not be strictly of sp² or sp³-type, but it will be a mixture of both. This is different from borophene, which clearly favors a sp²-like hybridization. Similarly, a mixed hybridization has been observed in some of the group IV elemental monolayers as well [23, 24, 26, 214–218].

Table 3.1 lists the results of binding energy per atom for all the studied systems. These data reveal that all the probed monolayers in β_{12} structure have negative binding energies and hence, each forms a bound system. Borophene possesses the highest (in magnitude) value of binding energy, with gallenene having the least value. This indicates that borophene is the

most stable system among the three group III based monolayers in β_{12} structure. The binding energy per atom for borophene in different structures reported in the literature i.e., for β_{12} , χ_3 and stripped (Pmmn) borophene are -6.15, -6.16 and -6.10 eV/atom, respectively [212]. Similar values for aluminene in different structures are -3.47 (P $\bar{3}$ m1), -2.94 (8-Pmmn), -3.02 (D2h-13 Pmnm), and -2.29 (P6/mmm) eV/atom (which matches with the literature) [70, 71, 219]. For the β_{12} structure, aluminene has a value of -2.68 eV/atom. Thus, it is clear that, for all the available configurations, aluminene possesses less binding energies than those of borophene structures.



Figure 3.2: Spatial distribution of valence charge density for the group III based monolayers. 0 (blue) and 1 (red) in the bar scale represent the charge deficit and the charge rich region, respectively. Bader charges on symmetrically inequivalent atoms (1(2), 3(4)) and 5, respectively, at the sites A, B and C) are shown.

For all the three cases, we show the valence charge density distribution in Figure 3.2. In order to gain insight into the bonding present in the system, we have also performed the Bader charge analysis [220]. The positive and negative signs show, respectively, the loss and gain of electrons by an atom. It is noted that electrons are acquired by the atoms at sites A (referred to as atoms 1 and 2). On the other hand, the atoms at sites B (atoms 3 and 4) and C (atom 5) act as electron donor in all the three monolayers. Notably, the C-site atom losses maximum number of electrons. For borophene and aluminene, an appreciable charge build-up between the atoms 3 and 4 compared to that between 4 and 5 has been observed. This can be attributed to the fact that, the bond distance between the former pair of atoms (d_1) is smaller (compared with the latter pair (d_2)). For gallenene, almost uniform distribution of charge density has been observed and the quantity of charge transfer between the constituent atoms is therefore lower (Figure 3.2).

3.2.1.2 Electronic Properties

Figure 3.3 presents the results of the electronic band structures for borophene, aluminene, and gallenene in β_{12} phase. All the three monolayers are found to be metallic in nature, exhibiting crossing of bands at the Fermi level. The energy versus momentum band dispersion is anisotropic along the high symmetry k-points in the Brillouin zone for all the three monolayers. As mentioned in the introduction, in the electronic band structures of borophene, existence of two Dirac cones is observed (which are characterized by the Dirac-like relativistic Hamiltonian) above the E_F . We find that these are around 0.5 eV and 2.0 eV along the S - Y direction and the $\Gamma - X$ direction, respectively. Further, the charge carriers close to the above mentioned linear dispersions are expected to move with the Fermi velocities (v_F) of 1.28 and 0.74 × 10⁶ m/s, respectively.



Figure 3.3: The electronic band structures of the group III based monolayers in β_{12} configuration. The blue circles indicate the locations of linear band crossings (Dirac-like cones). The Fermi energy is set to 0 eV.

Interestingly, we find that the Dirac cone around 0.5 eV has a far higher value of v_F

than that around 2.0 eV, and this value is even comparable to those of the charge carriers of graphene (0.85 - 3 × 10⁶ m/s) [221]. Further, these values are indeed higher than those observed for silicene (0.53 × 10⁶ m/s) [221], germanene (0.51 × 10⁶ m/s) [221] and CAs₃ (0.35 × 10⁶ m/s) [222] 2D monolayers. It is anticipated that the transport properties of borophene will be greatly affected by such large values of v_F.

For aluminene, we observe that the two linearly crossed bands have shifted nearer to the Fermi level compared to borophene and are found at around 0.8 and 0.3 eV, in the $\Gamma - X$ and S - Y directions, respectively. The corresponding values of v_F are 0.50 and 0.85 $\times 10^6$ m/s, respectively. Besides, we also note another linear E-k dispersion in the valence region at around -1.3 eV along the $\Gamma - X$ direction, and the v_F for the corresponding charge carriers has been calculated to be about 0.53×10^6 m/s.

Now we focus our attention to gallenene. Dirac cones are seen to be at lower energies, along the $\Gamma - X$ and S - Y directions. Further, we notice the signature of a similar crossing at around -0.03 eV along the S - Y direction and about -1.2 eV in the S - X direction. The v_F values for the charge carriers corresponding to the two cones along the S - Y and S - Xdirections are 0.82 and 0.55 × 10⁶ m/s, respectively. For the Dirac cones in the conduction region along the $\Gamma - X$ and $Y - \Gamma$ directions, values of 0.50 and 0.43 × 10⁶ m/s, respectively, have been found. Therefore, for both Al and Ga based 2D monolayers, we notice that one of the v_F values is comparable to the lowest value reported for graphene. Interestingly, we observe that in all the cases, the Dirac cone lying close to the Fermi level corresponds to the highest value of Fermi velocity.

It is well-known that the position of the Dirac cone as well as the Fermi velocity play a significant role in governing the transport properties. It is worth noting here that although the Fermi velocities are found to be somewhat lower for the charge carriers in aluminene and gallenene than borophene, the corresponding Dirac cones are much closer to the Fermi level than in borophene. Thus, we expect that all the three monolayers would exhibit interesting transport properties. Hence, overall, we conclude that two Dirac points along the $\Gamma - X$

and S - Y directions are present in all the three probed monolayers. Further, we observe that these points shift closer to the Fermi level as we go to higher atomic numbers of the constituent elements (from borophene to gallenene). It implies that the existence of buckling in the aluminene and gallenene structure does not influence the linear dispersion, which can be assumed as a characteristic feature of group III element based monolayers in the β_{12} configuration.

3.2.2 Effect of iso-electronic substitution

We now investigate the influence of iso-electronic substitution of group III elements (B to Tl) at the C-site (since this site tends to donate electrons to the system for its stabilization) on the structural and the electronic properties of borophene (B₅), aluminene (Al₅), and gallenene (Ga₅), in the β_{12} phase. The iso-electronic substitution at the C-site leads to a total of 15 probable monolayers: B₄X, Al₄X, and Ga₄X, where X (= B, Al, Ga, In and Tl) represents the iso-electronic element.

3.2.2.1 Geometric structure and energetic stability

First we explore the energetic stability (Figure 3.4) and geometric properties (Figure 3.5) of the B_4X , Al_4X , and Ga_4X cases. For the sake of completeness and comparison, along with the results of the substituted cases, we present the results of the pristine cases as well.

 $\mathbf{B}_4 \mathbf{X}$: Figure 3.4 illustrates the energetic stability of all the structures with iso-electronic substitution at the C-site in \mathbf{B}_5 . A decreasing (in magnitude) trend of E_B per atom is observed as X varies from B to Ga, followed by a saturation in the values for In and Tl. It should be noticed that, in comparison to pristine aluminene and gallenene, the iso-electronically substituted borophenes are more stable. Further, the iso-electronic substitution in borophene in the β_{12} configuration retains the planarity of borophene as is evident from the zero values of h_1 , h_2 , and h_3 for $\mathbf{B}_4 \mathbf{X}$ (Figure 3.5). We note a monotonically increasing trend for the lattice constants (*a* and *b*) with the increase in the atomic number of the substituted atom.



Figure 3.4: The binding energy of the group III based monolayers in β_{12} configuration as a function of iso-electronic substitution.

The b/a ratio has enhanced from a value close to $\sqrt{3}$ to 2.409, indicating a large degree of deformation in the hexagons. Indeed, we note a substantial deviation in the values of θ_1 and θ_2 , which indicates that an iso-electronic replacement by an element from group III with a larger atomic radius does not support sp² hybridization as in case of pristine borophene.

Al₄X and Ga₄X : Figure 3.4 depicts that all the probed systems with iso-electronic substitution at the C site of aluminene and gallenene are energetically stable systems. Identical to borophene, there is a pattern of systematic decrease in energetic stability, as larger group III elements are used as the substituent. On the other hand, when these two monolayers are replaced by smaller iso-electronic atoms, these systems become more stable. This is seen for Al₄B as well as Ga₄B and Ga₄Al monolayers. Hence, to summarize the above discussion: the B-based systems among all the three monolayer systems exhibit the highest stability. It is shown from Figure 3.5 that the variations of lattice constants (a and b) indicate a different behavior for both Al and Ga-based systems in contrast to the borophene cases. It is to note here that a (b) has the lowest (highest) values when the boron atom occupies the C-site. However, minor variations are observed for substitutions by atoms other than the B atom. As is evident from the non-zero values of h_1 , h_2 and h_3 , the aluminene and the gallenene systems exhibit buckling in their geometries. Notably, the values of h_2 are found to be very



Figure 3.5: Variation of geometrical parameters with iso-electronic substitution for the group III based monolayers in β_{12} configuration.

close to zero for the case when the atom at the C-site is replaced by the boron atom. This is because the boron atom is found almost on the same plane as the atoms at the B-site (i.e., Al and Ga atoms). Because of the increase in the heights (h_2 and h_3), the corresponding bond angle θ_4 centered around the X atom decreases from B to Tl. On the other hand, angles θ_1 , θ_2 and θ_3 do not change appreciably with the substitution.

Charge Analysis: To shed light into the bonding nature between the constituent atoms of iso-electronically substituted systems, we evaluate the Bader charges (Figure 3.6) on atoms at sites, A (atoms 1 and 2), B (atoms 3 and 4), and C (atom 5). The observations and findings from Figure 3.6 are:

(i) For B_4X , all the substituted atoms act as electron donor. Moreover, the quantity of charge transfer from the atom at the C-site is greater than that observed for B_5 . This clearly

shows that the substitution at the C-site plays almost the same role of stabilization of the structure in the β_{12} configuration via charge transfer. (ii) For all the three sets of monolayers, the atoms (1 and 2) at the A-site often act as electron acceptor, except for the cases of Al₄B and Ga₄B. This is because the electronegativity of B atom (2.04) is greater than Al (1.61) and Ga (1.81). In the case of B₄Al, this also explains the large quantity of charge lost by the Al atom. (iii) For the Al₄X series, the C-site atom always gains electrons from the system because Al atom possesses the lowest value for the electronegativity among all the group III elements probed. (iv) For most of the cases, atoms located at the B-site (atoms 3 and 4) loose electrons to the system. However, in comparison to the atoms at sites A and C, significantly less charge transfer occurs in case of the atoms at the B-site. (v) As the electronegativity of B atom is the greatest among all the group III atoms, we notice huge charge transfer between the B and the other constituent atoms. This can lead to strengthening of the ionic bonding between the constituent atoms of boron-based monolayers.



Figure 3.6: Bader charges on atoms (shown in the inset) in the β_{12} structure. Negative charge signifies that the atom has gained electron and positive charge represents that the atom has lost electron.

3.2.2.2 Electronic Properties

This subsection addresses the modifications in the electronic band structures of B_5 , Al_5 and Ga_5 as a result of iso-electronic substitution at the C-site. The band structures for the iso-
electronically substituted cases are shown in Figure 3.7. We note that, alike the pristine cases, the electronic band structures of B_4X , Al_4X and Ga_4X display metallic nature. Importantly, we note the presence of at least one linearly dispersed band situated nearer to the Fermi level when compared to the B_5 case.



Figure 3.7: The electronic band structures of group III based monolayers in β_{12} configuration with iso-electronic substitution. The blue circles indicate the locations of linear band crossings (Dirac-like cones). The Fermi energy is set to 0 eV.

 $\mathbf{B}_{4}\mathbf{X}$: When the B atom is substituted by the X atom, the band dispersion does not differ much from that of the pristine borophene system. It is worth mentioning here that the presence of Dirac dispersion above the Fermi level along the $\Gamma - X$ path in \mathbf{B}_{5} is preserved in all the iso-electronically substituted B_4X systems. The positions of the linearly crossed bands are around 2.0 eV, 1.3 eV, 1.1 eV, 1.4 eV, and 0.9 eV for B, Al, Ga, In and Tl, respectively. Shifting of various valence and the conduction bands towards the Fermi level, along with a greater number of linearly crossed bands have also been observed. For example, we note the appearance of two extra Dirac cones for the Al and In substituted borophene, in comparison to the pristine B_5 case. In fact, one of them lies almost at the Fermi level. Hence, it is found that tuning of the electronic structure in β_{12} borophene can be achieved via the iso-electronic substitution at the C site.

Al₄X and Ga₄X: It is observed that the features of the band structures of both, Al₄X and Ga₄X are reasonably similar, except for the case of B atom as substituent. The explanation for this anomaly can be attributed to the fact that Al₄B and Ga₄B have slightly different structure, with h_2 value equal to zero. Contrary to this, the rest of the other cases have h_2 value more than 1.0 Å. For all the systems in the Al₄X and Ga₄X series, we notice a Dirac dispersion along the S - Y path close to the Fermi level. Besides, few other linear band crossings, in the conduction as well as the valence regions, have been observed. Notably, the positions of Dirac features in the conduction band regions are shifted closer to the Fermi level in case of In and Tl substituted cases have clearly different dispersions, leading to the reduction in the number of Dirac like characteristics to two. Again, this disparity can easily be associated with the huge buckling seen in the substituted Tl systems, relative to the others. Overall, most of the Al₄X and Ga₄X systems, probed in this work, show one or more Dirac features (closer to the Fermi level) compared to borophene in the β_{12} configuration.

3.3 Summary

In this chapter, we have presented detailed analyses of structural and electronic properties of different group III (B, Al and Ga) based monolayers in β_{12} configuration. The results indicate that all the probed monolayers are energetically stable and possess metallic nature. Unlike the planar borophene case, the aluminene and gallenene systems are found to be non-planar. However, similar to borophene, these two monolayers also exhibit linear band crossings, though, the positions of linear crossing are much closer to the Fermi level compared to borophene. In addition, the Fermi velocities corresponding to the Dirac dispersions are found to be comparable to those observed for graphene.

Further, the influence of substitution of iso-electronic (B, Al, Ga, In and Tl) elements at the inequivalent C-site of β_{12} monolayers (borophene, aluminene and gallenene) has been probed. Interestingly, our findings indicate that all the pristine and iso-electronically substituted systems show Dirac cone like feature. In addition, when compared with pristine borophene, the positions of Dirac dispersion in all the substituted systems are found to lie closer to the Fermi level.

Finally, equipped with the calculated binding energies of various theoretically predicted 2D allotropes of aluminene from the present chapter, along with the data from the literature, we note that the hexagonal buckled aluminene possesses the highest binding energy, implying that this configuration is the most favorable amongst all. On the other hand, the planar aluminene system exhibits both geometrically and electronically close resemblance with those of graphene. Hence, both these configurations warrant further probing and analysis in terms of both fundamental understanding as well as possible applications. Thus, in the next few chapters, we study in detail, various methods of tuning the geometric, electronic and magnetic properties of only the buckled and the planar aluminene systems.

Chapter 4

Functionalization of 2D Aluminene

4.1 Introduction

As mentioned in the introduction chapter, because of the large surface area of 2D monolayer structures, functionalization of these in the form of adsorption, substitutional doping, intercalation, etc., plays a crucial role, not only in enriching the physics and chemistry of different compositions, but also in exploiting the multifunctionality of 2D materials toward various specific applications. The influence of functionalization includes modifications in the geometry and electronic structures of the 2D structures, also introduction of magnetism and spintronic behavior. These aspects can then be explored further for various promising applications, including storage and sensing of hazardous gases.

As concluded in the previous chapter, both buckled aluminene, being energetically the most stable and the planar aluminene, which can be regarded as highly hole-doped graphene, warrant further probing and analysis in terms of both fundamental understanding as well as possible applications. However, so far, functionalization of 2D aluminene have not been studied in the literature which motivated us to investigate in details, various methods of tuning the geometric, electronic and magnetic properties of these two different allotropes of aluminene as a result of functionalization. In this chapter, first the results of adsorption of transition metal (TM) atoms on aluminene have been presented, followed by the study of substitution in the consequent section. In the end, results of intercalation of TM atoms in bilayer of planar and buckled aluminene have also been presented.

4.2 Results and Discussion

4.2.1 Transition Metal Adsorbed Aluminene

This section is devoted to systematically examine the adsorption of first row TM atoms from Sc to Cu as well as the second-row TM atoms from Y to Ag (in total 18 different systems) on 2D monolayer of planar aluminene (Figure 4.1). A brief comparative analysis of the adsorption of different TM atoms on aluminene as well as on 2D monolayer materials across different classes is also carried out. To this end, we consider, for comparison, one 2D material each from groups IV and V, that is, silicene and arsenene.



Figure 4.1: Aluminene (planar): (a) bare and with TM atoms adsorbed at different sites namely (b) Hollow (H), (c) Top (T) and (d) Bridge (Br); top and side views are given in upper and lower panels respectively. Pink and blue balls represent aluminium and TM atoms, respectively. A and B represent two inequivalent Al atoms of the unit cell. (e),(f), (g) and (h) represent the same for bare silicene (arsenene) and TM adsorbed at different sites, respectively. Red and green balls represent silicon (arsenic) and TM atoms, respectively.

We study the adsorption of a single TM atom per unit cell of the 2D monolayers at three distinct crystallographically inequivalent sites, namely the hollow (H), the top (T), and the bridge (Br) sites. In what follows, we represent these composite systems, a TM atom adsorbed at the respective sites as TM@H, TM@T, and TM@Br, respectively. For arsenene and silicene, we have taken the buckled structure (ground state). There are two possible top positions for a buckled structure, described as T_A and T_B , where TM atoms are on top of the A and B sites, respectively. We denote the systems with TM atom adsorbed at these two different top sites as TM@ T_A and TM@ T_B , respectively.

Before discussing the adsorption of TM atoms on 2D monolayers, we wish to mention that our results of the lattice constants and binding energy (E_B) for the pristine 2D monolayer structures match well with the existing data in the literature. From our calculations, the equilibrium lattice constant (a) values obtained are 4.48 (4.49 [20]), 3.86 (3.87 [97]) and 3.61 (3.61 [30]) Å, respectively, for bare aluminene, silicene and arsenene. We obtained the following values of E_B /atom, -2.286 (-1.956 [20]), -3.903 (-3.958 [97]) and -2.981(-2.989 [30]) eV/atom for these three pristine 2D monolayers.

4.2.1.1 Analysis of Energetics and Geometry

Here we analyze the trend of binding of adsorbed TM atom on 2D aluminene, silicene, and arsenene, and the relative stability based on the $E_B/atom$, as a function of the atomic number Z of the adsorbed TM atom (Figure 4.2). We also discuss the geometrical parameters. A negative value of $E_B/atom$ means that the system is energetically stable. We note that the higher the magnitude of $E_B/atom$, the more stable the structure is. Additionally, the choice of the site for adsorption of different TM atoms on the 2D surface is analyzed in terms of the interaction energy determined for the most preferable adsorption site in each case.

The values of E_B /atom for 3d and 4d TM atoms adsorbed on aluminene are shown in Figure 4.2(a) and Figure 4.2(b), respectively. First, we analyze the case of TM atoms with adsorption of 3d electrons. We notice that each of the composite systems gives rise to a



Figure 4.2: Binding energy per atom (in eV/atom) for 3d ((a), (c), (e)) and 4d ((b),(d),(f)) TM atoms adsorbed on different sites of planar aluminene as well as buckled silicene and arsenene as a function of atomic number (Z) of the TM atom. In the inset, plot is given for interaction energy (in eV) for adsorption at the site, which corresponds to the lowest energy configuration, as a function of Z of TM atoms.

bound system. Our results indicate that the T-configuration is the most stable one for all the TM (Sc to Cu) atoms. It is important to note that the optimized structure of the TMadsorbed planar aluminene becomes buckled-like after adsorption of the TM atoms at the T site. In addition, the buckling distance in aluminene is also found to be very high (2.31 -2.44 Å, for the 3d and 2.25 - 2.43 Å, for the 4d TM atoms) when compared with the buckled systems like bare silicene (0.46 Å) [24] and arsenene (1.39 Å) [30]. However, it is of the order of the buckling distance of buckled aluminene (2.45 Å) [70]. Figure 4.2(b) summarizes the results of E_B /atom for the composite systems of 4d TM atoms adsorbed on aluminene and we note that all the systems are bound in nature. Also the trend for the lowest energy structures for 4d TM atoms is observed to be very similar to those of the composite systems of 3d TM atoms on aluminene. The TM@*H* configuration corresponds to the lowest energy case for Y atom. However, it is found to be energetically very close to the E_B for the case of *T* site. The TM@*T* structure corresponds to the most stable configuration, for Zr to Ag. Hence, the TM@*T* configuration is found to be the minimum energy one for both 3d and 4d TM atom adsorbed aluminene except for the Y case.

As in case of TM adsorption on aluminene, the stability of the TM atoms on silicene and arsenene at different sites is also analyzed on the basis of their relative $E_B/atom$. Figure 4.2(c,d), and 4.2(e,f) show the $E_B/atom$ for silicene and arsenene adsorbed with TM (3d and 4d) atoms, respectively. We observe that except for Ti, all the TM atoms with 3d electrons favor the *H*-site on silicene which matches very well with the results available in the literature [85]. Similarly, most of the 3d and 4d TM atoms prefer to reside at the *H*-site of 2D arsenene [219]**.

T configuration versus H configuration: To understand the relative stability between the H and T adsorption sites, we have calculated the number of first and second near-neighbors (NN) of the TM atoms and their distances for both the H and T configurations. We find that the T configuration has a greater number of NNs than the H case. For a more comprehensive explanation, we choose the Mn atom case as an example. Three Al atoms at a distance of 2.67 Å are the first NN of Mn, and the second set of NN atoms are six Mn atoms at a distance of 2.78 Å. It is worth noting here that there is a relatively small difference between the first and second NN distances, so we can assume that the effective

^{**}This published work is by the author of $_{\mathrm{this}}$ thesis and others inthe year Computational Condensed Matter belonging Elsevier Publishing 2018in to group. https://www.sciencedirect.com/science/article/abs/pii/S2352214318301709

number of close neighbors is nine in this case. On the other hand, when the Mn atom is adsorbed on the *H*-site of aluminene, the total number of first NN atoms is six. However, the second NN distance is 4.50 Å, which is very large as opposed to 2.67 Å (the first NN distance). Thus, in the *H* configuration, the effective number of NNs that can form chemical bonds is restricted to only six. This may be the likely reason as to why the *T* configuration (with more effective number of NN atoms) is energetically preferable over the *H* configuration. A similar argument based on the optimized geometry holds for the remaining 3d, and 4d TM atom adsorbed aluminene except for the Y atom. Alike the case of TM adsorbed aluminene, analysis of relative stability versus the number of NN justifies the observed preference of sites and the associated trend of E_B /atom for TM atom adsorbed on silicene and arsenene [219].

Interaction Energy: Though the values of E_B indicates the overall stability of a given system, we also calculate and compare the interaction energy to understand the relative ease of adsorption of various TM elements on different inequivalent sites of the 2D substrate aluminene, and compare the results with the cases of silicene, and arsenene substrates. It is noteworthy that in a few (Y and Nb for arsenene and Mo and Tc for silicene) cases, the optimization leads to a distorted structure in the lowest energy state. In these cases, we have considered the next lowest energy structure (which is H for the case of TM adsorbed arsenene and T_A for the case of silicene) for evaluating the interaction energy.

Our results of interaction energy for the minimum energy configurations are shown in the insets of Figure 4.2. First, we analyze the results of the aluminene, silicene, and arsenene systems for the TM atoms with 3d electrons. It is observed that for TM atoms Cr, Mn and Cu, all the three monolayer structures possess much smaller interaction energy than the other TM atoms, which matches well with the literature for the case of silicene [83]. Furthermore, it is seen that the trend for the higher interaction energy in the case of the TM atoms with 3d electrons is to some extent similar in all the three cases of aluminene, silicene, and arsenene. Ti and V atoms as well as Fe, Co, and Ni atoms are favored in

terms of interaction energy in all these three substrates from different groups. However, the trend for the 4d TM atoms adsorption on these three monolayers is found to be somewhat different, except for a few atoms of higher Z value. For the case of Ag atom, the adsorption leads to a much smaller interaction energy for all the three monolayer systems. It has been observed that the adsorption of Tc, Ru, and Rh give rise to higher interaction energy in all the three systems. Further, we note that in most of the cases, adsorption of the TM atoms with 3d electrons yields slightly higher interaction energy in the case of aluminene (-6.9 to -4.7 eV) when compared with silicene (-6 to -2.9 eV) and arsenene (-6.6 to -1.8 eV). Same trend is observed for the adsorption of TM elements with 4d electrons, where higher interaction energy in the case of aluminene (-7.2 to -1.8 eV) and arsenene (-7.2 to -3.6 eV). Hence, the above results suggest that aluminene is likely to fare better compared to the other two 2D materials in terms of ease of functionalization with TM atoms.

4.2.1.2 Analysis of Charge Distribution and Charge Transfer

To understand the nature of bonding between the constituent atoms in the composite system, and to gain more insight and quantify the amount of charge transfer, if any, between the TM atoms and monolayer material, we carry out the Bader charge analysis [220] for all the composite systems. The results of the net charge on each constituent atom in aluminene adsorbed with 3d, and 4d TM atoms are summarized in Figure 4.3. For the T configuration, as mentioned earlier, the two Al atoms do not remain in the same plane. As a result, the environments of the two Al atoms in the composite system are not the same, and we represent the Al atom, which is closer to the TM atom as Al2 and the other one as Al1. On the contrary, in the H configuration, there is no distinction between the two Al atoms as both the Al atoms have a similar environment.

In general, the charge transfer between two atoms of different electronegativity is discussed in the context of ionic bonding. Due to the difference in electronegativity values



Figure 4.3: Net charge on atoms using Bader method and electronegativity difference between TM and Al atoms as a function of Z is plotted for (a) 3d and (b) 4d TM atoms adsorbed on aluminene in the upper and lower panels, respectively for the T configuration for all systems except for Y (which favors *H*-site). (c) and (d) show the variation of electronegativity difference with Bader charges on 3d and 4d TM atoms. Dotted line is a guide to the eye. Charges on atom is obtained by taking the difference of the charge obtained from performing Bader analysis and the valence charge of the atom in the atomic limit (as defined in the atomic pseudopotential), i.e. positive charge on atom indicates electron deficiency and negatively charged atom represents electron rich atom.

between the Al and TM atoms, we expect a finite amount of charge transfer between them. For almost all the cases of 3d and 4d TM atom adsorbed aluminene material, the amount of transfer of charges is consistent with their respective electronegativity difference (Figures 4.3(c) and 4.3(d)). In the case of T configuration, the charge transfer occurs between the TM atom and the Al2 atom (which is closer to the TM atom), and the bonding exhibits an ionic-like character. From the Bader charge analysis, one can further conclude that the contribution of atom Al1 is negligible in this process of charge transfer. However, for the H configuration (applicable for Y adsorbed case), since both the Al atoms are in the same plane, both these atoms contribute appreciably to the charge transfer (to the TM atom). Therefore, one can conclude from the combined results of Bader charge analysis, that more of an ionic character (between the Al and TM atoms) prevails in all the configurations. The direction and the amount of charge transfer between the TM and Al atoms depend strongly on the atomic number. Hence, by varying the TM atom, it is possible to tune the polarity as well as the strength of the static electric field near the region just above the top of the 2D surface. This may h

4.2.1.3 Electronic and Magnetic Properties

In this subsection, we discuss the electronic and magnetic properties of the TM adsorbed aluminene system (Figures 4.4, and 4.5). It is observed that all the composite systems exhibit a metallic character since all these systems possess a finite amount of density of states (DOS) at the Fermi energy (E_F) . Though the observed metallic character is similar to that of pristine aluminene, the characters of the states in the composite system in the valence and conduction regions are expected to be different compared to the pristine case due to the adsorption of TM atom on aluminene. To explain the observed magnetic moments in these cases, we present spin resolved projected DOS for all the constituent atoms (Al1, Al2, and TM), shown in Figure 4.5.



Figure 4.4: Magnetic moment as a function of Z for 3d (left panel) and 4d (right panel) TM atom adsorbed aluminene at the three crystallographically inequivalent adsorption sites.

We discuss the magnetic behavior of the system first by analyzing the total magnetic moment in the unit cell of the composite system of aluminene adsorbed with the 3d and 4d TM atoms (Figure 4.4). We find that among the cases with adsorption of the 3d TM atoms, the composite systems with TM from Ti to Co exhibit magnetic nature, whereas, for the 4d atoms, only the composite case of Zr atom possesses magnetic moment. The PDOS analysis for the 3d TM adsorbed cases show that the major contribution of the magnetic moment arises from the 3d orbitals of the adsorbed TM atoms. Similar observations are seen for the 4d adsorbed cases [219].

Further, we note that the trend of charge transfer from one atom to another clearly explains the trend of the observed magnetic moments of the TM atom adsorbed on aluminene. It is observed from Figure 4.3 that from atoms Sc to V, the charge transfer takes place from the TM atom to the Al atom. Hence, we can expect a reduction in the moment of the TM atom. Similarly, from Cr to Cu, the charge is transferred from the Al atom to the TM atom. This charge contributes to the down spin moment of the TM atom since the up spin channel is already filled for these atoms. Thus, as is observed from the DOS, due to the compensation of the up and down spin moments, the magnetic moment of the composite system is less as compared to the isolated TM atom.

Next, we briefly discuss the relative stability of one configuration of TM adsorbed aluminene system over the other, on the basis of the analysis of total DOS. For that purpose, we separately analyze the total DOS obtained by adding up the DOS of both the spins of the three typical cases (TM atoms Co, Fe, and Ti). We choose H and T configurations and the results are shown in Figure 4.6. First, we analyze and compare the DOS for Co@H and Co@T. For the case of Co@H, we observe that there are large DOS contributions at and below the E_F . On the other hand, the DOS at the E_F for Co@T is relatively much smaller. If we integrate the DOS, we observe that states with higher DOS (more number of electrons) are closer to E_F in the case of Co@H as compared to that of Co@T. This implies that the states are comparatively further below the E_F in the Co@T case. In other words, overall, a spectral shift of the total DOS is observed in the case of Co@T in comparison to Co@H. This is expected to lead to the lowering of E_B in the case of Co@T over the Co@H case,



Figure 4.5: Spin-polarized (a) total density of states (TDOS) and (b), (c) and (d) partial density of states (PDOS) of 3d electronic orbitals for 3d TM atom adsorbed aluminene. The Fermi level has been set to zero and indicated by a vertical black dashed line. TDOS and PDOS are in the units of states/eV.

rendering the former to be the lowest energy structure. A similar explanation holds good for the case of Fe and Ti systems, as seen in Figure 4.6.



Figure 4.6: Comparison between the DOS of H and T-configuration for Co, Fe and Ti adsorbed aluminene.

Overall, the electronic structure results suggest that many composite systems turn out to be magnetic in nature due to the adsorption of TM atoms, whereas the pristine aluminene system exhibits no magnetic moment. Further, the stability of one particular configuration over another is also explained from the results of electronic DOS.

4.2.2 Transition Metal Substituted Aluminene

Similar to the study of adsorption, we investigate the geometries and the electronic as well as the magnetic properties when the Al atom in the planar aluminene lattice is substituted by a 3d TM atom (Sc to Cu) (Figure 4.7). Following the substitution we observe some distortion in the structure of the planar aluminene, leading to a buckled structure. Therefore, the following discussions are on the properties of TM-substituted buckled aluminene.

4.2.2.1 Geometric and Energetic Stability

The systems are found to be bound from energetic consideration (Figure 4.8(a)). The results of E_B /atom suggest that the Ti-substituted system is energetically the most stable (with the highest negative value) system, followed by the Co case among all the 3d TMsubstituted systems. The trends match with the available results in the literature on other 2D systems [107, 170, 219, 223–226]. For instance, for TM embedded silicene [107], Sc, Ti, and Co atoms have been found to exhibit the highest binding, while Zn shows the lowest binding. TM-substituted impurities in germanene and arsenene also exhibit a valley curve with Sc, Ti, Co and Ni showing the largest binding and Cr, Mn are the least-bound elements to germanene/arsenene surface [224, 225].



Figure 4.7: Schematic of top and side views of the optimized geometry of transition metal (TM = Sc-Cu) atom substituted 5×5 supercell of Aluminene. h is the height of the TM atom from the top layer of Aluminene. TM atom lies above and below the top layer of Aluminene lattice for (a) Sc, Ti and (b) V to Cu, respectively.

The trend of E_B /atom can be correlated to the number of d-shell electrons of the TM atoms. Because Cr, Mn, and Cu have half or fully filled d-orbitals, the binding is least for them. Because of the difference in the atomic radii of Al and TM atoms, we observe that the TM atom stabilizes at some elevation (height) with respect to the layer formed by one of the sublattices of buckled aluminene (Figures 4.7 and 4.8(b)). Sc and Ti atoms prefer to be at a height above the aluminene sheet as they possess the largest atomic radii among all the 3d TM atoms studied in this work. Beyond the Ti atom, the TM atoms are pushed below the top layer of the aluminene lattice because of the reduced atomic radii of the TM atoms. The observed trend can be justified from the values of covalent radii of the TM atoms reported in the literature [227] where the covalent radius of the TM atoms monotonically decrease from Sc to Ni and then increases for Cu atom. TM-substituted silicene also shows a similar trend for the height of TM atom with respect to the silicene sheet with height larger for Sc-Si (0.80



Figure 4.8: (a) Binding energy per atom (in units of eV/atom), (b) TM-Al bond distances and height of TM (in Å), (c) Bader charges on TM atoms (in units of e) and (d) magnetic moment (in units of μ_B) for 5×5 cell of TM-substituted Aluminene.

Å) and smaller for Zn-Si (0.32 Å) [107]. On the other hand, it is interesting to note here that the TM substitution in case of black and blue phosphorene show a peculiar behavior of E_B . A monotonic increase in the E_B has been reported from Sc to Cr, which is followed by a decrease from Mn to Ni where Cr shows the highest binding [226]. The authors explain this peculiarity of stronger binding for Sc-Cr with a decreasing trend of bond lengths (TM-P). Moreover, for Mn-Ni, the authors report the weakening of hybridization of orbitals of TM and P as TM-d shells are filled.

In Figure 4.8(b), the TM-Al bond distance has also been plotted. We observe that the range varies from 2.56 to 2.82 Å, in decreasing order from Sc-Co and then the bond distance increases for Ni to Cu. The values of bond distance show the formation of a strong bond, and hence the interaction is expected to be stronger (large $E_B/atom$). However, it is to be noted that the sum of the covalent radii of TM and Al atoms [227] lies in the range of 2.45-2.91 Å. Thus, the TM-Al bond character may be expected to be more ionic-like rather

than covalent. In the literature also, it has been observed that when the 3d TM atoms are substituted in germanene and arsenene, TM-Ge/As bond distances also reveal similar decreasing trend from Sc to Co, and then it increases for Ni and above as the binding gets weaker [224, 225].

4.2.2.2 Charge Analysis

We perform the Bader charge analysis [220] to estimate the nature of bonding between the Al and the TM atoms (Figure 4.8(c)). It is clear that Sc, Ti, and Cr atoms have lost electrons to the Al atoms of the aluminene lattice. On the other hand, the rest of the TM atoms have gained electrons. The variation of Bader charges on TM atoms shows the general linear dependence with the difference in electronegativity of the atoms, similar to the case of the above discussed TM adsorbed aluminene systems. On the contrary, for TM substitution in phosphorene [226] all the TM atoms have been found to loose electrons (maximum for Sc and least for Ni) with magnitude in the range of 1.5-0.16e. This is due to the fact that all the TM atoms have electronegativity less than that of the P atom. A large amount of charge transfer between the TM and Al atoms and the shorter bond distances (2.56-2.82 Å) suggest the existence of a mixed bonding (ionic and covalent) nature in TM-substituted aluminene systems.

4.2.2.3 Electronic and Magnetic Properties

Next, we analyze the induced magnetism in the TM-substituted systems (Figure 4.8(d)). We find that whenever moments are observed in a composite system, it is due to the TM atom, which is supported by the magnetization density plots [228]. From Figure 4.8(d), we note that V, Cr, Mn, and Fe-substituted systems possess a magnetic moment, whereas the rest are non-magnetic in nature. Similar tuning of magnetism has been observed when 2D non-magnetic systems are functionalized with TM atoms [107, 224–226]. For example, the magnetism of silicene has been modulated by embedding different TM atoms, with moments

1.6, 2, 3, 3.7 μ_B for V, Cr, Mn, and Fe-substituted silicene, respectively [107]. Less than 1 μ_B has been observed for the Co case. However, a non-magnetic state has been observed for Sc, Ti, and Ni systems. In the lietrature, the fractional spin moments are found in V-Co (1.026 - 3.384 with maximum for Mn and minimum for Co) substituted germanene with zero spin state for Sc, Ti and Ni systems [224]. The electronic DOS shown in Figure 4.9 also validates the magnetic moments observed in TM-substituted aluminene. Further, similar to the TM adsorbed aluminene systems, all the TM-substituted systems are also found to be metallic in nature.

To further gain insight into observed magnetism in the system, we plot the electronic DOS in Figure 4.9. In this direction, the total DOS and the TM PDOS have been resolved into spin up and down components. All TM-substituted systems are found to be metallic in nature. Sc and Ti have large number of unoccupied d-orbitals with electronic configuration of $3d^{1}4s^{2}$ and $3d^{2}4s^{2}$, respectively. Thus, the corresponding dominant DOS peaks lie in the conduction region above the E_F . As seen from Figure 4.9, these two systems have degenerate spin up and down DOS and hence exhibit zero magnetic moment. Because of the increase in number of 3d valence electron for V, more spin-up states appears in the valence region close to E_F in comparison with the Ti case, leading to a magnetic moment in the system. As we move towards Cr and Mn, we note that majority of the spin-up states lie in the occupied region (below E_F), however, the spin-down states remain in the unoccupied region. This large asymmetry in the up and the down states (large exchange splitting) leads to a large moment in the system. From Fe onwards, the down-spin states start filling up and as a result, the magnetic moment decreases compared to the Mn-substituted system. For Co, Ni and Cu, however, the DOS of the two spin channels are again same leading to zero magnetism in the system. Thus, the magnetism in aluminene based composite systems can be controlled by the suitable choice of the TM atoms.

A comparative study of AM atom (Li, Na and K) substituted planar aluminene [229]**.

^{**} Reproduced from "Strain Induced Magnetism and Half-Metallicity In Alkali Metal Substituted Aluminene", D. Pandey, C. Kamal, A. Chakrabarti, AIP Conference Proceedings, **2019**, 2115, 030351 with the



Figure 4.9: Total density of states (DOS) and partial density of states (PDOS) (in units of states/eV) for TM-substituted aluminene systems.

reveals a slightly different trend from the geometric point of view. We find that the optimized

permission of AIP Publishing. https://aip.scitation.org/doi/abs/10.1063/1.5113190

structure for Li atom substituted planar aluminene converges to a buckled structure. However, Na and K substitution retain the planarity of the aluminene lattice after full geometry optimization. The study of electronic structure shows that the AM atom substituted systems are non-magnetic and metallic in nature. Moreover, it is observed that the application of strain in the AM substituted system induces magnetism in the cases of substitution of Na and K, with half-metallicity being observed for 15% bi-axial tensile strain.

4.2.3 Intercalation of Transition Metals in Aluminene bilayers

Having discussed the effect of adsorption and substitution on the geometry, electronic and the magnetic properties of 2D monolayers of aluminene, in this section, we probe the influence of intercalation of TM atoms in bilayer aluminene. To this end, we first investigate various possible stacking arrangements of bilayers of both buckled and planar allotropes of aluminene, which is discussed below. Further, we intercalate few 3d TM atoms (Ti, Cr, Mn, Fe, Co, and Ni) in bilayer of unit cell aluminene systems and study the effect of the same on various physical properties.

4.2.3.1 Pristine bilayer aluminene

Analysis of Energetic Stability and Geometry: We first probe the possible atomic arrangements for bilayer aluminene. Following that, the results of various physical properties of these are discussed. We note that two possible stacking configurations for planar bilayer exist and these are named as AA_p and AB_p . These structures are similar to those of graphene bilayers. Five different stacking configurations are possible for the buckled case. These are differentiated by using the subscript *b* and superscript prime (') as shown in Figure 4.10. We note that the buckled A(B) monolayer is mirror image of A'(B').

The above considerations account for seven possible unique configurations for pristine bilayer aluminene made up of monolayers of aluminene. These cases are named as follows: 1) case I: AA-stacking made of planar configuration (\mathbf{AA}_p) ,



Figure 4.10: Top and side views of different starting configurations of pristine mono-layer buckled aluminene.

- (2) case II: AB-stacking made of planar configuration (\mathbf{AB}_p) ,
- (3) case III: AA-stacking made of buckled configuration $(\mathbf{A}\mathbf{A}_b)$,
- (4) case IV: AA'-stacking made of buckled configuration (\mathbf{AA}'_b) ,
- (5) case V: AB-stacking made of buckled configuration (\mathbf{AB}_b) ,
- (6) case VI: A'B-stacking made of buckled configuration $(\mathbf{A'B}_b)$,
- (7) case VII: A'B'-stacking made of buckled configuration $(\mathbf{A}'\mathbf{B}_b)$

The top and side views of valence charge density distribution (VCDD) for the optimized structures of all these above-mentioned cases are displayed in Figure 4.11(a-g). It is observed that after full geometry optimization, the AB_p case exhibits a buckled configuration (Figure 4.11 (b)). However, the name of the case (AB_p) is retained throughout the chapter. The geometrical parameters (lattice constant (a), intralayer distance (d_1), distance between two layers (d_2)), energetic information (E_B/atom and the formation energy (E_{form})) are listed in Table 4.1.

From our calculations, all the structures have been found to possess energetic stability which is evident from the negative values of $E_B/atom$ associated with all the seven cases. In pristine monolayer buckled aluminene, the buckling height is large (2.45 Å) [70], hence, the bond length, d_1 (2.92 Å) is larger than the lattice constant, a (2.75 Å). Therefore, it may be expected that similar results will be obtained for a and d_1 of bilayer buckled aluminene.

From Table 4.1 we observe that, the lattice parameter values for a and b are larger in the

Table 4.1: Geometric and energetic data for different configurations (case I through case VII) of pristine bilayer aluminene. d_1 and d_2 represent intra and interlayer (vertical) Al-Al distances, respectively. Values in parentheses are results from calculations performed with van der Waals interaction. The values of lattice constants a and b are same, $\alpha = \beta = 90$ and $\gamma = 120$ degrees. Values of a, d_1 and d_2 are in Angstrom. E_B/atom is binding energy per atom in units of eV/atom. E_{form} is the formation energy in units of kJ/mol.

Case	a	d_1	d_2	$E_B/atom$	E_{form}
AA_p	4.48	2.58	2.70	-2.72	71.87
	(4.45)	(2.57)	(2.68)	(-2.84)	(60.64)
AB_p	4.24	2.67	1.17	-2.85	60.07
	(4.18)	(2.66)	(1.19)	(-3.01)	(44.90)
AA_b	2.78	2.93	2.45	-3.28	18.43
	(2.76)	(2.94)	(2.47)	(-3.48)	(-0.52)
AA'_b	2.78	2.93	2.79	-3.24	21.64
	(2.76)	(2.93)	(2.72)	(-3.44)	(2.38)
AB_b	2.78	2.92	2.78	-3.24	21.63
	(2.76)	(2.92)	(2.71)	(-3.44)	(2.39)
$A'B_b$	2.79	2.93, 2.91	2.41	-3.28	17.81
	(2.77)	(2.94)	(2.43)	(-3.48)	(-1.050)
$A'B'_b$	2.79	2.91	2.40	-3.29	17.00
	(2.78)	(2.91)	(2.39)	(-3.49)	(-1.83)

planar structures as compared to those of the buckled configurations. Therefore, a larger binding is observed in case of all the buckled configurations in comparison to the planar cases. Further, it is found that the $\mathbf{A'B'_b}$ conformation shows the lowest formation energy among all the structures. We also observe that while planar structures exhibit positive and high formation energy, all the five buckled cases possess positive but lower formation energies. Interestingly, it is observed that while all the results of binding and formation energies obtained from the DFT-D2 level of calculations show substantial lowering in the values, for few of the buckled cases, the formation energy even turns out to be negative.

Valence Charge Density Distribution: VCDD is expected to help in understanding the nature of bonding between the two layers. Therefore, we calculate and present the results of VCDD in Figure 4.11. Substantial amount of charge is found to be present in the layer as well as between the two layers, though less compared to the intralayer region, in case of bilayered planar aluminene with AA stacking. This difference suggests that the three Al-Al bonds present in each layer are more covalent-like in comparison to the single Al-Al bond, present between the two layers in this case. However, the case of planar aluminene with AB-stacking seems different. After the full geometry optimization, the Al atoms in a single layer in this case are not in their respective planes. This leads to a buckling in the material. Further, accumulation of charge is not significant between the two layers; but this is expected due to the distance between the Al atoms in the two layers (Al atom of bottom layer is below the Al atom of the top layer). However, signature of a more covalent-like bonding among the Al atoms of each layer is observed (Figure 4.11).



Figure 4.11: Different stacking configurations of pristine bilayer aluminene. (a)-(g) First and second panels from the top give the top and side views of the valence charge density distributions of the seven different configurations. (h)-(n) Third (bottom) panel exhibits the results of ELF calculations along (110) plane.

Next, we concentrate on the discussion of the five (case III to VII) buckled configurations. The VCDD shows that the amount of charge density between the two monolayers for AA_b , $A'B_b$ and $A'B'_b$ configurations is insignificant, which indicates the lack of covalent nature of bonding between the two Al atoms of the upper and lower layers. However, VCDD is comparatively higher for cases IV and V which suggests a covalent-like bonding in the interlayer region. The observation corroborates with the structural geometry where the interlayer distance (distance between the Al atoms of the upper and lower layers) is found to be less as compared to the intralayer Al-Al distance (Table 4.1).

Electronic Structure: The results of band structures of various bilayer aluminene are depicted in Figure 4.12. We observe that all the seven cases show metallic behavior. Further, the band structures of the buckled bilayer aluminene cases are quite similar to that of the buckled monolayer case [70]. Nearly-free-electron (NFE) like band dispersions are found around the Γ point for the buckled cases (III to VII). Electronic localization functions (ELF) [230], which exhibit values between 0 and 1, have been calculated and analyzed to gain more in-depth understanding of the electronic structure of various cases. These results of ELF, presented in Figure 4.11, to a large extent corroborate with the NFE-like bands around the E_F . From Figure 4.11, specifically for the cases III, VI and VII, it is observed that, the values of ELF are primarily around the value which is obtained for the homogeneous electron gas (0.5), both in and between the layers. Two regions of exception are there. One is close to the atoms where ELF exhibits values which are close to zero. The other region is near the surfaces. In these surface regions, large amount of accumulation of charge is observed, which is attributed to the presence of surface potential. Overall, the results of ELF and the presence of NFE-like bands indicate that a metallic-like bonding nature is prevalent in these systems.

The band structure of the AA_p configuration is very similar to that of planar aluminene [20]. Unlike the case of graphene bilayer, the dispersion curves of the bilayer planar aluminene are found to be non-degenerate. This is due to the fact that the interaction between two layers in case of aluminene is much stronger than the graphene bilayer, where the layers are bound only by a weak van der Waals interaction. Further, more bands are found to be crossing the E_F in the bilayer case, as compared to the monolayer aluminene. Therefore, the



Figure 4.12: Electronic band structures for different configurations of pristine bilayer aluminene. Red (solid line) and blue (dashed line) colored bands represent bands without and with van der Waals dispersion correction, respectively. E_F is set to 0 eV.

larger number of Fermi surfaces as well as NFE-like bands (Figure 4.12) are expected to play an important role in tuning the transport properties of these bilayer systems. Since the AB_p structure is quite distorted from the planar geometry, the corresponding band structure is rather different from that of the planar monolayer.

To inspect the role of van der Waals interaction (VDWI), which is seen to play an important role in stabilizing some of the well-known multi-layered systems [231], we include such interactions in our calculations. The results of our calculations suggest that the VDWI does not alter the results of energetics and geometry to a considerable extent for the systems.

4.2.3.2 TM-intercalated bilayer aluminene

As per the primary aim of the work, we intercalate different TM atoms between the two layers of both the planar and buckled configurations and study its effect on the various physical (geometric, electronic and magnetic) properties of these bilayer structures. It should be noted here that after full geometry optimization, the AB_p structure has been found to converge to the A'B'_b structure [232]**. Hence, for further study, the case II (AB_p) is not considered, and we intercalate six different TM atoms (Ti, Cr, Mn, Fe, Co and Ni) between the two layers of the remaining six configurations (cases I to VII, except II). A total of fourteen configurations based on various possible inequivalent sites for all the six structures have been identified (see Figure 4.13).



Figure 4.13: Top and side views of initial geometries (schematic) of various possibilities of TM intercalation in different stacking configurations of pristine bilayer aluminene. Solid black line represents the unit cell.

Analysis of Energetics and Geometry: In Figure 4.14, we present the fully optimized geometries and the E_B /atom of the same for all the TM atoms. We wish to point out here that, for the pristine bilayer case, the A'B'_b configuration is found to possess the lowest energy.

^{**} Reproduced from "Intercalation of transition metals in aluminene bi-layers: An ab initio study", **D. Pandey**, C. Kamal, A. Chakrabarti, The Journal of Chemical Physics, **2019**, 150, 194702 with the permission of AIP Publishing. https://aip.scitation.org/doi/full/10.1063/1.5093945

However, when TM atoms are intercalated, the AA-type buckled cases exhibit the lowest energy. For the TM atoms with close to half-filled d shells (Cr, Mn and Fe) cases, AA_{b2} structure yields the lowest energy, which has a trigonal symmetry. However, for TM atoms, Ti, Co and Ni, after full geometry optimization, the starting configuration of AA_{p2} is seen to converge to a buckled configuration (AA'_{b2}), which has the lowest energy. Furthermore, the initial (starting) trigonal symmetry has also been found to change to a tetragonal symmetry (Figure 4.14). Unlike the preferred AA configuration for TM intercalation in the bilayer aluminene, our results of TM-intercalated silicene (TM = Mn, Fe and Co) reveals that Fe and Co marginally favor the AB stacking whereas Mn has a slight preference of the AA over the AB configuration when intercalated in bilayer silicene [233]**.



Figure 4.14: (a) Optimized structure and (b) Formation energy (E_{form}) and binding energy per atom (E_B/atom) for TM intercalated bilayer aluminene. Blue balls represent Al atoms and different colored balls represent various TM atoms. Angle between a and b axes is 90° for Ti, Co and Ni cases.

We observe that the Co and Cr composite systems exhibit the highest and lowest $E_B/atom$, respectively (Figure 4.14(b)). We note that, Wang *et al.* [234] have also observed similar trend for aluminium clusters doped with various doping concentrations of different TM atoms. The Cr-Al clusters have been seen to be the least stable one, which is followed by the Mn-Al clusters. These clusters have been found to exhibit less stability as compared to

^{**}Reproduced from "Transition metal intercalated bilayer silicene", **D. Pandey**, C. Kamal, A. Chakrabarti, AIP Conference Proceedings, **2018**, 1942, 050096 with the permission of AIP Publishing. https://aip.scitation.org/doi/abs/10.1063/1.5028727

Table 4.2: Geometrical parameters and magnetic moment for lowest energy configurations of TM-intercalated bilayer aluminene. d'_1 represents intralayer Al-Al distance. d'_2 signifies the minimum distance between the TM and the closest Al atom. d'_3 represents the TM-TM distance. NN lists number of few near neighbors with distances and the last column represents the magnetic moment of the system (in units of μ_B). Lattice constants a and bhave same values as well as angles α and β have same values of 90 degrees. Values of a, d'_1 , d'_2 , d'_3 and near neighbor distances are reported in Angstrom. Angle γ (degrees) is 120 and 90 for AA_{b2} and AA'_{b2}, respectively.

TM	Configuration	a	d'_1	d'_2	d'_3	NN	Moment
Ti	AA'_{b2}	2.78	2.91,	2.84	2.78	4 Ti@2.78, 1Al@2.84,	0.00
			2.91			2Al@2.85	
Cr	AA_{b2}	2.76	2.88	2.60	2.76	3Al@2.60, 6Cr@2.76	0.61
Mn	AA_{b2}	2.76	2.89	2.58	2.76	3 Al@2.58, 6Mn@2.76	1.95
Fe	AA_{b2}	2.77	2.88	2.54	2.77	3Al@2.54, 6Fe@2.76	1.94
						,	
Co	AA_{h2}'	2.77	2.92	2.46	2.77	2Al@2.46, 1Al@2.47,	0.00
	02					4Co@2.7689	
Ni	AA_{h2}^{\prime}	2.75	2.92	2.52	2.75	1Al@2.52, 2Al@2.52,	0.00
	02					4Ni@2.75	

the Fe-Al, Co-Al and Ni-Al clusters, as found by the authors. Close to half-filled d-orbitals of Cr and Mn may have led to the reduced tendency of formation of TM-Al clusters [234].

It is interesting to find that, the composite systems with Ni and Co TM atoms exhibit negative formation energies in their lowest energy phases. Further, a small positive formation energy is found for the Ti system. However, high positive formation energy is observed for the Cr, Mn and Fe systems (Table 4.2). Hence, from analysis of the E_{form} values, it is expected that experimental synthesis of the Co and Ni based cases may be feasible.

Charge Analysis: To predict the nature of bonding between the Al and the TM atom, which possess different electronegativities, Bader charge analysis has been carried out [220]. The variation of charge on a TM atom with the difference between the electronegativities (EN) of TM and Al atom is depicted in Figure 4.15(a). We observe that unlike Ti, all

the other TM atoms have gained electron. A somewhat linear relationship is found to exist between the difference of electronegativity (between the Al and TM atom) and the charge on the TM element. From our studies, possibility of tuning the quantity of charge transfer and polarity by functionalizing the bilayer aluminene with different TM atoms is predicted which may find importance in the field of gas sensing. Similar results on monolayer aluminene functionalized via adsorption/substitution of TM atoms have also been obtained, as discussed above.



Figure 4.15: Plot of (a) Bader charge versus electronegativity difference and (b) ELF for TM intercalated bilayer aluminene along (110) plane for minimum energy configurations.

Electronic Structure and Fermi-Surface for TM-intercalated systems: It is to be noted here that, while AA_{b2} is the lowest energy structure for the composite systems with Cr, Mn and Fe atoms, the lowest energy phase is AA'_{b2} for Ti, Co and Ni atoms. Hence, on the basis of our results on energetics and geometric properties, the TM-intercalated systems are divided into two categories. Category (i) includes bilayer aluminene systems intercalated with Cr, Mn and Fe elements having trigonal symmetry. Category (ii) includes bilayer aluminene systems intercalated with Ti, Co and Ni atoms having tetragonal symmetry. In what follows, we discuss the magnetic and electronic structures for the two categories in detail.

category(i) The electronic structures of Cr, Mn and Fe intercalated systems (with lowest energy phase AA_{b2}) reveal that the composite system with Cr atom exhibits a magnetic moment of ~0.61 μ_B . For Mn and Fe intercalated cases, the calculated moments are found to be ~1.95 μ_B and ~1.94 μ_B , respectively (Table 4.2). We note here that Zhang *et al.* [235] have also observed that there is high magnetic moment in Cr, Mn and Fe intercalated bilayer graphene (with various TM/carbon hexagon ratios). On the contrary, our study of TM-intercalated silicene displays that a significant net magnetic moment is observed in cases of Mn-intercalated silicene bilayers, whereas Fe and Co have zero moment [233].

category(ii) The electronic structures of Ti, Co and Ni intercalated systems reveals that all the three systems are non-magnetic in nature. The Ti-intercalated system, has an underlying AA'_b configuration, however, the band structure of the latter (pristine case) gets modified subsequent to the intercalation as is observed from Figure 4.16(a). Close to the high symmetry k-point S, near E_F , a hole and an electron pocket as well as parabolic-like bands in both the valence and conduction regimes have been observed. Figure 4.16(b) shows the case of Co-intercalation. Along the Γ -X direction, at around E_F , hole and electron pockets are observed. A shift towards higher binding energy is more pronounced in the Ni-intercalated system (Figure 4.16(c)).

The evidence of greater stability (from E_{form} values) and observation of electron and hole pockets around the E_F in the systems under category (ii) motivates us to calculate the Fermi surface (FS) for these materials (Figure 4.16). Different dispersion of the bands crossing the E_F leads to dissimilar FS. To identify which electronic bands correspond to FS, momentum vectors are marked in the band structures (Figure 4.16). We wish to mention here that FS has been plotted using XCrySDen software [236].

For Ti-intercalated system (Figure 4.16(a)), the parabolic bands around Γ (k_{12} and k_{13}) form circular like FS along the Γ -S direction. Moreover, the hole-like NFE bands centred



Figure 4.16: Fermi surface for (a) Ti, (b) Co and (c) Ni intercalated bilayer aluminene. Red colored arrow shows the probable nesting vector. Momentum vectors corresponding to the first (leftmost) and the last (rightmost) bands crossing E_F are marked in this figure. k-vectors corresponding to bands crossing between the leftmost and rightmost bands are numbered in the ascending order, which are marked in the Fermi surface plot adjacent to the band structure. Due to lack of space, only the leftmost and rightmost k-points are marked in the left panels (band structures), and the numbers increase from left to right. In the right panels which depict the FS though, we mark almost all the k-point vectors.

around S-point lie very close to it and hence the corresponding circular FS has very small radius. Further, because of the crossing of only one band, we observe one FS along the Γ -X

direction. In the Co-based system, we observe the Γ -centred hole-like bands between the k_1 and k_2 points and electron-like bands between the k_3 and k_4 points along the Γ -X direction. As has already been mentioned above, we observe the NFE-like bands around Γ and S points, which is reflected in the topology of FS where we observe distorted circular shapes around the Γ and S points. Around the S-point, we observe hole-like bands crossing the E_F at k_7 and k_8 . Because of the absence of bands along the Γ -X direction in Ni-intercalated system as compared to that of Co system, we observe only one FS along the Γ -X direction. However, similar to the Co-system, we observe free-electron like circular FS around the S-point which may play a crucial role in transport of electrons in this system.

From Figures 4.16(b) and 4.16(c), we observe that the Co and Ni intercalated systems exhibit parallel parts of FS which may lead to its nesting [237–239]. Presence of nesting in the FS may lead to electronic instability and consequently, to the formation of charge density wave (CDW) in the system. Interestingly, CDW is found to be common in low-dimensional systems [237–241]. Equipped with the data from the literature and from the FS plots for Co and Ni intercalated bilayer aluminene (Figure 4.16), we conjecture that there is an interesting possibility of formation of CDW in these composite systems.

4.3 Summary

In this chapter, we explore the effect of functionalization of planar as well as buckled aluminene on various physical properties by different means, like, adsorption, substitution and intercalation of TM and AM atoms. Along this direction, first we present the results of our study on adsorption of first (3d (Sc-Cu)) and second (4d (Y-Ag)) row TM atoms on aluminene at different in-equivalent crystallographic sites (hollow, top and bridge). We have also investigated various properties when TM atoms are adsorbed on silicene and arsenene and these results are compared with the data obtained in case of aluminene. The results of $E_B/atom$ indicate that all the probed composite systems studied in the present work are energetically stable.

Further, the analysis of interaction energy reveals that, in most of the cases, adsorption of TM atoms typically yields higher interaction energy in case of aluminene when compared with silicene and arsenene systems. Among all the 3d and 4d TM atoms adsorbed on aluminene, Ti, V, Fe, Co, Ni (among 3d) and Tc, Ru, Rh (among 4d) composite systems are found to possess high interaction energy. Induced magnetism (TM-derived) is observed in some of the composite systems. From the charge analysis, we infer that the amount of charge transfer (between TM and aluminene), and even the polarity can be tuned by varying the TM atom.

Similar to the study of adsorption, we investigate the geometries and the electronic as well as the magnetic properties when Al atom in the planar aluminene lattice has been substituted by the 3d TM atoms. We observe that substitution of 3d TM atoms in planar aluminene leads to a buckled structure, like the case of adsorption. From the binding energy (E_B/atom) , we find the Ti and Co substituted systems to be the most bound systems with highest E_B/atom and with non-magnetic metallic ground state, and Cr based system shows the least binding with large magnetic moment. From the charge analysis, it is seen that Sc, Ti and Cr have lost the electrons to Al atoms of the aluminene lattice. On the other hand, the rest of the TM atoms have gained the electrons. Overall, alike the case of 3d TM adsorption on the aluminene, similar trend of energetics, charge transfer and magnetism has been observed for 3d TM-substituted aluminene. In addition, substitution of alkali atoms (AM=Li, Na and K) in planar aluminene are also investigated, and it is found that the application of strain in the AM substituted system induces magnetism in the cases of substitution of Na and K, with half-metallicity being observed for 15% bi-axial tensile strain.

Having discussed the effects of adsorption and substitution, effect of intercalation of TM atoms (Ti, Cr, Mn, Fe, Co, and Ni) in bilayer aluminene is also explored in this thesis. We first investigate various possible stacking arrangements of bilayer aluminene. Unlike the case of graphene, the interaction between the layers is found to be quite strong in the bilayer structure of aluminene. Further, we calculate valence charge density and electron localization function to ascertain the nature of bonding present in both the pristine and TM-intercalated composite systems. Among all the six atoms, intercalation of Cr, Mn and Fe atoms results in a magnetic ground state for the composite system (moments being in the range of 0.61 to 1.95 μ_B). Interestingly, for Ti, Co, and Ni-intercalated systems, after full geometry optimization, the starting trigonal symmetry has been seen to change to a tetragonal symmetry. In addition, the plots of Fermi surface for Ti, Co and Ni-intercalated systems in their lowest energy configurations have been presented. Among these, except for the Ti case, the results of Co and Ni intercalated systems indicate the presence of Fermi surface nesting in these systems.

Chapter 5

Aluminene based van der Waals heterostructures

5.1 Introduction

In the last chapter, we have explored the influence of functionalization (primarily by TM atoms) on the geometric and electronic structure of aluminene (in planar and buckled configuration). We have observed various interesting changes in the physical properties, which include induced magnetism following the adsorption of and substitution by TM atoms, structural transformation upon intercalation of TM atoms in bilayer aluminene and the signature of Fermi surface nesting in some of these intercalated bilayer systems. Although the ways of functionalization mentioned above serve efficiently for tailoring the geometric and electronic structures of planar and buckled aluminene, it does not lead to a change in the fundamental electronic (metallic) nature of aluminene.

It is worth noting here that it has been established in the literature that due to the semimetallic nature of graphene, it fails to be of importance in the field of electronic devices [14, 16]. To surmount this problem, various experimental as well as theoretical approaches have been used to induce a bandgap in graphene [150–159]. In this direction, a system made
of monolayer of hexagonal boron nitride (BN) was proposed to be a suitable substrate for graphene to produce a gap in the system [150]. In the graphene/BN heterostructure, the interlayer interaction gives rise to non-equivalent carbon sublattices which induces a gap of 0.12 eV in the system [156]. In trilayer BN/graphene/BN structure as well, a stacking-dependent bandgap was observed [157].

The similarity of the geometric and electronic structure of graphene with planar aluminene (a system like highly-hole-doped graphene [20]) and also the changes in the electronic nature of graphene by constructing graphene/BN van der Waals (vdW) heterostructure [156, 157] have motivated us to investigate the heterostructures of planar aluminene and BN monolayers and also compare the results with those of the heterostructures of graphene/BN. We investigate the stability, structural properties and electronic nature of aluminene/BN heterostructures. Since for the study of multilayer heterostructures, vdW interaction has been found to play an important role in case of various systems, we consider the effect of long-range vdW interaction included via the D2 dispersion term given by Grimme [199].

5.2 Results and Discussion

In this section, we discuss the results of the structural and energetic stability followed by the electronic properties of the bilayer aluminene/BN heterostructures, and the respective trilayer heterostructures.

5.2.1 Aluminene/BN Bilayer heterostructures

Study of Geometry and Stability: The lattice constant of BN monolayer is reported to be 2.5 Å and the B-N bond length is 1.45 Å [242]. The lattice parameter of aluminene monolayer is 4.48 Å where the Al-Al bond length is 2.59 Å [20]. Since the lattice constants of aluminene and BN monolayer are quite different, we employ the "commensurate"

supercell approach for our calculations to optimize the lattice mismatch between the two 2D monolayers. We have chosen a (1×1) unit cell of aluminene and a (2×2) unit cell of BN monolayer. These form a commensurate heterostructure as shown in Figure 5.1. In this periodic supercell arrangement of the bilayer, though the Al-Al bond length has increased from 2.59 to 2.90 Å, the B-N bond distance remains the same.



Figure 5.1: Top and side views of aluminene/BN in AA, AB and AB' stacking configurations. E_B is the binding energy per atom and d is the interlayer distance. Green, grey and pink colored balls represent B, N and Al atoms, respectively.

The stacking arrangements in aluminene/BN heterostructure (shown in Figure 5.1) can be categorized (following the case of graphite [156]) as: (i) AA (Al atoms on top of the B and N atoms), (ii) AB (an Al atom is on top of the N atom and the other Al atom is directly on top of the hollow site of the hexagon), and (iii) AB' (an Al atom is on top of the B atom while another one is directly on top of the hollow site of the hexagonal monolayer).

The binding energy values of the aluminene/BN bilayer obtained using DFT-D2 method are presented in Table 5.1 and Figure 5.1. The binding energy per atom, E_B , has been calculated as

$$E_B = [E_{tot} - E_{aluminene} - E_{BN}]/N \tag{5.1}$$

where E_{tot} , $E_{aluminene}$ and E_{BN} are the total energy of the composite system as well as the energies of the aluminene and BN sheet, respectively. N is the total number of atoms present in the unit cell.

	Interlayer distance, d	E_B	Bandgap
	(Å)	(eV/atom)	(eV)
Aluminene/BN			
AA	3.13	-0.03	$\operatorname{metallic}$
AB	3.03	-0.04	$\operatorname{metallic}$
AB'	3.33	-0.03	metallic
BN/Aluminene/BN			
AAA	3.08	-0.04	$\operatorname{metallic}$
ABA	2.90	-0.05	≈ 0.13
AB'A	3.27	-0.03	metallic
ABC	2.88, 3.23	-0.04	$\operatorname{metallic}$

Table 5.1: Geometric, energetic and electronic properties of aluminene/BN heterostructures calculated at the DFT-D2 level of theory.

The interlayer distance has been found to increase in going from AB to AA to AB'-stacked configuration. However, the intralayer (Al-Al and B-N) distances remain virtually the same in the respective monolayers. The observed higher stability of AB over the AB' configuration can be attributed to the shorter interlayer Al-N distance (3.03 Å) in AB stacking as compared to the Al-B distance of 3.33 Å in case of the AB' stacking. In contrast, AB' has been found to be the lowest energy configuration for the graphene/BN heterostructure where the interlayer distance is 3.02 Å, obtained using the DFT-D2 method [156].

Importance of van der Waals interaction in stabilization of the structures -To examine and establish the nature of interaction between aluminene and BN monolayer, calculations using the PBE exchange-correlation functional without the incorporation of vdW interaction have also been performed. For AA-stacked bilayer, the E_B and the interlayer distance have been found to be 0.002 eV and 3.98 Å, respectively. On the other hand, we observe from Table 5.1 that the E_B and the interlayer distance are -0.03 eV and 3.13 Å, respectively, with the inclusion of vdW interaction via DFT-D2 level of theory. Thus, our results indicate that the vdW interactions between the constituent layers is one of the stabilizing factors for the bilayer. A similar analysis with graphene as a substrate reveals that the AA stacking with interlayer distance of 2.74 Å is slightly preferred over the AB stacking for aluminene/graphene bilayers. The E_B is found to be -0.04 eV/atom and this indicates that the interlayer interaction is primarily governed by the vdW interactions in these aluminene-based heterostructures [243]**.



Figure 5.2: Top and side views of the calculated valence charge density distribution (VCDD) for the aluminene/BN bilayers in different stacking configurations, with an isovalue of 0.03 e/A³. Yellow colored region depicts the electron rich region.

Analysis of Charge Density: To elucidate the nature of bonding between the constituent layers in the aluminene-based bilayer heterostructures, we present the spatial distribution of valence charge density distribution (VCDD) in Figure 5.2. The figure displays the distinctive features of the layered system with absence of charge density at the interface and accumulation of more charge densities in the basal planes containing intralayer covalent bonds between the atoms. Therefore, the charge distribution results suggest that the interaction is weak, as has been reported for the case of graphene/BN heterostructure [156] and this corroborates with the results of E_B (Table 5.1).

Study of Electronic Structure: We now discuss the electronic structures of aluminene/BN bilayer heterostructure. Here we also assess the effect of increased bond length between two Al atoms in the commensurate supercell. To this end, we begin the discussion first with comparing the results of the strained and strain-free aluminene monolayer. It is

^{**}This published by the author of this thesis work is and others $_{in}$ the year 2020 inComputational Material Science belonging to Elsevier Publishing group. https://www.sciencedirect.com/science/article/abs/pii/S0927025620304432

found that the Dirac cones are located at around -4.1 and 1.4 eV for the strained aluminene case, whereas these values are -4.2 and 1.6 eV for the strain-free aluminene case (Figure 5.3). Furthermore, we note that the Al-s derived parabolic band (of strain-free aluminene) at 2.8 eV around the Γ -point above the Fermi energy (E_F) (Figure 5.3(a)) shifts downward and becomes degenerate with the other bands present above E_F at the Γ -point (Figure 5.3(b)) in the strained case.



Figure 5.3: Orbital projected density of states and band structure for (a) pristine monolayer aluminene with intralayer Al-Al bond distance of 2.59 Å, (b) strained monolayer aluminene with intralayer Al-Al bond distance of 2.90 Å. Fermi energy (E_F) has been set to 0 eV.

The band structures of aluminene/BN bilayer heterostructures are displayed in Figure 5.4. We find that the aluminene/BN bilayer heterostructures are non-magnetic and also metallic in nature. The Dirac-like dispersion (around K-point) is not observed in the aluminene/BN case due to the hybridization of Al-p states with both the N-p states and B-p states (Figure 5.4).



Figure 5.4: Orbital projected band structures of AA, AB and AB' configurations of aluminene/BN. Fermi energy (E_F) is set to 0 eV. Insets represent the band dispersions for AA, AB and AB'-stacked configurations in the energy interval of -0.2 to 0.2 eV. Red, green, blue and orange colored bands represent the Al-s, Al-p, B-p and N-p orbitals, respectively (as shown in legend in the AA case).

We find that for AA-configuration, the degeneracy of the band at point **a** (see Figure 5.4) is lifted when compared to strained aluminene (Figure 5.3(b)). The band corresponding to point **a** is dominated by the Al-s orbital with some contribution from the N-p states. On the contrary, point **b** is found to be associated with the Al-p orbitals alongwith the N-p and B-p orbitals. A non-negligible splitting of bands occur along the Γ -K (at point (c)) and K- Γ -M paths (along the direction **e-f**).

In AB configuration, the contributions of the states at point \mathbf{a} are found to get inverted and these are now dominated by the B-p orbitals. This may be supported by the fact that the direct bonding of Al and B atoms is non-existent in the AB configuration. We find that there is no band splitting at points \mathbf{c} , \mathbf{e} and \mathbf{f} for the AB'-configuration, unlike the cases of AA and AB configurations. Furthermore, the two non-degenerate bands observed at \mathbf{a} and \mathbf{b} points in AA and AB configurations are found to become degenerate in case of AB' configuration.

The splitting of the energy bands around the Γ -point can be considered to be a measure of the strength of interlayer coupling in the bilayer. A relatively large splitting in AB configuration indicates the presence of a stronger interlayer interaction which may be due to the affinity of the Al atom (with the valence configuration of $3s^2 3p^1$) for the N atom (with valence configuration of $2s^2 2p^3$) [244].



Figure 5.5: Evolution of band structures of AB and AB' stacking configuration of aluminene/BN bilayers with a variation in the interlayer distance (d) in Å. Fermi energy (E_F) has been set to 0 eV.

To substantiate that the interaction of aluminene (via the Al atoms) with BN monolayer (via the N atoms) induces the band splitting near E_F , we analyze the evolution of band structures of AB (i.e. Al atom on top of N atom) and AB' (i.e. Al atom on top of B atom) configurations (Figure 5.1) with a variation in the interlayer distance. These are displayed in Figure 5.5. As we reduce the interlayer distance and consequently increase the interaction strength, a larger degree of the band splitting around the Γ -point is observed for the AB stacked configuration. It is found that a gap opens up at the interlayer distance of 2.30 Å. This is not observed in the case of AB' configuration and no such opening of the gap can be predicted. This result clearly indicates that a vital role is played by the interaction between the Al and N atoms in causing the band splitting around the Γ -point near E_F in the bilayer heterostructures. Similar to the case of aluminene/BN, the aluminene/graphene bilayers are

88

also found to be metallic in nature [243], and the bands close to the E_F exhibit contributions from both the Al and C orbitals.

5.2.2 BN/Aluminene/BN Trilayer heterostructures

Study of Geometry and Stability: A trilayer comprising BN and aluminene has more stacking possibilities as compared to those in case of the bilayer systems. The possible stacking configurations which are probed to find the energetically preferred configuration for BN/aluminene/BN, namely AAA, ABA (N-top), AB'A (B-top) and ABC, are shown in Figure 5.6.



Figure 5.6: Top and side views of BN/aluminene/BN stacked in AAA, ABA, AB'A and ABC configurations. R (Å) is the thickness of the heterostructure. E_B is the binding energy per atom. Green, grey and pink colored balls represents B, N and Al atoms, respectively.

Our results show that the ABA configuration is energetically slightly preferred and has an interlayer distance of 2.90 Å (Table 5.1). In AAA and AB'A configurations, the interlayer distances converge to 3.08 and 3.27 Å, respectively. In case of ABC configuration, the asymmetry between the top and the bottom BN layers yields bond distances of 3.23 Å for Al-B and 2.88 Å for Al-N. It is observed that the intralayer B-N bond distance (1.45 Å) remains independent of the stacking arrangements of the heterostructure. It is interesting to note that the overall results for BN/aluminene/BN are in agreement with those for BN/graphene/BN

where the ABA and ABC stacked configurations are found to be the preferred configurations with nearly degenerate binding energies [157]. It is to note here that the results of E_B predict that the case of AAA stacking with the interlayer distance of 2.88 Å is energetically slightly preferred for graphene/aluminene/graphene system [243], which is in contrast to the case of BN/aluminene/BN for which the ABA stacking is found to be preferred.

It is seen that for the BN/graphene/BN case, the AAA stacking arrangement is predicted to have a larger gap of 116 meV, which is followed by a value of 57 meV for ABA case [157]. The reason for the opening up of the gap in these systems are due to the asymmetry present in the carbon lattices (being greatest in the AAA case) of the middle graphene layer. The case of BN/aluminene/BN is, however, different, where we find a gap only in the case of ABA configuration. The difference in these two cases can be attributed to the interaction of Al atom with the N atom (due to their electronic configuration) in case of BN/aluminene/BN, which is not found to be the case for C and N interaction in BN/graphene/BN system.

Analysis of Charge Density: Figure 5.7 displays the VCDD for BN/aluminene/BN case, which indicates a weak bonding at the interfaces [243], as has also been seen in case of the respective bilayer heterostructures. Similar to the bilayer cases, no charge is accumulated between the BN monolayer and the aluminene planes.



Figure 5.7: Top and side views of the valence charge density distribution (VCDD) for the BN/aluminene/BN heterostructures in AAA, ABA, ABA, AB'A, and ABC stacking configurations, with the isovalue of 0.03 e/A^3 . Yellow colored region denotes the electron rich region.

Study of Electronic Structure: The electronic band structure shown in Figure 5.8



Figure 5.8: Orbital projected band structures of (a) AAA, (b) ABA, (c) AB'A and (d) ABC stacked configurations of BN/aluminene/BN. Fermi energy (E_F) is set to 0 eV. Insets in (b), (c) and (d) represent the band dispersions for ABA, AB'A and ABC stacked configurations in the energy interval of -0.6 to 0.6 eV, respectively. Red, green, blue and orange colored bands represent the Al-s, Al-p, B-p and N-p orbitals, respectively (as shown in legend in (a)).

reveals that it is dependent on the nature of stacking arrangement as was also observed in the literature for other heterostructures [24, 157]. The band dispersions of AAA stacked BN/aluminene/BN are similar to those of AA stacked aluminene/BN. A small but sizable reduction is observed in the width of the bands, which are crossing E_F (Figure 5.8 (a)). This may be because of a slightly smaller interlayer distance in the AAA case in comparison with that of AA configuration of the bilayer. This in turn may lead to a relatively large degree of interaction between the layers in the former case. Figure 5.9 validates this as the width of the bands crossing the E_F has appreciably increased for a larger interlayer distance of 3.56 Å in the AAA stacked heterostructure.

Similarly, the band structures for AB'A and AB' configurations are rather close to each



Figure 5.9: Calculated band structure for AAA stacked configuration of BN/aluminene/BN trilayer with interlayer distance of 3.08 and 3.56 Å. Fermi energy (E_F) has been set to 0 eV.

other. The only difference observed between the two is that point **b** in the latter case has shifted below E_F . This yields Dirac-points slightly above and below E_F along the Γ -M and Γ -K directions, respectively (Figure 5.8(c)). The calculated band structure of the ABCconfiguration is similar to that of the AB configuration. In case of trilayer, the point **a** comes very close to E_F and the parabolic band at **b** around the Γ -point is shifted below the Fermi level.



Figure 5.10: Comparison of DOS for ABA configuration for BN/aluminene/BN case (lowest energy configuration) with GGA-PBE and HSE06 hybrid functionals. Fermi energy (E_F) has been set to 0 eV.

The most important observation is related to the energetically preferred ABA configuration. The band structure of this case shows a finite gap of 0.13 eV at the Γ -point (Table 5.1, and Figure 5.8(b)). As discussed previously in the case of aluminene/BN bilayers, the enhanced interaction of the Al and N atoms (resulting in a larger degree of overlap of Al and N orbitals) leads to a larger degree of band splitting near the Γ -point which eventually gives rise to the opening up of the gap (Figure 5.5). Thus, the opening of the gap in ABA configuration can be anticipated due to the fact that the Al atoms experience the presence of N atoms, of the top and bottom BN layers.

As it is well known that the standard PBE functional form underestimates the bandgap, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [194, 195] has been used to perform calculations for the ABA configuration (Figure 5.10). The gap from the HSE06 functional has been obtained to be 0.48 eV, thus confirming that the ABA configuration of BN/aluminene/BN heterostructure is clearly semiconducting in nature.



Figure 5.11: The I-V characteristics and density of states for AB stacked bilayer and ABA stacked trilayer heterostructures of aluminene and BN. Al/BN stands for aluminene/BN heterostructures.

5.2.3 Tunneling current and I-V characteristics

Since the tunneling current is sensitive to the local electronic properties of atoms at the surface, we probe the electron tunneling charateristics of the layered heterostructures. Figure 5.11 displays the current-voltage characteristics of the aluminene based heterostructures. The calculations have been performed based on the scanning tunneling microscope (STM) theory of Tersoff and Hamann [245] as expressed by Lang [246] and implemented by He *et.al* [247]. In an STM-like setup, the sample and the probing tip are typically separated by a vacuum gap to mimic the non-bonding configuration of the tip with the sample. The tip is taken to be an Au₁₃ cluster being placed at a distance of 5 Å, above the surface of the sample. Note that the tunneling current is dependent on the convolution of the DOS

of the Au₁₃ cluster tip and the surface under study. At a certain positive (negative) bias voltage, the electrons tunnel from the occupied bands of the tip (sample) to the unoccupied bands of the sample (tip). As is seen from the literature, this approach has been successfully applied to determine the electron tunneling characteristics in various systems e.g. (PbS)₃₂ quantum dot, Sn monolayers, BN monolayers etc. [248–251]. It is evident from Figure 5.11 that the aluminene monolayer exhibits the highest current. Prominent negative differential resistance (NDR) is observed for aluminene/BN system (beyond 0.26 V) for the positive bias regime. The diode like characteristic is observed for the semiconducting ABA stacked BN/aluminene/BN case. Contrary to the case of BN/aluminene/BN, a large tunneling current for aluminene/BN is found due to the presence of a finite DOS near the Fermi level.

5.3 Summary

In this chapter, using vdW dispersion corrected DFT, we have investigated the stability, structural and electronic properties of aluminene/BN heterostructures. The results of E_B and charge density indicate that the stability of the heterostructures is governed by the van der Waals interactions between the constituent layers, making these systems van der Waals heterostructures. We have observed a strong dependence of the electronic structure on the stacking arrangements as well as on the number of layers in the heterostructure. The bilayer heterostructures comprising aluminene and BN monolayers are found to be non-magnetic and metallic in nature. From the GGA-PBE level of theory, ABA stacked BN/aluminene/BN is found to be semiconducting in nature. Further, Dirac cones have also been observed for the AB'A stacked configuration of BN/aluminene/BN. The results of electron tunneling characteristics validate the metallic or semiconducting nature of the heterostructures considered.

Chapter 6

Prediction of Two-Dimensional Binary Monolayers Based on Mo and W

6.1 Introduction

In the last few chapters, our study was focused on 2D monoelemental monolayer, mainly aluminene. We explored and investigated various methods of tuning the geometric and electronic properties of aluminene primarily, via different methods of functionalization, such as adsorption, substitution and intercalation. Besides, we also probed the heterostructures of aluminene and BN monolayers, and achieved a bandgap opening in planar 2D elemental aluminene trilayer heterostructure.

As previously stated in Chapter 1, in addition to numerous studies on elemental 2D monolayers, extensive research on binary 2D monolayers, inlcuding group III-VI [39], group IV-VI [34,40], group III-V [41] and several other type of binary monolayer systems [42], exist in the literature. These materials have been of increasingly expanding interest due to their possible application in the areas of semiconductors, optoelectronics, photoelectronics, etc.

It has been observed that, much of these studies are focused on the 2D binary monolayers consisting of chalcogens, which have been commonly found to bind with metal atoms having s and p electrons (like Ga, Sn etc). The chalcogens form bonds with the transition metal (TM) atoms (having d electrons, for example: Mo, W) as well, as has been observed in cases of transition metal dichalcogenides (TMDCs). Since the last few decades, 2D monolayer TMDCs have been the topic of immense interest to the scientific community [75, 252–259], and MoS_2 and WS_2 are well studied among all 2D TMDCs. Hence, it would be interesting to investigate the possibility of 2D binary monolayers of monochalcogenides (monosulfides) of Mo and W. Furthermore, it is noted that 2D binary monosilicides or monoarsenides of Mo and W are yet to be explored. Hence, in this chapter, we investigate and study the 2D binary monolayers of monosulfides, monosilicides and monoarsenides with TM atoms Mo and W. We explore various relevant configurations, which are generally found in the literature for monolayers, for these 2D binary monolayers to establish their lowest energy state. This chapter, thus, is divided into two parts. (1) We investigate the possibility of 2D monolayer of monochalcogenides of Mo and W, with "sulfur" atom as a chalcogen. We examine the stability of various structures in this stoichiometry, both from the points of view of energetic and dynamical stability. Further, we analyze the geometric configurations and the associated electronic properties for the lowest energy configurations of MoS and WS. (2) We also explore the possibility of formation of 2D binary monolayers of monosilicides and monoarsenides with TM atoms Mo and W, in various configurations.

6.2 Results and Discussion

We note from the literature that many of the monochalcogenides have phosphorene-like puckered or buckled structures [34, 40, 260–271]. We, therefore, probe both these probable configurations for sulfides, arsenides and silicides studied in this thesis. Besides the aboveidentified structures, we also examine the planar configuration, to probe for the lowest energy state of these systems. Further, we wish to mention here that, different relative positions of Mo/W atoms with respect to the S/Si/As atoms have been investigated to examine the lowest energy states of the binary monolayers in the puckered structure [272]** and only the most stable configurations have been considered for further discussion.

6.2.1 Two-dimensional monochalcogenides: MoS and WS

6.2.1.1 Structure and Energetics

As stated earlier, different configurations have been investigated to probe the lowest energy configuration for the MoS and WS monolayers (Figure 6.1). We determine the E_B /atom to examine and compare the electronic stability of the structures and their values are presented in Table 6.1.



Figure 6.1: Schematics of different possible configurations for XS (X = Mo, W): (a) planar, (b) buckled and (c) puckered configuration. The solid line indicates the unit-cell. Gray and red balls represent Mo/W and S atoms, respectively.

It is clear from the table that, the puckered configuration is the lowest energy configuration for both, MoS and WS, followed by the buckled configuration. The energetically lowest (puckered) configuration is found to be the structure where Mo/W atom is positioned at the adjacent sites, and S prefers the edge sites (Figure 6.1). We wish to mention here that the puckered structure having the lowest energy possesses a different geometry than the other

^{**}This is published by the work author of this thesis and others in year 2019inPhysics Letters А belonging to Elsevier Publishing the group. https://www.sciencedirect.com/science/article/abs/pii/S0375960119305535

Structure	MoS	MoS	MoS	WS	WS	WS
	Planar	Buckled	Puckered	Planar	Buckled	Puckered
$E_B/atom$	-4.296	-4.949	-5.462	-4.853	-5.838	-6.266

Table 6.1: Binding energy per atom (E_B/atom) in units of eV/atom for different configurations for MoS and WS monolayers.

2D monochalcogenides, reported in the literature [34, 265–267, 271]. Further, we find that for MoS and WS, the energy difference between the (lowest energy) puckered and buckled configurations correspond to 0.51 and 0.43 eV per atom, respectively. Therefore, we consider only these two lower energy configurations for further discussion on these monochalcogenides.

Analysis of the spatial valence charge density distribution (VCDD) (Figure 6.2(a)-Figure 6.2(d)) has been carried out to examine the nature of bonding prevailing in the systems. We find more charge localization on the atoms, indicating that the dominant bonding is essentially ionic-like. Additionally, we have performed Bader charge [220] analysis, which also provides a more in-depth insight into the chemical bonding between the atoms constituting the system. From this analysis, we find that a large amount of charge transfer occurs between the X (= Mo, W) and S atoms for the probed monochalcogenides (Table 6.2), and thus, these results corroborate well with the VCDD results. Further, it has been found that the direction of charge transfer is consistent with the electronegativity (EN) difference (since $EN_{Mo/W} \leq EN_S$). It is worth-mentioning that similar ionic-like bonding is seen for Mo and W dichalcogenides as well [253]. For instance, in MoS_2 , Mo act as an electron donor losing 0.90e, and each S accepts 0.45e, [253]. These values have a close resemblance with what we observe for MoS (Table 6.2).

6.2.1.2 Phonon Dispersion

A crystal lattice stays in the ground state at 0K temperature, with no phonon contribution in the system. However, the study of phonons becomes crucial at finite temperatures, as they contribute significantly in governing the thermal and electrical properties of a material.

Table 6.2: Geometric and energetic data for the buckled and puckered configurations of MoS and WS monochalcogenide. E_B /atom and a represent the binding energy per atom (in eV/atom) and the lattice constants, respectively. Δ is the buckling parameter, d_1 and d_2 represent X-S and X-X bond distances, respectively. Values of a, Δ , d_1 and d_2 are in Angstrom. α and β represent the bond angles (in degrees) S-X-X and S-X-S, respectively, where X = Mo and W. ΔQ shows the amount of Bader charge transfer between the X and S atoms in the units of e.

Structure	E_B/atom	a	Δ	d_1, d_2	α,β	ΔQ
MoS-buckled	-4.949	3.00	1.58	2.34	79.6	0.50
WS-buckled	-5.838	2.98	1.62	2.66	78.18	0.55
MoS-puckered	-5.462	3.12	-	2.45, 2.36	116.1, 78.9	0.76
WS-puckered	-6.266	3.08, 3.01	-	2.45, 2.47	$105.9,\ 77.9$	0.78

Moreover, the stability of a structure is also based on the phonon modes. We have adopted a finite displacement method using the VASP [196,197] and PHONOPY packages [204,205] to evaluate the phonon dispersion of the systems under investigation. A supercell of 6×6 has been employed for the calculation of phonon spectra and the structural stability. For a system to be dynamically stable, all the phonons must vibrate with positive frequencies [273]. The phonon dispersion plotted in the high symmetry k-point direction (Γ -K-M- Γ for buckled case and Γ -X-S-Y- Γ for puckered case) has been shown in Figure 6.2((e)-(h)).

Buckled cases: We know that there exist a total of 3N phonon modes corresponding to N number of atoms in a unit cell. For MoS-buckled and WS-buckled configurations, we notice six phonon modes, as the unit cell contains two atoms. The three low-lying frequency dispersions refer to the acoustic mode, and the rest three having a non-zero frequency at the Γ -point correspond to the optical mode. All phonon modes exhibit positive frequencies, with the exception of one mode, which at the Γ - point has a negligible imaginary frequency value. But this small imaginary frequency present in the systems has a numerical rather than a physical origin, as has been explained in the literature [41].

Puckered cases: The MoS and WS systems in the puckered configuration possess 12 phonon modes in total. We note from Figure 6.2(h) that one of the phonon modes has a relatively high imaginary frequency for the WS-puckered case. Hence, structural stability



Figure 6.2: Valence charge density distribution (VCDD) for optimized geometry for (a) MoSbuckled, (b) WS-buckled, (c) MoS-puckered and (d) WS-puckered configurations. The solid line indicates the unit-cell. Gray and red balls represent Mo(W) and S atoms, respectively. Note that the yellow region indicates the electron rich region, consequent to that, the gray color of Mo(W) is not clearly visible. (e), (f), (g) and (h) represent the phonon dispersion curves for MoS-buckled, WS-buckled, MoS-puckered and WS-puckered configurations, respectively. WS-puckered case (h) exhibits negative frequency with substantial values, near the Γ point.

is likely to be absent for this system. The imaginary frequency could be related to the lower symmetry of the WS-puckered structure. In contrast, MoS-puckered is predicted to be structurally stable, with all the phonons oscillating with positive frequencies. Because of the dynamical instability observed for the WS-puckered case, we will not pursue this system for further analysis.

6.2.1.3 Electronic Structure

We now discuss the results of the electronic density of states (DOS) and band structure shown in Figure 6.3 for the monolayers of monochalcogenides. Further, the partial DOS (PDOS) of the atoms constituting the system has also been analyzed to gain in-depth insight into the contribution of orbitals of various atoms. From the results of electronic structure, it is observed that all the three predicted structures are non-magnetic in nature. Moreover, except for WS-buckled configuration (which is semimetallic), the other three systems exhibit metallic behavior. The observations and results for the buckled-monochalcogenides are discussed first, followed by the puckered-cases.



Figure 6.3: Band structure, partial density of states (PDOS) and bands with spin-orbit interaction. (a)-(c) show the band structure plot, (d)-(f) represent the PDOS and (g)-(i) exhibit the band with the inclusion of spin-orbit coupling. X in the figure reperesents Mo and W. MoS-buckled, WS-buckled and MoS-puckered cases are shown in left, middle and right panels respectively. (i) and (ii) in the inset of (b) and (c), respectively, show the Brillouin zone for the buckled and the puckered system, respectively.

MoS-buckled: We note from the plot of PDOS (Figure 6.3(a), Figure 6.4(a)) that a

dominant contribution around the Fermi energy (E_F) comes from the Mo-d states. Thus, the band edges consist of states derived from the d-orbitals of Mo atoms with a minor contribution from p orbitals of S atoms. However, it is observed that the Mo-d and S-p states are hybridized to a greater extent below -2eV (in the valence region). The orbital projected DOS for MoS along with the band decomposed partial charge density (PCD) corresponding to the C Γ -point (which represents the Γ -point in the conduction band regime) of the conduction band is shown in Figure 6.4. It is evident from the figure that the electronic bands in the vicinity of the Fermi level have significant contribution from Mo- $d_{x^2-y^2}$ and d_{xz} orbitals with minimal S-p orbital contributions. The observation is further supported by the PCD analysis, which exhibits the contribution of the Mo-d orbitals to the DOS and bands slightly above the Fermi level.



Figure 6.4: Orbital projected density of states (DOS) for buckled monolayer of (a) MoS and (b) WS. DOS is in units of states/eV. Inset shows partial charge densities corresponding to band point $C\Gamma$ shown in Fig.5(b,d).

To establish the role of absence of one S atom from MoS_2/WS_2 in the MoS/WS systems, we provide the comparison of the band structures for dichalcogenides as well as monochalcogenides, which is shown in Figure 6.5. The monolayer dichalcogenides, MoS_2 and WS_2 , exhibit direct bandgaps of 1.65 eV and 1.84 eV, respectively, which match well with the literature [253]. We observe that the monochalcogenide, MoS, lacks a bandgap. In addition, for MoS_2 , the valence band maximum (VBM) and the conduction band minimum (CBM) lie at the same momentum value, in contrast to the MoS case. Furthermore, relative to the corresponding dichalcogenides, we find that the Mo-d bands lying in the conduction region are located near the Fermi level for MoS. The difference in the electronic structure between the mono and dichalcogenides can be due to the absence of one S atom which leads to the dissimilarity in the hybridization between the corresponding states of the Mo (the cation) and S (the anion) atoms.



Figure 6.5: Atom projected partial band structure for buckled monolayer of (a) MoS_2 and (b) MoS, (c) WS_2 and (d) WS. X in the legend corresponds to Mo and W atoms. C Γ and $V\Gamma$ represent the Γ -point in the conduction and valence band regimes, respectively.

WS-buckled: We find from our calculations that this monochalcogenide is semimetallic in nature, with the VBM (at *M*-point) and CBM (in the Γ -K path), lying at different kpoints. Alike the MoS-buckled monochalcogenide, the DOS in the vicinity of E_F has a dominant contribution from the W-d states. A greater hybridization between the W-d and S-p states has been observed deeper down the Fermi level. On the other hand, as opposed to the corresponding MoS case, the S-p orbitals also contribute above the Fermi-level along with the W-d states. This is reaffirmed with the help of the respective PCD, which exhibits charge density localization in the neighborhood of the S-atom as well, for WS case.

We also note a rearrangement of the bands in case of WS monochalcogenide, identical to the results of the comparative study of MoS₂ and MoS. Thus, the rearrangement of bands and further, the differences in the hybridization between the W and S atoms prevailing in the two systems lead to the differences in the electronic bonding between the mono and dichalcogenides. We have also investigated the influence of spin-orbit coupling (SOC) since it may play a crucial part in altering the electronic structure of a system [274–277]. Wang *et al.* [276] have shown that for graphene-based systems, WS₂ can serve as a substrate and provides a possibility for topological states of matter. It has been well established that the degeneracy of energy levels is raised by the inclusion of SOC. Similar splitting of the energy levels of the monochalcogenides has been observed (Figure 6.3((g)-(i))). Due to the incorporation of SOC in WS (Figure 6.3(h)), we notice a minimal band splitting corresponding to the CBM in the Γ -K direction. The influence of SOC in the WS-buckled case has been found to be more significant than the MoS case since it is well known that the interaction governed by the spin-orbit coupling is more pronounced for the higher atomic number (Z) elements.

MoS-puckered: For this case also, the results of electronic band dispersion and the DOS show that the dominant states in the proximity of E_F are primarily due to the Mo-d electrons. Negligibly small splitting has been observed in the Γ -X and Γ -Y direction (as both the directions are symmetric) as well as at the S-point (at about -1.2 eV) as a result the inclusion of SOC.

6.2.1.4 Bandgap engineering by application of strain

It has been well studied in the literature that application of strain (either tensile or compressive) on the system play a crucial part in modifying the electronic structure of a material [255,278–282]. Since the WS-buckled monochalcogenide possesses an (indirect) semimetallic nature, the effect of application of strain on its band structure is worth probing. Therefore, we have applied bi-axial strain (as discussed in Chapter 2) on this system. We apply tensile and compressive strain, with the magnitude of 5%, 6%, and 8%, to study its influence on the bonding and the electronic properties of the system. The effect of distortion obviously is well reflected in the changed geometric parameters (bond distances, bond angles, and the buckling parameter) of the WS structure, which further affects the electronic structure. Notably, an opening of an indirect bandgap has been observed for the bi-axial tensile strain (Figure 6.6). No such gap opening is seen on the application of compressive strain.



Figure 6.6: Evolution of band structure due to bi-axial tensile and compressive strain on WS-buckled system. Tensile strain causes opening of a bandgap.

The evolution of the VBM (at *M*-point) and the CBM (along the Γ -K path) on the application of strain explain the bandgap. We note that the VBM located at the high symmetry *M*-point moves below the E_F level with increasing bi-axial tensile strain. Further, the CBM (observed along the Γ -K direction) shifts far from the E_F . This noticeable movement of the bands has the following origin. Figure 6.3 (b) and 6.3 (e) show that the band edges have a predominant contribution from the W-d states along with a minimal contribution of the S-p orbital. Enhanced tensile strain tends to cause an increment in the lattice constant, and thus, consequently, the bond distances, W-W, W-S, or S-S are also lengthened (Table 6.3). As a result of this, the overlap of W and S orbitals and, hence, the existing hybridization between W-d states and S-p states is reduced (Figure 6.7(b)), leading to a gap. It should be mentioned that along with the increase in the tensile strain, the C Γ (located at 0.46 eV above E_F) and V Γ (at about -1 eV with respect to E_F) points are lowered and lifted up, respectively, towards the E_F . However, we wish to point out here that the maximum strain applied (i.e. +8% tensile strain) is not adequate to induce the Fermi level crossing of bands corresponding to the Γ -point. Consequently, an indirect semiconducting nature for the WS-buckled monochalcogenide is observed. A complete reverse behavior for the band evolution is found for the case of compressive strain application. The Fermi level is crossed by the CBM and VBM, leading to a metallic nature of the system. It is worth mentioning that dissimilar to the WS-buckled case, no sign of any metal-semiconductor transition has been observed for the MoS-buckled monochalcogenide [272], and the application of strain preserves the metallic nature in the latter case.

Table 6.3: Lattice constant (a), buckling parameter (Δ), W-S bond distance (d_1), W-S-W bond angle (α) and the bandgap (E_g) are tabulated for different tensile bi-axial strain. a, Δ , d_1 are in Å, α in degrees, E_g is in eV units.

Strain (%)	a	Δ	d_1	α	E_g
5%	3.12	1.56	2.38	81.9	0.14
6%	3.15	1.54	2.39	82.7	0.17
8%	3.21	1.52	2.40	84.1	0.20

We have also evaluated the $E_B/atom$ (Figure 6.7(c)) for MoS and WS monochalcogenides in the buckled configuration under the influence of strain. We observe the parabolic nature when energy is plotted against the applied bi-axial strain and the lowest energy state is exhibited by the system without strain. It is evident from Figure 6.7(c), however, that as a whole, the systems under the tensile strain have relatively higher (more negative) E_B in comparison to the compressively strained systems. Hence, the possibility to stretch the system is likely to be energetically more favorable than to compress it.



Figure 6.7: Orbital projected DOS (in units of states/eV) corresponding to +8% tensile strain for buckled (a) MoS and (b) WS. (c) Binding energy per atom (eV/atom) of monolayer buckled MoS and WS as a function of strain.



Figure 6.8: Comparison of band structure of monolayer buckled MoS and WS with GGA-PBE and HSE06 hybrid functionals. Fermi energy (E_F) has been set to 0 eV.

6.2.1.5 Effect of Hybrid functional on the electronic band structure

Since WS-buckled case exhibits semimetallic nature, we wish to probe the influence of the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [194, 195] on its electronic structure. For the sake of comparison and completeness, we also consider calculating the electronic band structure of MoS-buckled case using the same hybrid functional. From the results using the HSE06 hybrid functional, interestingly, we find that both, WS-buckled and MoS-buckled, cases have indirect bandgaps of 0.62 eV, and 0.34 eV, respectively. Like silicon and germa-

nium which are indirect bandgap semiconductors and used in the field of semiconductors, these indirect bandgap semiconductors may be expected to find potential application in the semiconductor industry.

6.2.2 Two-dimensional monolayers of Arsenides and Silicides : MoAs/WAs and MoSi/WSi

As mentioned above, similar to the monochalcogenides, MoS and WS, we present and briefly discuss here the results of 2D binary Mo/W arsenides and silicides in the planar, buckled and the puckered configurations.



Figure 6.9: (a) Optimized geometry for the Mo/W arsenides and silicides in the (I) buckled and (II) puckered configurations. Brown and blue colored balls represent Mo/W and Si/As atoms, respectively. (b) Difference charge density (DCD) for (I) buckled configuration and (II) puckered configuration, respectively. Yellow and cyan colors denote the electron rich and deficit regions, respectively.

6.2.2.1 Energetics, Geometry and Charge Analysis

Similar to the case of monosulfides, the planar geometry is the least stable structure for all the systems. Thus, in this work, we analyze and report the geometric (Figure 6.9 and Table 6.4)

and electronic properties of only the buckled and puckered structures for Mo/W arsenides and silicides. From Table 6.4, it is clear that the puckered configuration has the lowest energy for all the systems, identical to those of above discussed MoS and WS monosulfides, however, with different relative positions of the atoms in the unit cell (Figure 6.9(a)).

We note from Table 6.4, that for the arsenide systems, because of the larger atomic radii of As as compared to Si, bucking height tends to be more to facilitate an effective overlap between the As and Mo/W orbitals. The greater buckling leads to reduced lattice parameters. Difference charge density (DCD) analysis reveals the dominant covalent-like nature of bonding between the Mo/W and As/Si atoms (Figure 6.9(b)).

The optimized geometries for the puckered configurations suggest that MoSi and WAs systems form a square lattice. On the other hand, WSi and MoAs form a rectangular lattice with $a \neq b$ (Table 6.4). Similar to the case of buckled configuration, a covalent-like bonding exists in the puckered configurations (Figure 6.9(b)) along the d_1 and d_2 bonds. For the MoAs case, a covalent character between the Mo-d and As-sp orbitals is present along the d_2 bond and absent along the d_1 bond. This is expected because d_2 is smaller than d_1 for this case (Table 6.4). The characteristic features of Mo/W-d and As/Si-sp orbitals are evident from the DCD plots.

The calculation of phonon dispersion reveals that MoSi, WSi and WAs have positive phonon frequencies only for the puckered configurations [283]^{**} (Table 6.4). On the contrary, MoAs has stable buckled as compared to the puckered configuration. It is evident from the literature that the effect of substrate as well as application of strain have an immense effect on the lattice vibrations of the 2D materials and could be sufficient enough to tailor the thermal lattice vibrations [284, 285]. Hence, we can conjecture that it may be possible to stabilize the soft phonon modes in buckled MoSi and WSi using strain or using different substrates.

^{**}This work is published by the author of this thesis and others in the year 2020 in AIP Conference Proceedings belonging to AIP Publishing group. https://aip.scitation.org/doi/abs/10.1063/5.0016628

Table 6.4: Structural parameters and energetic data for different configurations of MoY and WY (Y = Si, As) binary systems. $E_B/atom$ and a, b represent the binding energy per atom (in eV/atom) and the lattice constants, respectively. Δ is the buckling parameter, d_1 , d_2 represent the Mo/W-Y bond distances. Values of a, b, Δ, d_1, d_2 are in units of Å. α, β , γ, δ (in deg) represent the angles shown in Figure 6.9. Last column indicates whether the structure is dynamically stable from the phonon dispersion calculation or not.

Structure	$E_B/atom$	a, b	Δ	d_1, d_2	$lpha,eta,\gamma,\delta$	Phonon stability
MoSi-buckled	-4.01	3.22	1.42	2.34	86.9	Unstable
WSi-buckled	-4.77	3.21	1.45	2.35	86.0	Unstable
MoAs-buckled	-3.90	2.90	1.96	2.58	68.5	Stable
WAs-buckled	-4.76	2.88	2.03	2.62	66.6	Unstable
MoSi-puckered	-5.19	3.24	-	2.50, 2.72	66.3, 80.8, 113.7	Stable
WSi-puckered	-6.04	3.15, 3.33	-	2.54, 2.74	64.4, 76.5, 115.7, 115.6	Stable
MoAs-puckered	-4.53	2.88, 4.00	-	2.69, 2.54	66.6, 64.9, 113.3, 113.3	Unstable
WAs-puckered	-5.42	3.24	-	2.70, 2.91	58.2, 74.0, 121.5, 122.0	Stable

6.2.2.2 Electronic Structure

In this section, we discuss in brief the electronic band structure for Mo/W arsenides and silicides in the buckled and the puckered configurations (Figure 6.10). All the systems under investigation are found to be non-magnetic in nature. The calculations predict indirect bandgaps for the buckled MoSi and WSi cases with bandgaps of 0.22 eV and 0.38 eV, respectively. On the other hand, metallic nature is revealed for the MoAs and WAs systems in buckled configuration. We observe interesting features in the band structures for the puckered cases (Figure 6.10(II)). Linear Dirac-like characteristics are observed for the MoSi and WSi cases along the Γ -X direction. The other directions in the Brillouin zone do not possess this interesting band-crossing features near E_F . This indicates direction-dependent charge carriers and consequently, the transport properties. We wish to mention here that the application of strain was also probed for the silicides and the arsenides in their energetically and dynamically stable structures. However, no bandgap opening was observed for these cases.



Figure 6.10: Band structures along the high symmetry directions for (I) buckled and (II) puckered configuration respectively. Fermi energy (E_F) has been set to 0 eV.

6.3 Summary

In conclusion, in this chapter, we discuss the possibility of stability of monolayered 2D monosulfides, arsenides, and silicides of Mo and W based systems. Different initial configurations, like planar, buckled and puckered structures, have been examined to probe for the lowest energy state of these systems. The buckled and the puckered structures are found to be the two most stable configurations, as is evident from the results of calculations of the binding energies. For all the three binary systems, MoY and WY (Y = S, As and Si), the puckered structure is energetically the most favorable structure. In the case of sulfides, the MoS system exhibits dynamical stability in both the configurations. On the other hand, the WS case in the puckered configuration is seen to have dynamical instability. From the analysis of dynamical stability for all the silicides and the arsenides probed in this study, it is established that, considering both energetic and dynamical stabilities, MoAs is stable in the buckled and the other arsenide and the silicides are stable in the puckered configuration.

A non-magnetic metallic nature has been observed for puckered structures of both MoS and WS. On the contrary, an indirect semimetallic with non-magnetic behavior is observed for the WS-buckled system. Interestingly, we observe Dirac-like features close to E_F for MoSi and WSi in puckered configurations. Further, an effect of application of strain has been probed for MoS-buckled and WS-buckled configurations. An electronic transition from semimetal to an indirect bandgap semiconductor is found for the WS-buckled system upon applying tensile strain.

We wish to point out here that besides exhibiting interesting physical and electronic structure properties, 2D nanostructures have also gained significant interest in gas sensing applications due to their high surface-to-volume ratio and specific chemi- or physisorption capabilities. Further, to enhance the sensitivity of gas molecules, the 2D surfaces are activated through foreign atom (especially transition metal (TM)) adsorption, substitutions, etc. Hence, in the next chapter of the thesis, we explore the possibility of two types of 2D systems serving as efficient gas sensors. We probe one monoelemental system, namely, aluminene, and one set of binary systems, namely, Mo/W based monochalcogenides (MoS/WS). We wish to mention here that since for MoS/WS cases, one of the terminating layers consist of a TM atom (Mo, W), we restrict ourselves to probe the adsorption of gas molecules (on top of the TM atom) on the pristine surfaces only.

Chapter 7

Gas Adsorption on 2D Surfaces

7.1 Introduction

It is well known that sensing and storage of various important gas molecules are nowadays an important field of research which is primarily relevant from the point of view of environment as well as application, for example, detecting leakage of toxic gases (carbon monoxide (CO), nitric oxide (NO), ammonia (NH₃), etc.), monitoring air quality, controlling the emission of gases, etc. [160, 286–289], and also storage of useful gases like hydrogen (H₂), that can be used as an alternative to the fossil fuels [290].

As already discussed in Chapter 1, extensive studies on gas molecule adsorption on monoelemental 2D materials, like graphene, silicene, phosphorene, germanene, etc., have been reported till date in the literature [162,164–168,291]. The strength of adsorption (and hence physisorption versus chemisorption) of gas molecules on the surfaces of interest has been proved to be an important aspect from the points of view of both fundamental understanding as well as application. Further, it has been shown in the literature that the introduction of defects and doping in the 2D surfaces often leads to a significant improvement in the adsorption behavior [169–171, 175, 176]. Therefore, we have studied and presented the results in Chapter 4 of various aspects of functionalization to tailor the geometric and electronic properties of pristine 2D aluminene in the buckled and planar structures. One of the prime motivation behind these studies of functionalization (via adsorption of or substitution or intercalation by, mainly, TM atoms) is because it leads to improvement in sensing and adsorption of gas molecules on 2D surfaces, discussed in the literature [169–179].

Taking the work further, in this chapter, we present the results of our study on adsorption of few environmentally important gas molecules on both pristine and TM functionalized aluminene. We probe the possibility of the ease of adsorption of three gas molecules, namely, H_2 , CO, and NO, on TM functionalized buckled aluminene surface. We concentrate on TM atoms as candidates for substitution since these have been shown to be promising in earlier studies for other 2D surfaces. In this regard, we take four typical cases of TM-substituted aluminene (results presented in Chapter 4): non-magnetic Ti and Co-substituted systems and magnetic Cr and Fe-substituted systems. Further, a brief comparative study of gas adsorption on binary 2D monochalcogenides, MoS, and WS (results of predictive studies of pristine surfaces have been presented in Chapter 6) has also been carried out and discussed in this chapter. We wish to mention here that, in what follows, we use the word - Aluminene - to represent pristine 2D buckled aluminene surface.

7.2 Results and Discussion

7.2.1 Gas Adsorption on Aluminene and TM-substituted Aluminene

Probing the binding strength (i.e., the adsorption energy) of different gas molecules with the substrate is necessary to identify a suitable material for gas sensing and/or storage. In this section, we analyze the strength of binding of three different gas molecules (CO, NO, and H_2) on pristine as well as TM-substituted Aluminene system. It is found from the literature that the charge transfer between graphene and the considered adsorbates does not depend much on the adsorption site. Instead, strong dependence on the orientation of the adsorbate with respect to the graphene surface is found [162]. To this end, we probe different configurations for the adsorption of CO and NO molecules (hetero-nuclear) and H_2 molecule (homo-nuclear) on pristine (Aluminene) and TM-substituted surfaces (Ti-Aluminene, Cr-Aluminene, Fe-Aluminene, and Co-Aluminene) as discussed below.

For the first and second configurations, the CO/NO molecule is placed perpendicular to the Aluminene as well as the TM-substituted Aluminene surface. We place the C/N (O) atom on top of the Al atom in the pristine case and on top of the TM atom in the substituted cases for the first (second) case. A third configuration is also possible where the CO/NO gas molecule is parallel to the 2D surface. We assign the following nomenclature for the different configurations:

- (a) A-configuration (perpendicular orientation with N/C facing Al/TM)
- (b) **B**-configuration (perpendicular orientation with O facing Al/TM)
- (c) **C**-configuration (parallel orientation)

We optimize the geometries for the \mathbf{A} , \mathbf{B} and \mathbf{C} configurations. It is to be noted here that the systems mentioned in Tables 7.1, 7.2 and 7.3 are named as per the starting/initial orientation of the gas molecule on the 2D surfaces for the configurations discussed above. Unlike the \mathbf{A} , \mathbf{B} and \mathbf{C} configurations for the cases of adsorption of hetero-nuclear CO or NO molecules, understandably, adsorption of homo-nuclear H₂ molecule gives rise to only two configurations, namely, \mathbf{A} and \mathbf{C} (A and B being same).

7.2.1.1 Adsorption of H_2 gas molecule

As mentioned above, the configurations probed for the adsorption of H₂ molecule are **A** and **C** (Figure 7.1). After performing full geometry optimization of these two configurations, the H-H bond length is found to be 0.75 Å. Table 7.1 lists the adsorption energy (E_{ads} , defined in Chapter 2) to establish the possibility of adsorption of H₂ gas molecule on pristine and TM (TM = Ti, Cr, Fe and Co) substituted Aluminene. It is well-known that a higher adsorption energy (negative values of E_{ads} and absolute values being of the order of around 1 eV or more)

suggests the occurrence of chemisorption, where a chemical bond is typically characterized by charge transfer between the 2D surface and the adsorbate molecule. We observe that configuration **A** is favorable for Aluminene with a very small E_{ads} of -0.062 eV, and hence, it indicates physisorption. Moreover, both **A** and **C** configurations may be possible for this case, since the difference between the two is rather small (about 12 meV). A large value of distance between the molecule and the surface is observed in both the configurations, which corroborates with the energetics (Table 7.1).

Table 7.1: E_{ads} is the adsorption energy, Δq is the Bader charge on H₂ gas molecule. H-H is the distance between the two H atoms in H₂ molecule after adsorption. D is the moleculesurface distance after optimization. Negative value of Δq indicates that the gas molecule has gained electron from the 2D surface.

Configurations	E_{ads}	Δq	H-H	D
	(eV)	(e)	(Å)	(Å)
Al-H-H (\mathbf{A})	-0.062	-0.02	0.75	2.92
H-Al-H (\mathbf{C})	-0.050	-0.01	0.75	3.16
Ti-H-H(A)	-0.666	-0.13	0.82	1.94
H-Ti-H (\mathbf{C})	-0.666	-0.13	0.82	1.94
Cr-H-H(A)	-0.069	-0.02	0.76	2.82
H-Cr-H (\mathbf{C})	-0.654	-0.20	0.91	1.69
Fe-H-H (\mathbf{A})	-0.074	-0.02	0.75	3.15
H-Fe-H (\mathbf{C})	-0.538	-0.17	0.96	1.58
Co-H-H (\mathbf{A})	-0.073	-0.05	0.76	3.12
H-Co-H (\mathbf{C})	-0.205	-0.11	0.91	1.59

We find evidence of negligible charge transfer from Bader charge analysis. Further, an insignificant change in the H-H bond distance has been observed when compared to the respective value in the isolated gaseous form. All these results put together give evidence of a weak interaction (that is physisorption) between the 2D Aluminene sheet and the H₂ gas molecule. We wish to point out here that, Villagracia *et al.* [292] have studied the adsorption of H₂ molecule on Mg, Ca and K doped planar aluminene. They have also reported that H₂ molecule is physisorbed on doped aluminene with small value of E_{ads} in the range of -0.023 eV to -0.081 eV. Hydrogen adsorption has also been studied on other 2D structures like

pristine graphene, phosphorene, borophene, etc [175, 293–298]. Zhang *et al.* have reported H_2 adsorption on pristine graphene and the adsorption energy is reported to be 0.067eV [294]. For pristine phosphorene, the adsorption energies are found to be -0.130 eV and 0.060 eV, from the works of Zhang *et al.* [297] and Yu *et al.* [298], respectively. Therefore, based on the results from the literature as well as our work, it can be conjectured that the adsorption of H_2 gas molecule on various pristine monoelemental 2D substrates is weak.



Figure 7.1: Schematic of optimized geometry (top and side view) of H_2 gas molecule adsorption on Aluminene and TM-Aluminene (TM = Ti, Cr, Fe and Co). Blue, cream and green colored balls denote Al, H and TM atoms, respectively.

When a surface is functionalized with different metals, an enhancement in adsorption of H_2 gas molecule is observed as reported in the literature. According to Zhang *et al.* [294], H_2 adsorbed on Ti-doped graphene has an adsorption energy of -0.3 eV. Li and Na doped silicene have been predicted to be suitable for storage of hydrogen (the adsorption energies are -0.46 and -0.48 eV for Li and Na cases, respectively) [175]. In general, it is argued in the literature that a molecule having a strong σ -bond, as in the case of H_2 molecule, is inert towards a stable binding with a metal. It is well-known that transition metals are used for catalysis, which involves H_2 molecule [299] where electrons from σ orbitals are donated from
H_2 to the metal. It is then stabilized further by the back donation of electrons from metal d-orbitals to the hydrogen, which helps in the catalytic process of hydrogenation. This well-known interaction is called Kubas interaction [299]. This process is generally characterized by an enhancement of the bond length of the H_2 molecule, but without breaking the H-H bond. In what follows, we discuss the presence of this interaction in case of adsorption of H_2 on TM-Aluminene surfaces, studied in this thesis.

From Table 7.1 it is observed that there is an enhancement in the strength of adsorption when Aluminene is functionalized with TM. First we consider the non-magnetic cases. In the case of Ti-Aluminene, configuration **A** converges to the **C** configuration (Figure 7.1). Further, the increase in the strength of adsorption is evident from the E_{ads} (-0.666 eV) value. We find that, the H-H bond distance shows slight increament of 0.82 Å from 0.75 Å, which is observed in the gaseous state. For the Co-Aluminene system also, **C** is the favorable configuration (which has parallel orientation of H₂ molecule with respect to the 2D surface) with E_{ads} of -0.205 eV (Table 7.1 and Figure 7.1). The H-H distance increases to 0.91 Å. Further, we note that, a smaller distance between the Co-Aluminene surface and the H₂ molecule indicates a higher adsorption energy in the **C** configuration as compared to the **A** configuration.

We observe that the H-H distances for the Co-Aluminene and Ti-Aluminene cases (in their energetically favorable configurations) lie in the range of about 0.8 to 0.9 Å. Interestingly, this is the range in which true Kubas complexes are known to be formed [299]. Besides, the charge transferred to the H₂ molecules suggests the back donation of electrons from the TM atom when compared to the pristine case. Thus, it gives an indication that Co-Aluminene and Ti-Aluminene cases favor hydrogen adsorption through the well-known Kubas interaction. Hence, the adsorption of hydrogen molecule on these systems is likely to be stabilized via such an interaction.

Identical to the non-magnetic Ti and Co-Aluminene cases, it has been observed that the magnetic Cr and Fe-Aluminene systems also prefer the C configuration for adsorption, where

the H_2 molecule is parallel to the 2D surface. The H-H bond distances are 0.91 and 0.96 Å, respectively, for Cr and Fe-Aluminene systems in their lowest energy configurations. This shows that these systems also favor the H_2 adsorption through the Kubas interaction. The bonding between the H_2 molecule and the TM atom is stabilized by the transfer of electrons from an occupied TM-d orbital to the H atoms. This consequently leads to the weakening and lengthening of the H-H bond.

Next, we summarize in brief the difference in the H-H bond distance resulting due to adsorption of H₂ on TM-Aluminene surfaces with the two TM atoms that have less than d^5 configuration, i.e., Ti and Cr. Since Ti contains fewer d-electrons than Cr, less charge is transferred in the former case. Therefore, only a slight increase in the H-H bond distance for the Ti-Aluminene case is observed. On the contrary, H-H bond distance exhibits appreciable lengthening (0.91 Å) in Cr-Aluminene due to larger charge transfer to the molecule. Comparing the cases with elements having more than half-filled d-shell (i.e., Fe and Co), we observe similar behavior: the more the charge transfer to the gas molecule, the more the H-H bond distance.

We wish to note here that, as reported in the literature, for the storage of H_2 molecule, the ideal range of absolute values of adsorption energy per H_2 molecule is 0.2 to 0.7 eV [294]. Interestingly, the values of adsorption energy obtained by us for H_2 adsorbed on all the TM-Aluminene systems studied here lie in this range. Therefore, it can be expected that all these systems may have the potential for hydrogen storage.

Next, to understand the bonding nature in detail, we have performed difference charge density (DCD) analysis (Figure 7.2(a)). It is observed that a considerable amount of electron density is found to be accumulated near the H₂ molecule (red-colored region), which is a clear evidence of the fact that the gas molecule has gained electrons (see Table 7.1). The results of DCD are consistent with the results of Kubas interaction and the Bader analysis in all these systems (Δ q value in Table 7.1).

Electronic Density of States: From the total density of states (DOS), it is found



Figure 7.2: (a) Difference charge density (DCD) for H_2 adsorbed Aluminene and TM-Aluminene (TM=Ti, Cr, Fe and Co) systems. Red and green colored regions show electron rich and electron deficit regions, respectively. The DCD are plotted with 0.002 e/A³ for Aluminene and TM-Aluminene, respectively, for all the cases of gas adsorption. (b) and (c) represent total density of states (DOS) and partial density of states (PDOS) of H_2 gas adsorbed systems. The Fermi level has been set to zero and indicated by a vertical black dashed line. The brown-shaded area in (b) corresponds to the DOS of H_2 adsorbed systems with red colored boundary.

that all the composite systems are metallic in nature (Figure 7.2 (b and c)). A negligible change in the total DOS of Aluminene upon the adsorption of H_2 is observed. This indicates

that a weak interaction exists between the molecule and the 2D surface. On the contrary, significant changes in the total DOS have been observed for H_2 adsorbed TM-Aluminene systems. Therefore, a stronger adsorption of H_2 molecule is evident from both the total DOS as well as energetics and charge analyses (discussed above). Interestingly, it is seen that the Cr and Fe-Aluminene cases (which were magnetic before the gas adsorption) turn out to be non-magnetic in nature after the adsorption of the H_2 gas.

7.2.1.2 Adsorption of CO gas molecule

Results of geometry and energetics for the case of CO gas adsorption are presented in Figure 7.3 and Table 7.2. In the case of Aluminene, the **A**-configuration is the most favorable one. The CO gas molecule is perpendicular to the Aluminene surface and the C atom points towards the sheet, with highest E_{ads} of -0.548 eV among all three configurations. The preferred orientation of CO gas on the Aluminene surface matches well with a previous report in the literature [181]. From Bader charge analysis, it is found that about 0.45 e charge is transferred from Al to CO molecule (since C has more electronegativity than Al). Upon the adsorption of the molecule on the Aluminene surface, the C-O bond-distance has increased slightly to 1.16 Å in comparison to the isolated case, where it is 1.14 Å [300,301]. Similar enhancement of the C-O bond-distance (1.16 Å) has already been reported in the case of 2D borophene [180], indicating a very slight activation of the CO molecule.

Next, we discuss the adsorption of CO gas on the TM-substituted surfaces. Results reported in Table 7.2 show that substitution of TM favors the adsorption of CO molecule on the surface. A higher E_{ads} as compared to Aluminene is observed in these cases. This indicates enhanced adsorption of CO molecule on the TM-substituted Aluminene. It is to be noted that similar to Aluminene, all the TM-Aluminene cases favor the **A**-configuration. The higher E_{ads} and reduced molecule-sheet distances put together suggest a greater affinity of the CO molecule towards the TM-substituted Aluminene systems. Among the four TM-Aluminene systems, Cr-Aluminene possesses the highest E_{ads} with the maximum amount of



Figure 7.3: Schematics of optimized geometry (top and side view) of adsorption of CO gas molecule on Aluminene and TM-Aluminene. Blue, brown, red and green colored balls denote Al, C, O and TM atoms, respectively.

charge transfer of 0.46 e and C-O bond distance of 1.18 Å.

The bonding of CO molecule to the TM atom occurs through the frontier orbitals, namely the 5σ (HOMO) and 2π orbitals (LUMO) of CO molecule, according to the Blyholder model [302]. The process starts by charge donation from CO 5σ orbital to the metal atom, which is then followed by the back donation to 2π orbital of the CO molecule. The charge added to this orbital through the back-donation from TM element causes the stretching of the C-O bond, thus exhibiting a dissociative behavior of the C-O bond. The amount of charge transfer from the TM atom depends on the electronegativity difference as well as on the degree of the overlap between the TM-d-states with the molecular orbitals. We note that the electronegativity differences between the C atom and the TM atoms Ti and Cr are larger compared to those in cases of Fe and Co. Thus, Ti and Cr-Aluminene cases are associated with a significant amount of charge transfer from the 2D surface to the molecule.

System	E_{ads}	Δq	C-O	D
	(eV)	(e)	(Å)	(Å)
Al-C-O (\mathbf{A})	-0.548	-0.45	1.16	2.01
Al-O-C (\mathbf{B})	-0.046	-0.01	1.14	3.94
C-Al-O (\mathbf{C})	-0.139	-0.08	1.15	3.89
Ti-C-O (\mathbf{A})	-1.790	-0.42	1.17	2.06
Ti-O-C (\mathbf{B})	-0.380	-0.14	1.16	2.23
C-Ti-O (\mathbf{C})	-0.922	-1.18	1.24	2.20
$Cr-C-O(\mathbf{A})$	-2.205	-0.46	1.18	1.85
$Cr-O-C(\mathbf{B})$	-0.056	-0.01	1.14	3.53
C-Cr-O (\mathbf{C})	-0.624	-1.07	1.23	2.04
Fe-C-O (\mathbf{A})	-2.113	-0.39	1.18	1.76
Fe-O-C (\mathbf{B})	-0.046	-0.01	1.14	3.71
C-Fe-O (\mathbf{C})	-2.113	-0.36	1.18	1.76
$Co-C-O(\mathbf{A})$	-1.658	-0.28	1.17	1.75
Co-O-C (\mathbf{B})	-0.047	-0.01	1.14	3.69
C-Co-O (\mathbf{C})	-1.660	-0.32	1.17	1.75

Table 7.2: E_{ads} is the the adsorption energy, Δq is the Bader charge on CO gas molecule. C-O is the distance between C and O atoms in CO molecule after adsorption. D is the molecule-sheet distance after optimization.

The DCD for all the CO adsorbed composite systems (Figure 7.4(a)) have also been calculated. An electron-rich region around the C atom of the CO gas molecule is observed. The charge transfer is found to be more for the Aluminene, Ti-Aluminene, and Cr-Aluminene systems as there are electron deficit regions (indicated by green color) around the Al as well as Ti and Cr atoms, which are closer to the C atom of CO molecule, respectively. For Fe and Co-Aluminene cases, an electron-rich region around the TM atoms is observed with a reduced electron localization around the C atom. These results corroborate with the Bader charge analysis (Table 7.2).

Electronic Density of States: We now discuss the effect of CO adsorption on the DOS of Aluminene and TM-Aluminene. Figure 7.4(b and c) depicts the DOS plots of these systems. It is clear from the figure that all the systems exhibit metallic nature with a finite DOS at E_F . Figure 7.4(b and c) show the total DOS and partial DOS (PDOS) for Aluminene and TM-Aluminene with CO molecule adsorbed on the surfaces. We note a slight change



Figure 7.4: (a) Difference charge density (DCD) for CO adsorbed Aluminene and TM-Aluminene (TM=Ti, Cr, Fe and Co). Red and green colored regions show electron rich and electron deficit regions, respectively, for all the cases of gas adsorption. (b) and (c) represent total density of states (DOS) and partial density of states (PDOS) of CO gas adsorbed systems. The Fermi level has been set to zero and indicated by a vertical black dashed line. The brown-shaded area in (b) corresponds to the DOS of CO adsorbed systems with red colored boundary.

in the electronic structure following the adsorption of CO gas molecule, specifically in the valence band region. Moreover, from Figure 7.4(c), it is evident that the majority of C-p and O-p orbitals lie in the unoccupied region, and hence have negligible interaction with

Al-s and p orbitals in the energy interval of -6 eV to 2 eV. On contrary to slight changes in DOS for pristine Aluminene, CO adsorption on TM-Aluminene leads to appreciable changes in the electronic DOS. A clear signature of hybridization of C-p and O-p orbitals with TM-d orbitals is observed. This indicates the existence of a strong interaction of the adsorbate with the TM-substituted surfaces. Finally, the above-discussed results (along with the values of E_{ads}) show weaker interaction of CO adsorbate with the Aluminene surface as opposed to the TM-Aluminene cases.



Figure 7.5: Partial density of states (PDOS) of TM (=Ti, Cr, Fe and Co) atoms $(d_{z^2}$ or d_{σ} and d_{π} or $d_{xz,yz}$) and molecular orbitals (5σ and 2π) for the comparison of CO gas molecule before and after adsorption. PDOS for each TM atom has sub-figures (from upper to lower panel) corresponding to CO 5σ (2π) orbitals in isolated and in adsorbed cases and TM- d_{σ} (d_{π}) states with and without gas adsorption. Note that the DOS corresponding to the CO-adsorbed case is the sum of the C and O contributions.

Now to understand the general trend of reactivity of the CO gas molecule towards the TM atom, we analyze how the orbitals of CO molecule interact with the TM-d orbitals. Due to this interaction, each orbital of the CO molecule splits into the bonding and antibonding states. The occupancy of the states governs the bond strength. The more unoccupied the antibonding orbitals are, the stronger the bond is and vice-versa. Therefore, the reactivity

of the CO molecule depends on the position of the d-bands of the TM atoms relative to E_F since this factor decides the position and the degree of filling of both the bonding and antibonding states [303]. Hence, we compare the PDOS of the CO molecule before and after the adsorption on the 2D surfaces (Figure 7.5). To visualize the hybridization between the TM-d states and CO σ and π states, we assume the z-axis to be normal to the TM surface and CO molecule is adsorbed perpendicular to the surface, thus the σ and π states result as the consequence of mixing of C and O orbitals, which are defined as

$$\sigma = C_s + C_{pz} + O_{pz}$$
 and $\pi = C_{px} + C_{py} + O_{px} + O_{py}$

The d_{z^2} or the d_{σ} of the TM atoms are pointed towards the 5 σ orbitals of the CO molecule. Because of the interaction of TM d_{σ} and CO 5 σ , the d_{σ} states are depleted and shifts above E_F . Further, the 5 σ peak of the CO molecule is significantly suppressed in comparison to that of the free CO molecule as there is charge transfer from 5 σ to the d_{σ} states (Figure 7.5). Along with the changes in the electronic structures of TM d_{σ} and CO 5 σ orbitals, significant modifications in the densities of TM d_{π} or $d_{xz,yz}$ and CO 2 π orbitals have been observed. From the figure, it is clear that TM d_{π} orbital is depleted of the electron density as the PDOS shifts away from E_F towards higher energy. Moreover, the 2 π orbital of CO gains electron and exhibits the density buildup below E_F . Thus, DOS results explain the back-donation mechanism of charge from the TM atom to the CO molecule. This results in slight elongation of the C-O bond following adsorption (1.14 Å for free CO molecule and 1.17-1.18 Å for the adsorbed CO molecule).

Next, we discuss the effect of bonding of the CO molecule to the surface when the atomic number of the TM atom increases. It is well-known that the surfaces of TM atoms having less than half-filled d levels show a higher tendency of chemisorption of CO molecule when compared to the more than half-filled cases [304, 305]. This is because in the former cases, the d orbitals are comparatively more diffused. Consequently, more charge transfer from the d-states to the CO 2π orbitals may occur. This results in greater chemisorption of CO gas molecule on the early TM atom surfaces. This argument supports the minimum value of E_{ads} observed for Co-Aluminene among all the TM-Aluminene cases probed for CO gas adsorption in this thesis.



Figure 7.6: Variation of E_{ads} and d-band centre (dbc with respect to Fermi level (0 eV)) as a function of TM atoms for the CO adsorbed systems.

To reaffirm the finding, we plot the d-band centre (dbc) relative to E_F as well as the E_{ads} for each TM studied here (Figure 7.6). We find that the smaller the magnitude of dbc (Cr having the smallest dbc), the more is the adsorption of CO. Along with the dbc, the spread of the d-band also plays a vital role in governing the adsorption of the molecule. The adsorption of CO molecule is mainly governed by the back-donation charge transfer to the CO 2π orbital and their interaction with the TM d_{π} orbitals. Figure 7.5 reveals that the d_{π} orbitals of Cr-Aluminene has the greatest d-band width and for the Co case, the width is the least. This enables the mixing and strong hybridization with CO 2π orbitals over a long-range for the Cr, Fe, and Ti-Aluminene cases in comparison to the Co-Aluminene case.

7.2.1.3 Adsorption of NO gas molecule

Here we present the results of adsorption of NO gas on Aluminene and TM functionalized Aluminene. From the E_{ads} values presented in Table 7.3, we observe that, compared to the adsorption of CO, adsorption of NO gas molecule seems to be more probable. The reduced molecule-sheet distances (presented in the table) give a clear indication of higher possibility of adsorption of NO molecule compared to CO. Overall, because of the smaller distances (D) and larger interaction of NO and the 2D sheet, it is found that more charge transfer takes place in the NO adsorbed systems as compared to the CO adsorbed systems (see Tables 7.2 and 7.3). A similar observation of preference of adsorption of NO over CO gas molecule has been reported in the literature for other 2D monolayers as well [162–164, 180]. This observation can be attributed to the stronger electron affinity of NO gas molecule which is due to the fact that both N and O atoms have very high electronegativity.

Table 7.3: E_{ads} is the adsorption energy, Δq is the Bader charge on NO gas molecule. N-O is the distance between N and O atoms in the NO molecule after adsorption. D is the molecule-sheet distance after optimization.

System	E_{ads}	Δq	N-O	D
	(eV)	(e)	(Å)	(Å)
Al-N-O (\mathbf{A})	-1.051	-0.68	1.21	1.83
Al-O-N (\mathbf{B})	-2.399	-1.79	1.47	1.79
N-Al-O (\mathbf{C})	-1.597	-1.66	1.29	2.02
Ti-N-O (\mathbf{A})	-2.826	-0.57	1.20	1.86
Ti-O-N (\mathbf{B})	-1.389	-0.43	1.22	1.93
N-Ti-O (\mathbf{C})	- 3.182	-1.87	1.43	2.11
$Cr-N-O(\mathbf{A})$	-3.143	-0.54	1.20	1.70
$Cr-O-N(\mathbf{B})$	-1.112	-0.43	1.19	1.79
N-Cr-O (\mathbf{C})	-2.632	-1.78	1.40	1.90
Fe-N-O (\mathbf{A})	-2.480	-0.38	1.19	1.65
Fe-O-N (\mathbf{B})	-0.518	-0.40	1.19	1.79
N-Fe-O (\mathbf{C})	-2.510	-0.43	1.19	1.65
Co-N-O (\mathbf{A})	-1.640	-0.36	1.18	1.66
Co-O-N (\mathbf{B})	-1.566	-1.29	1.27	2.88
N-Co-O (\mathbf{C})	- 1.554	-1.30	1.27	2.06

Now we compare the results of different cases of pristine and TM-substituted Aluminene. From Table 7.3, we note that the preferred configuration of NO adsorption on Aluminene is the configuration with **B** as the starting geometry. After geometry optimization, the starting geometry of **B**-configuration has got somewhat distorted. As a result, the N atom has come closer to the Aluminene sheet and the molecule has a tilted orientation (Figure 7.7(a)). The E_{ads} value has been found to be -2.399 eV. The N-O bond length shows large stretching to 1.47 Å (from the value of 1.16 Å in its gaseous phase). An appreciable amount of charge transfer (1.79 e) has taken place between the gas molecule and the 2D surface. All these observations put together indicate a stronger bonding and hence chemisorption of NO on Aluminene surface. Next, we focus our attention on the adsorption of NO gas on TM-functionalized Aluminene. The electronic configuration of NO is such that the atom N has one unpaired electron, and thus can show the tendency to accept electrons from the TM-d orbitals. As a result, the bonding of NO molecule with the TM could occur through the attachment of N atom to the TM atom. From Table 7.3, it is observed that except for Ti-Aluminene, which favors a tilted orientation of NO molecule (Figure 7.7(a)), all other TMsubstituted Aluminene systems prefer **A** as the lowest energy configuration. Typically large values of E_{ads} are observed for adsorption of NO molecule on Aluminene and TM-substituted Aluminene (Table 7.3). Hence, overall, the results indicate a tendency of chemisorption of NO on all the Aluminene surfaces, although it is more for the early 3d TM cases (Ti and Cr) than the Fe and Co-based systems. A similar decreasing trend for the binding energy and bond length of NO molecule has been observed in the literature in the case of interaction of NO molecule with 3d metal dimers (Sc-Zn) [306].

DCD for all the systems have been calculated (Figure 7.7(a)). It is evident that the region between N and O atoms is a more charge deficit region for the Aluminene and Ti-Aluminene case. This clearly shows that the strength of covalent bonding between the atoms in the NO molecule in its isolated phase has reduced upon adsorption on the Aluminene and Ti-Aluminene surfaces. This observation corroborates with the enhanced bond lengths (Table 7.3), indicating the activation of NO molecule to a great extent when adsorbed on these two 2D-sheets. On the other hand, the scenario is different for Cr, Fe, and Co-Aluminene cases. We note that a lesser amount of charge transfer between the NO molecule and the surfaces occurs for these cases. This is clearly seen from the N-O bond distance of NO molecule, which upon adsorption changes to a maximum of 1.20 Å (from 1.16 Å), with the least N-O distance of 1.18 Å for Co-Aluminene. Thus, it is evident that NO is comparatively weakly activated on the Co-Aluminene sheet compared to the other 2D surfaces.



Figure 7.7: (a) Difference charge density (DCD) for NO adsorbed Aluminene and TM-Aluminene (TM=Ti, Cr, Fe and Co). Red and green colored regions show electron rich and electron deficit regions, respectively, for all the cases of gas adsorption. (b) and (c) represent total density of states (DOS) and partial density of states (PDOS) of NO gas adsorbed systems. The Fermi level has been set to zero and indicated by a vertical black dashed line. The brown-shaded area in (b) corresponds to the DOS of NO adsorbed systems with red colored boundary.

Electronic Density of States: Figure 7.7 (b and c) shows the DOS for the cases of NO adsorption on Aluminene and the TM-functionalized aluminene in their most preferred

configurations. Unlike the case for CO adsorption on Aluminene, the DOS for NO adsorbed Aluminene is significantly different from that of Aluminene. This supports the stronger interaction between the NO molecule and the Aluminene sheet. A strong hybridization between the TM-d, N-p and O-p orbitals has also been observed for the TM-substituted Aluminene cases. Similar to the CO cases, the reactivity trend of adsorption of NO molecule can be explained by evaluating the positions of bonding and the antibonding orbitals formed by the interaction of NO 2π with TM d_{π} orbitals (partially occupied) which plays a major role in the adsorption mechanism [228]^{**}. When we consider the 3d TM atoms from lower to higher Z value, the d-bands shift towards more negative binding energy (below E_F), and hence the possibility of back donation decreases. As a result, the N-O bond strength increases, and bond distance decreases when we go from left to right in the 3d TM series. This is evident from the N-O bond distance, which clearly shows a decreasing trend (largest for Ti-Aluminene and smallest for Co-Aluminene) in the respective lowest energy configurations (Table 7.3). To reaffirm the reactivity of NO on TM-substituted Aluminene, dbc has been calculated for Cr, Fe, and Co-Aluminene cases (since these three prefer similar adsorption configuration). The values of dbc (with respect to E_F) are -0.08, -1.15, and -1.68 eV for Cr, Fe, and Co-Aluminene, respectively. Thus, dbc lies very close to (far away from) E_F for Cr (Co) and therefore Cr (Co) has the highest (lowest) E_{ads} among the three TM-substituted cases. It is worth mentioning here that the filling of unoccupied antibonding molecular orbital (due to charge transfer from the surface) leads to the weakening of the N-O bond and lowering of spin moment of NO molecule. If there is sufficient charge transfer such that the unoccupied orbitals of NO molecule get completely filled, spin-polarization present in isolated NO molecule disappears. Thus, in the present study, chemisorption of NO with the surface causes it to loose its spin magnetization. Similar disappearance of magnetism of NO has been reported when it is chemisorbed on Pt(111) surface [307].

^{**}This published work isby the author of this thesis and others inthe 2020 inApplied Surface Science belonging Elsevier Publishing to group. vear https://www.sciencedirect.com/science/article/abs/pii/S0169433220321218

7.2.2 Potential for Gas Sensors

In this subsection, to probe the possibility of Aluminene and TM-substituted Aluminene as useful gas sensors, we correlate the calculated adsorption properties, like E_{ads} , charge transfer leading to any change in the electronic DOS and subsequently in the electrical conductivity with the factors like sensitivity, stability, selectivity, and recovery time, which serve as important characteristics for an efficient gas sensor [308].

If the gas molecule adsorbs chemically on the 2D sheets having substantial E_{ads} (leading to chemisorption), the sheet may turn out to be an efficient gas sensor for the detection/sensing of gas molecules. From Tables 7.1, 7.2 and 7.3, we note that most of the systems exhibit significant values of E_{ads} , which span a long-range (from -0.062 to -0.666 eV for H₂, from -0.548 to -2.205 eV for CO, and from -1.640 to -3.182 eV for NO gas adsorption). Thus, the appreciable values of E_{ads} indicate that the gas molecules are mostly chemisorbed on Aluminene and TM-functionalized Aluminene, except for a few cases, specifically, the H₂ gas adsorption on Aluminene with E_{ads} of -0.062 eV, which favors physisorption. These results reveal the sensitivity of the respective surfaces towards the absorbed gases.

Along with the adsorption parameters like the E_{ads} , charge transfer, and the changes in the DOS upon gas adsorption, the sensitivity of a gas sensor can be further probed by evaluating the change in the electrical conductivities (σ) of the systems before and after the gas adsorption because of remarkable modulation in the electronic properties due to adsorption of gases. The electrical conductivity has been calculated using the semi-classical Boltzmann transport theory (BoltzTraP software [206]) under the relaxation time (τ) approximation. The percentage change in the conductivity ($\sigma' = \sigma/\tau$) (Table 7.4) has been defined as [289]

$$\Delta \sigma' = \left[\left(\sigma'_q - \sigma'_{wq} \right) / \sigma'_{wq} \right] \times 100 \tag{7.1}$$

where σ'_g and σ'_{wg} are the values with and without gas molecules on the surfaces, respectively. We wish to mention here that our further discussion will include only the systems where no significant distortion in the geometry after gas adsorption has been observed. Therefore, our following discussion excludes the cases of adsorption of NO on Aluminene and Ti-Aluminene surfaces.

The variation in the electrical conductivity reveals high sensitivity and the possibility of detection of H_2 on the TM-substituted systems. It is clear from the table that an appreciably large change in conductivity has been observed for the CO adsorbed Aluminene (23.6%) compared to the case of adsorption of H_2 gas molecule (11.5%). Thus, the detection of CO gas molecule on the Aluminene surface seems to be feasible. On the other hand, H_2 gas adsorption on the TM-substituted systems with TM = Cr, Fe, and Co leads to large changes in conductivity (16.3 - 87.9%), but not for the Ti-Aluminene case. Thus, overall, the analysis suggests that H_2 molecule adsorption on all the probed surfaces exhibit a maximum change in conductivity upon adsorption with respect to the corresponding surfaces before adsorption and hence can possibly be sensed and detected. Further, Cr and Fe-substituted Aluminene, which are magnetic in nature, upon adsorption of the probed gases turn into non-magnetic surfaces. Thus, the change in magnetic properties of these 2D functionalized sheets also can indicate their sensitivity towards the probed gases.

Table 7.4: Percentage change (%) in the quantity σ' for the H₂, CO and NO gas adsorbed systems in the lowest energy configurations calculated using Eq. 7.1.

System	H_2	CO	NO
Aluminene	11.5~%	23.6%	-
Ti-Aluminene	1.2%	3.1%	-
Cr-Aluminene	87.9%	87.4%	22.8%
Fe-Aluminene	13.8%	0.78%	15.0%
Co-Aluminene	16.3%	4.37%	17.7%

Besides sensitivity, another important characteristic of an effective gas sensor is the stability of the surface. If there is no significantly large structural distortion upon gas adsorption, the sheet is expected to exhibit stability. From Figure 7.7(a), we observe that except for the cases of NO adsorption on Aluminene and Ti-Aluminene, no other cases show significant structural deformation after the adsorption of the gas molecules. Hence, except these two cases, stated above, all the other probed substrates can be considered to be stable towards adsorption of the gases under consideration.

As far as the selectivity of any gas molecule on a sheet is concerned, the gas molecules for which greater E_{ads} is observed, are preferred over the other gas molecules. As is evident from our results, NO gas molecules exhibit the highest adsorption on the probed surfaces, followed by the adsorption of CO and then H₂ molecule (Tables 7.1, 7.2 and 7.3). The selectivity of NO over CO and H₂ is also evident from a large amount of charge transfer between the NO gas molecule and the surface as well as significant change in the electronic DOS after adsorption of NO gas as compared to the other two gas molecules. However, for a significant E_{ads} , the desorption becomes difficult and a device may require a long recovery time, which we have calculated for the systems. From the transition state theory, the recovery time (R_t) is defined as

$$R_t = \nu_0^{-1} \exp\left(-E_{ads}/k_B T\right)$$
(7.2)

where ν_0 is the attempt frequency, E_{ads} represents the adsorption energy, k_B and T are Boltzmann's constant and temperature, respectively. For the calculation of R_t at room temperature (300 K), we consider that all the gas molecules possess the same attempt frequency (of the order of 10^{12} s⁻¹) [181].

The expression 7.2 shows that greater E_{ads} (more negative) leads to longer R_t , in turn, resulting in a long desorption process of gases from the 2D surface. As mentioned above, it is preferred to have a smaller value of R_t for an efficient reversible gas sensor. On the other hand, stronger adsorption with larger E_{ads} leads to higher value of R_t which in turn makes the surface useful for disposable gas sensors. From our studies, it is observed that only a few systems, namely, Al-H-H, H-Co-H, H-Fe-H, H-Cr-H, H-Ti-H (Table 7.1) possess smaller R_t values of 11.0×10^{-12} , 2.8×10^{-9} , 1.1×10^{-3} , 0.1, 0.2 and 1.6×10^{-3} seconds, respectively. On the other hand, because of large E_{ads} for CO and NO adsorption on Aluminene and TM- substituted Aluminene (except for CO adsorbed Aluminene case), these systems possess values of R_t ranging from several minutes to hours. Thus, the estimation of R_t precludes any possibility of the probed 2D sheets as a reusable gas sensor for CO (except for the Aluminene case) and NO gas molecules. As a consequence, serving as a disposable gas sensor (for CO and NO) may be a possibility for the studied surfaces.

7.2.3 Gas adsorption on MoS and WS

Besides extensive research on gas adsorption on 2D monoelemental systems, the binary monolayers are also studied as prospective candidates for gas sensing applications [309, 310]. 2D planar GaN sheet has been probed for the adsorption of various gas molecules. It is found that this surface is highly sensitive and selective towards NH_3 gas molecules with small value of R_t . Moreover, it is also predicted as efficient magnetic gas sensor for the NO molecule [309]. Additionally, 2D monolayers, for instance, GaS and InN show selectivity towards gas molecules like SO_2 , NO_2 , etc. AsP and ZnS 2D surfaces hold promises as H_2S and NH_3 gas sensors, respectively [310]. This motivates us to probe the suitability of the 2D binary surfaces of pristine MoS and WS monolayers as a substrate for gas sensing. Thus, this section investigates and briefly discusses the adsorption of H_2 , CO, and NO gas molecules on these monosulfides. We probe various configurations for the gas adsorption, similar to gas adsorption on Aluminene.

7.2.3.1 Adsorption of H_2 gas molecule

As mentioned above, the configurations probed for H_2 molecule adsorption are **A** and **C** (Figure 7.8). However, we observe that, similar to TM-Aluminene case, the configuration **A** converges to **C** for both the surfaces following the geometry optimization. From Table 7.5, we note that the values of E_{ads} for both MoS and WS surfaces are negative, which signifies that adsorption is an exothermic process and is energetically favorable (stable).

As is evident from Table 7.5, among MoS and WS surfaces, the latter surface (with



Figure 7.8: Top and side views of the optimized geometry for the H_2 adsorbed MoS/WS system.

 E_{ads} of -0.92 eV) exhibits a slightly greater tendency towards the adsorption of H₂ molecule as compared to the former one (with E_{ads} of -0.87 eV). For both the surfaces, the H-H bond distance (of around 0.89 Å) shows an enhancement from 0.75 Å, which is observed in its gaseous state. The smaller distance between the sheets and the H₂ molecule and the appreciable value of E_{ads} indicate a strong adsorption of the molecule on the surfaces.

Table 7.5: E_{ads} is the adsorption energy. Δq is the Bader charge on H₂ gas molecule. d_{H-H} is the distance between the two H atoms in the H₂ molecule after adsorption. Δh is the vertical distance between the sheet and the molecule.

	MoS				W	7 S		
System	E_{ads}	Δq	d_{H-H}	Δh	E_{ads}	Δq	d_{H-H}	Δh
	[eV]	[e]	[Å]	[Å]	[eV]	[e]	[Å]	[Å]
H-Sheet-H (A/C)	-0.87	-0.15	0.88	1.82	-0.92	-0.13	0.89	1.81

Similar to the case of TM-substituted Aluminene, we note that the H-H distances (after adsorption on MoS and WS) lie in the range of about 0.8 to 0.9 Å, which is the range in which true Kubas complexes form [299]. Also, the charge transferred to H₂ molecules supports the back donation of electrons from TM atoms (Mo and W), consequently, indicates stabilization of the process of hydrogenation in these systems.

Unlike the strong adsorption of H_2 on the MoS and WS surfaces, it is shown in the literature that this gas molecule is physisorbed on 2D MoS₂, and WS₂ surfaces [311, 312]. The H_2 gas molecule prefers the perpendicular orientation (and is located on top of Mo site) for the adsorption on MoS_2 with the adsorption energy of -82 meV [311]. Ganji *et al.* have also reported about a weak interaction of H_2 gas molecule with 2D MoS₂ and WS₂ surfaces, having adsorption energies of -131.61 meV and -169.44 meV, respectively [312]. The larger values observed here are due to the ease of formation of Kubas complexes due to the proximity of H_2 molecule with the TM atoms (Mo/W). Interestingly, like the greater sensitivity of WS₂ as compared to MoS₂ surface towards the H₂ adsorption, the 2D WS surface probed in this thesis is also expected to exhibit larger sensitivity towards H₂ gas than the MoS surface.



Figure 7.9: (a) 3D and 2D (slice) plots for difference charge density (DCD). Red and green (blue for 2D slice) region show the charge accumulated and depleted regions, respectively. (b) Total density of states (DOS) for the H_2 adsorbed MoS/WS system for the lowest energy configuration.

We perform the DCD analysis to shed light on the bonding nature of the gas molecules upon adsorption (Figure 7.9(a)). Overall, it is observed that the charges are accumulated around the H₂ molecule (which corroborates with the Bader analysis), which is a clear evidence of the fact that the gas molecule has gained electrons (see Table 7.5). Interestingly, we see a charge deficit region between the two H atoms as a result of enhancement of H-H bond distance upon adsorption. On the other hand, huge charges are localized in the bonding region between the H and TM atoms. Also, the neighboring TM atoms (Mo and W) have lost electrons. As a whole, these observations affirm that the adsorption of H_2 is stabilized via Kubas complex formation in these systems.

Electronic Density of States: To further explore the influence of gas adsorption on the electronic properties of the MoS/WS monolayer, we analyze the DOS for the H₂ adsorbed monolayers along with that of the pristine MoS/WS system (Figure 7.9(b)). A zero bandgap (semimetallic) nature is observed for pristine WS monolayer. We note that upon adsorption of H₂ molecule on both the binary surfaces, the states in the total DOS are slightly shifted towards higher energy, which is an indication that the surfaces have lost electrons to the H₂ molecule. It is interesting to note here that the semimetallic nature of pristine WS shows a transition to a semiconducting character upon the adsorption of H₂, with a tiny gap of around 0.03 eV at the GGA-PBE level of calculation, which may lead to a change in the electrical conductivity. Hence, the modifications in the electronic structure upon adsorption of H₂ indicate the sensitivity of these surfaces towards this gas molecule.

7.2.3.2 Adsorption of CO and NO gas molecule

For the adsorption of CO and NO gas molecules on MoS/WS sheet, three above-mentioned configurations, namely, **A**, **B** and **C**, have been probed (Figure 7.10). Tables 7.6 and 7.7 list the E_{ads} , the sheet to molecule vertical distance (Δ h), and the C-O/N-O) bond distances (d) after adsorption, for all the probed configurations. We first present and discuss the results of adsorption of CO gas molecules on the two surfaces, which is followed by the discussion on the NO gas adsorption.

We observe that the parallel orientation of CO molecule (with respect to the surface) in the configuration \mathbf{C} , after optimization, is changed to a tilted orientation, and it is the preferred configuration for the adsorption (see Table 7.6 and Figure 7.10). This configuration has a highest value of E_{ads} and a small value of Δh of 1.56 Å. We observe that, after the



Figure 7.10: Top (and side) views of the optimized geometry for the CO/NO adsorbed MoS/WS system for all the three probed configurations.

adsorption, the CO molecule is slightly activated, which is evident from the enhanced C-O bond distance (from 1.14 Å to 1.23 Å). This agrees well with the studies in literature where the tilted configuration leads to the elongation of C-O bonds [313–315]. A huge amount of charge transfer also supports the strong chemisorption of CO molecule on the MoS/WS surfaces.

The results of our calculations show that MoS and WS surfaces exhibit comparable sensitivity towards the CO gas molecule, as shown in Table 7.6. Similar to the CO adsorption case, NO molecule prefers the tilted orientation (with N being closer to the sheet) for its adsorption on MoS/WS surfaces (Figure 7.10). The MoS and the WS monolayers prefer the NO adsorption over the CO gas molecule with a huge difference in E_{ads} . The reduced molecule-sheet distances (Δ h) and the greater amount of charge transfer for the NO adsorbed case also support this (see Table 7.7). Similar preference of adsorption of NO over the CO gas molecule has been reported for other 2D monolayers in the literature [162, 164, 180, 291]

Table 7.6: E_{ads} is the adsorption energy. Δq is the Bader charge on CO gas molecule. d_{C-O} is the distance between C and O atoms in the CO molecule after adsorption. Δh is the vertical distance between the sheet and the molecule (atom of the molecule facing the sheet).

	MoS			WS				
System	E_{ads}	Δq	d_{C-O}	Δh	E_{ads}	Δq	d_{C-O}	Δh
	[eV]	[e]	[Å]	[Å]	[eV]	[e]	[Å]	[Å]
Sheet-C-O (A)	-2.33	-0.42	1.17	2.02	-2.43	-0.40	1.17	2.03
Sheet-O-C (\mathbf{B})	-0.35	-0.15	1.16	2.28	-0.32	-0.14	1.16	2.27
C-Sheet-O (C)	-2.49	-0.82	1.22	1.56	-2.45	-0.87	1.23	1.56

Table 7.7: E_{ads} is the adsorption energy. Δq is the Bader charge on NO gas molecule. d_{N-O} is the distance between N and O atoms in the NO molecule after adsorption. Δh is the vertical distance between the sheet and the molecule (atom of the molecule facing the sheet).

	MoS				WS				
System	E_{ads}	Δq	d_{N-O}	Δh	E_{ads}	Δq	d_{N-O}	Δh	
	[eV]	[e]	[Å]	[Å]	[eV]	[e]	[Å]	[Å]	
Sheet-N-O (A)	-3.04	-0.58	1.19	1.88	-2.80	-0.49	1.19	1.89	
Sheet-O-N (B)	-1.11	-0.40	1.20	2.02	-0.97	-0.34	1.19	2.02	
N-Sheet-O (C)	-4.02	-1.21	1.38	1.22	-4.08	-1.33	1.42	1.25	

and has been observed for TM-substituted Aluminene sheets studied in this thesis.

We note here that, Shokri *et al.* also observed an inclined orientation of CO and NO molecules when adsorbed on MoS_2 monolayer. Further, an appreciable strength of adsorption is observed on this surface with adsorption energies of -0.45 eV for CO and -0.56 eV for NO adsorption [316]. Slightly smaller adsorption energies of -0.13 eV and -0.21 eV have been observed, when CO and NO gas molecules, respectively, are adsorbed on WS₂ monolayer [317]. Our results suggest that similar to the case of H₂ adsorption, the monochalcogenides (MoS and WS) exhibit a greater tendency towards the adsorption of CO and NO gas molecule as compared to their dichalcogenide analogues.

Further, there has been an extensive study of adsorption of CO molecule on the transition

metal surfaces, especially on Mo and W surfaces [313–315]. CO molecules are found to be tilted with respect to the Mo(112) surface with E_{ads} of 2.10 eV (in magnitude) at low coverage. However, with the increased coverage, a vertical orientation with the carbon atom facing the surface is seen to be the most stable configuration because of lateral interactions. The tilting of the CO molecule results in the C-O bond being slightly elongated to 1.20 Å [313]. A similar observation has been reported for CO adsorption on Mo (110) surface [314]. Likewise, the most stable configuration for low CO coverage on W(100) is the one where the CO molecules have been tilted with respect to the surface by an angle of 58°. In this configuration, the corresponding value of E_{ads} is -3.01 eV [315]. Moreover, the C-O bond is stretched to 1.41 Å, leading to the activation of the molecule. However, at higher coverages of above 0.5 monolayer, the CO molecules also begin to reside on the on-top sites and all the CO molecules are positioned on the top-site of the surface and have the adsorption energy of -1.63 eV for the full coverage.

The above studies on CO adsorption on Mo or W surfaces suggest that for low concentration of CO molecule, the tilted orientation is preferred for adsorption with appreciably large adsorption energies and elongated C-O bond distances. Interestingly, we also observe similar results for our case (preference of tilted configuration for adsorption of a single CO gas molecule). Thus, we conjecture that upon an increase of coverage of CO molecules on the probed MoS and WS monochalcogenide surfaces, the tilted orientation of CO molecule may converge to the configuration \mathbf{A} occupying the on-top sites of TM atoms.

The DCD analysis reveals that electron accumulation is around the CO/NO molecule with the depletion around the MoS/WS surface (Figures 7.11(a) and 7.12(a)). Thus, the polarization of both the monolayers and the gas molecules occur because of the charge redistribution in real space. DCD analysis corroborates well with the Bader charge analysis, which reveals the nature of CO/NO molecules to be charge acceptors (Tables 7.6 and 7.7). We wish to mention here that, from the analysis of DCD, we observe a maximum charge redistribution and, consequently, polarization for the NO adsorbed cases, followed by the



Figure 7.11: (a) Difference charge density (DCD). Red and green region show the charge accumulated and depleted regions, respectively. (b) Total density of states (DOS) for the CO adsorbed MoS/WS system for the lowest energy configuration. (c) represents the partial DOS corresponding to the CO molecule in the isolated (blue dashed line) and adsorbed (red colored) phase. Note that the DOS corresponding to the CO-adsorbed case is the sum of the C and O contributions.

CO gas molecule adsorption. Minimum polarization is seen for the H_2 adsorbed cases. This is supported by the largest and least values of E_{ads} for NO and H_2 adsorption, respectively.

Electronic Density of States: To further explore the influence of gas adsorption on the MoS/WS monolayer, we analyze the electronic DOS for the CO adsorbed surfaces along with that of the pristine MoS/WS system (Figure 7.11(b)). It is interesting to note here that the semimetallic nature of pristine WS shows a transition to a semiconducting character upon CO adsorption, with a very small gap of around 0.05 eV at the GGA-PBE level of calculation. An observable change in the electronic DOS has been observed upon CO adsorption, which indicates that the surfaces are sensitive towards the adsorbed gas molecule. The significant contribution in the DOS comes from the TM-d and S-p orbitals of MoS/WS with a small contribution from C and O atoms around the E_F . Moreover, Figure 7.11(c) shows the PDOS for the CO molecule before and after the adsorption on the surface. The shift of the orbitals towards more negative energy reveals the electron-accepting nature of the CO



Figure 7.12: (a) Difference charge density (DCD). Red and green region show the charge accumulated and depleted regions, respectively. (b) Total density of states (DOS) for the NO adsorbed MoS/WS system for the lowest energy configuration. (c) represents the partial DOS corresponding to the NO molecule in the isolated (blue dashed line) and adsorbed (red colored) phase. Note that the DOS corresponding to the NO-adsorbed case is the sum of the N and O contributions.

molecule, which is consistent with the DCD and the Bader analysis. The electronic DOS of NO adsorbed WS monolayer is shown in Figure 7.12(b). We observe a significant change in the electronic DOS after the adsorption of the NO molecule. It is to note here that although NO molecule (in its isolated phase) carries a magnetic moment of 1 μ_B , after adsorption, no magnetism is observed in the composite system. From Figure 7.12(c), we observe that LUMO of NO (located at E_F) has shifted below E_F as the charge has been transferred from the MoS/WS monolayers to the NO molecule. This explanation is validated from the DCD (Figure 7.12(a) where charge accumulated region is around the NO molecule) and Bader charge analyses.

To shed light on the charge transfer mechanism occurring between the gas molecules and the probed surfaces, we examined the position of the HOMO and LUMO of the gas molecule, along with the E_F of the substrate (in our case, MoS and WS) (Figure 7.13). To explain the mechanism, we consider the case for CO adsorption on the WS surface as an example. It is seen that the molecular LUMO for the CO molecule (at -2.162 eV) is lower than the E_F of WS monolayer (-2.157 eV), thus rendering the electrons to drift from WS to CO molecule, which again is consistent with the Bader charge analysis. A similar explanation holds for the rest of the gas adsorbed surfaces.

Thus, from the combined results of E_{ads} , Bader charges and electronic DOS, we predict the presence of strong interaction of H₂, CO and NO gas molecules with the MoS and WS surfaces. Hence, these surfaces may serve as efficient substrates for sensing of these gases.



Figure 7.13: Molecular LUMO and HOMO levels and Fermi-level (E_F) of the pristine MoS and WS monolayers. The arrow represents the direction of transfer of charge from the sheet to the LUMO of the molecule.

As discussed above, factors like sensitivity, stability, selectivity, and recovery time serve as important characteristics for an efficient gas sensor. Since 2D MoS and WS surfaces exhibit large values of E_{ads} , significant charge transfer and appreciable changes in the electronic structure, they prove to be sensitive to the absorbed gases. Moreover, structural stability is found to be retained upon the adsorption of gases. As far as the selectivity of a gas molecule is concerned, both the 2D monochalcogenides prefer NO over the other two gas molecules. However, the large value of E_{ads} results in longer recovery time. Thus, these two surfaces may not be suitable for gas storage but might be viewed as disposable gas sensors, for the studied gas molecules.

7.2.4 Comparison of gas adsorption on different 2D surfaces

Table 7.8 presents the values of E_{ads} for H₂, CO and NO gas adsorption on different 2D nanostructures from the literature as well as for systems discussed in this chapter. From the table, it is evident that for all the three gas molecules (H₂, CO, and NO), graphene exhibits the least binding of gas molecules because of its chemical stability. Further, the value of E_{ads} for silicene (semimetal), arsenene, and phosphorene (semiconductors) indicate appreciable adsorption of the molecules on these 2D surfaces. However, among all the listed monoelemental 2D surfaces, borophene and Aluminene (both metallic in nature) have a much greater sensitivity towards the CO and NO gas molecules than other mentioned 2D surfaces. A comparison of the relevant results of 2D monoelemental, TM dichalcogenides and the probed TM monochalcogenides from the table suggest that the 2D surfaces probed in this thesis may fare better in terms of adsorption and sensing of H₂, CO, and NO gas molecules.

Table 7.8:	Comparison	n of the listed	l adsorption	energy v	values (E_{ads})	in eV) for 1	H_2, CO	and
NO gas ad	sorption on	different 2D	nanostructu	res from	literature,	and studies	carried	out
in this the	sis.							

System	H_2	CO	NO
Graphene [162, 169, 294]	0.067	-0.01, -0.12	-0.03, -0.30
Silicene $[164, 165]$	-0.1	-0.18	-0.35
Arsenene [318, 319]	-0.069	-0.23	-0.15
Phosphorene $[320]$	-0.130	-0.31	-0.32
Borophene [180, 321, 322]	-0.045	-1.38, -0.84	-1.79, -1.11
Aluminene	-0.062	-0.548	-2.399
MoS_2 [312, 316]	-0.13	-0.45	-0.56
$WS_2 [312, 317]$	-0.17	-0.13	-0.21
MoS	-0.87	-2.49	-4.02
WS	-0.92	-2.45	-4.08

7.3 Summary

Using van der Waals dispersion corrected density functional theory, the adsorption of three environmentally important gases, namely, H_2 , CO, and NO on pristine Aluminene and TM (Ti, Cr, Fe, and Co) atom substituted Aluminene surface has been studied. Preferred orientation and the energetic stability have been predicted by evaluating the adsorption energy (E_{ads}), Bader charge and the difference charge density analyses. Interestingly, we observe enhanced adsorption of all the gases for the TM-substituted Aluminene when compared to the pristine case. It has been found that the Kubas interaction plays an important role in stabilizing the H_2 adsorption on TM-substituted systems. CO and NO adsorption on TM-Aluminene surfaces have been successfully explained from the Blyholder model of the bonding of molecule to the TM atom through the frontier orbitals of molecules. Moreover, the reactivity trend of TM-Aluminene surfaces for CO/NO adsorption has been discussed based on the position of the TM d-band centre with respect to E_F and the spread of the TM d-bands. From the analyses of recovery time the percentage change in electrical conductivity , it is observed that H_2 adsorbed systems have smaller R_t values, and also exhibit maximum change in electrical conductivity, in general.

Further, a comparative investigation of adsorption of these three gas molecules on binary 2D monochalcogenides, MoS and WS, has also been performed. Similar to the case of TM-substituted Aluminene, H₂ adsorption on MoS and WS surfaces is stabilized via Kubas complex formation. Moreover, we found that both the CO and NO molecules prefer the tilted orientation for their adsorption on the 2D MoS and WS sheets with C and N, respectively, closer to the sheet. We find that these surfaces exhibit appreciable values of E_{ads} and charge transfer, which is larger in comparison to those of pristine and TM-substituted Aluminene. Charge transfer theory has been discussed to study the direction of charge transfer from the sheet to the molecule and the results are found to be consistent with the Bader charge analysis. The density of states results reveal a semimetallic to semiconductor transition in case of adsorption of H₂ and CO gas molecule on the WS monolayer. Moreover, significant changes in the electronic states of MoS and WS have been observed upon gas adsorption, which reveal that the 2D MoS and WS surfaces may serve as prospective systems for the sensing of the studied gas molecules. Further, a comparation of gas adsorption demonstrates that compared to the pristine 2D systems studied in the literature, the 2D surfaces probed in this thesis, namely, pristine (and TM-substituted) Aluminene as well as the monochalcogenides (S being the chalcogen atom) based on Mo/W atoms may prove better for the adsorption and sensing of these gas molecules.

Bibliography

- [1] R. P. Feynman, Engineering and Science, vol. 23, p. 22, 1960.
- [2] R. Saito, G. Dresselhaus, and M. Dresselhaus. Imperial College Press, 1998.
- [3] E. Wolf. Wiley, 2015.
- [4] M. Pagliaro. Wiley, 2010.
- [5] S. Trudel, *Gold Bulletin*, vol. 44, p. 3, 2011.
- [6] V. Georgakilas, J. A. Perman, J. Tucek, and R. Zboril, *Chemical Reviews*, vol. 115, p. 4744, 2015.
- [7] P. Antoniammal and D. Arivuoli, Journal of Nanomaterials, vol. 2012, p. 415797, 2012.
- [8] S. D. Singh, Ph.D. dissertation, Homi Bhabha National Institute, 2012.
- [9] H. Qian, M. Zhu, Z. Wu, and R. Jin, Accounts of Chemical Research, vol. 45, p. 1470, 2012.
- [10] G. Li and R. Jin, Accounts of Chemical Research, vol. 46, p. 1749, 2013.
- [11] T. Movlarooy, Materials Research Express, vol. 5, p. 035032, 2018.
- [12] C. Weisbuch and B. Vinter. Elsevier Science, 2014.
- [13] A. K. Geim and K. S. Novoselov, Nature Materials, vol. 6, p. 183, 2007.
- [14] M. I. Katsnelson, *Materials Today*, vol. 10, p. 20, 2007.
- [15] P. R. Wallace, *Phys. Rev.*, vol. 71, p. 622, 1947.
- [16] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.*, vol. 81, p. 109, 2009.
- [17] E. P. Randviir, D. A. Brownson, and C. E. Banks, Materials Today, vol. 17, p. 426, 2014.
- [18] F. Xia, D. B. Farmer, Y.-m. Lin, and P. Avouris, Nano Letters, vol. 10, p. 715, 2010.
- [19] A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, and N. P. Guisinger, *Science*, vol. 350, p. 1513, 2015.
- [20] C. Kamal, A. Chakrabarti, and M. Ezawa, New Journal of Physics, vol. 17, p. 083014, 2015.
- [21] V. Kochat, A. Samanta, Y. Zhang, S. Bhowmick, P. Manimunda, S. A. S. Asif, A. S. Stender, R. Vajtai, A. K. Singh, C. S. Tiwary, and P. M. Ajayan, *Science Advances*, vol. 4, p. e1701373, 2018.
- [22] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. Le Lay, *Phys. Rev. Lett.*, vol. 108, p. 155501, 2012.
- [23] C.-C. Liu, H. Jiang, and Y. Yao, Phys. Rev. B, vol. 84, p. 195430, 2011.
- [24] C. Kamal, A. Chakrabarti, A. Banerjee, and S. K. Deb, Journal of Physics: Condensed Matter, vol. 25, p. 085508, 2013.
- [25] M. E. Dávila, L. Xian, S. Cahangirov, A. Rubio, and G. L. Lay, New Journal of Physics, vol. 16, p. 095002, 2014.

- [26] A. Acun, L. Zhang, P. Bampoulis, M. Farmanbar, A. van Houselt, A. N. Rudenko, M. Lingenfelder, G. Brocks, B. Poelsema, M. I. Katsnelson, and H. J. W. Zandvliet, *Journal of Physics: Condensed Matter*, vol. 27, p. 443002, 2015.
- [27] F.-f. Zhu, W.-j. Chen, Y. Xu, C.-l. Gao, D.-d. Guan, C.-h. Liu, D. Qian, S.-C. Zhang, and J.-f. Jia, *Nature Materials*, vol. 14, p. 1020, 2015.
- [28] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, *Nature nanotechnology*, vol. 9, p. 372, 2014.
- [29] A. Castellanos-Gomez, L. Vicarelli, E. Prada, J. O. Island, K. L. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. V. Alvarez, H. W. Zandbergen, J. J. Palacios, and H. S. J. van der Zant, 2D Materials, vol. 1, p. 025001, 2014.
- [30] C. Kamal and M. Ezawa, *Phys. Rev. B*, vol. 91, p. 085423, 2015.
- [31] S. Zhang, Z. Yan, Y. Li, Z. Chen, and H. Zeng, Angewandte Chemie (International ed. in English), vol. 54, p. 3112, 2015.
- [32] E. Aktürk, O. U. Aktürk, and S. Ciraci, Phys. Rev. B, vol. 94, p. 014115, 2016.
- [33] Y. Zhang, A. Rubio, and G. L. Lay, Journal of Physics D: Applied Physics, vol. 50, p. 053004, 2017.
- [34] C. Kamal, A. Chakrabarti, and M. Ezawa, *Phys. Rev. B*, vol. 93, p. 125428, 2016.
- [35] L. T. Hoa, H. N. Tien, V. H. Luan, J. S. Chung, and S. H. Hur, Sensors and Actuators B: Chemical, vol. 185, p. 701, 2013.
- [36] P. K. Kannan, D. J. Late, H. Morgan, and C. S. Rout, Nanoscale, vol. 7, p. 13293, 2015.
- [37] K. Khan, A. K. Tareen, M. Aslam, R. Wang, Y. Zhang, A. Mahmood, Z. Ouyang, H. Zhang, and Z. Guo, J. Mater. Chem. C, vol. 8, p. 387, 2020.
- [38] D. Tyagi, H. Wang, W. Huang, L. Hu, Y. Tang, Z. Guo, Z. Ouyang, and H. Zhang, *Nanoscale*, vol. 12, p. 3535, 2020.
- [39] H. L. Zhuang and R. G. Hennig, *Chemistry of Materials*, vol. 25, p. 3232, 2013.
- [40] L. C. Gomes, A. Carvalho, and A. H. Castro Neto, *Phys. Rev. B*, vol. 94, p. 054103, 2016.
- [41] H. Şahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R. T. Senger, and S. Ciraci, *Phys. Rev. B*, vol. 80, p. 155453, 2009.
- [42] J.-H. Lin, H. Zhang, X.-L. Cheng, and Y. Miyamoto, Phys. Rev. B, vol. 96, p. 035438, 2017.
- [43] M. Derivaz, D. Dentel, R. Stephan, M.-C. Hanf, A. Mehdaoui, P. Sonnet, and C. Pirri, Nano Letters, vol. 15, p. 2510, 2015.
- [44] L. Kou, C. Chen, and S. C. Smith, The Journal of Physical Chemistry Letters, vol. 6, p. 2794, 2015.
- [45] M. Pumera and Z. Sofer, Advanced Materials, vol. 29, p. 1605299, 2017.
- [46] F. Reis, G. Li, L. Dudy, M. Bauernfeind, S. Glass, W. Hanke, R. Thomale, J. SchÄfer, and R. Claessen, Science, vol. 357, p. 287, 2017.
- [47] D. Akinwande, N. Petrone, and J. Hone, *Nature communications*, vol. 5, p. 5678, 2014.
- [48] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tomnek, and P. D. Ye, ACS Nano, vol. 8, p. 4033, 2014.
- [49] L. Tao, E. Cinquanta, D. Chiappe, C. Grazianetti, M. Fanciulli, M. Dubey, A. Molle, and D. Akinwande, *Nature Nanotechnology*, vol. 10, p. 227, 2015.
- [50] Z. Ni, Q. Liu, K. Tang, J. Zheng, J. Zhou, R. Qin, Z. Gao, D. Yu, and J. Lu, *Nano letters*, vol. 12, p. 113, 2012.
- [51] N. D. Drummond, V. Zólyomi, and V. I. Fal'ko, Phys. Rev. B, vol. 85, p. 07542, 2012.

- [52] M. Ezawa, New Journal of Physics, vol. 14, p. 033003, 2012.
- [53] L. Zhang, T. Gong, Z. Yu, H. Dai, Z. Yang, G. Chen, J. Li, R. Pan, H. Wang, Z. Guo, H. Zhang, and X. Fu, Advanced Functional Materials, p. 2005471, 2020.
- [54] J. Nevalaita and P. Koskinen, *Phys. Rev. B*, vol. 97, p. 035411, 2018.
- [55] H. Liu, H. Tang, M. Fang, W. Si, Q. Zhang, Z. Huang, L. Gu, W. Pan, J. Yao, C. Nan, and H. Wu, Advanced Materials, vol. 28, p. 8170, 2016.
- [56] T. Ling, J.-J. Wang, H. Zhang, S.-T. Song, Y.-Z. Zhou, J. Zhao, and X.-W. Du, Advanced Materials, vol. 27, p. 5396, 2015.
- [57] Y. Ma, B. Li, and S. Yang, Mater. Chem. Front., vol. 2, p. 456, 2018.
- [58] S. Yan, X. Zhu, J. Dong, Y. Ding, and S. Xiao, Nanophotonics, vol. 9, p. 1877, 2020.
- [59] T. Zhang, P. Cheng, W.-J. Li, Y.-J. Sun, G. Wang, X.-G. Zhu, K. He, L. Wang, X. Ma, X. Chen, Y. Wang, Y. Liu, H.-Q. Lin, J.-F. Jia, and Q.-K. Xue, *Nature Physics*, vol. 6, p. 104, 2010.
- [60] F. Yin, S. Kulju, P. Koskinen, J. Akola, and R. E. Palmer, *Scientific Reports*, vol. 5, p. 10065, 2015.
- [61] B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, and K. Wu, Nature Chemistry, vol. 8, p. 563, 2016.
- [62] R. Wu, I. K. Drozdov, S. Eltinge, P. Zahl, S. Ismail-Beigi, I. BoÅoviÄ[‡], and A. Gozar, *Nature Nan-otechnology*, vol. 14, p. 44, 2019.
- [63] W. Li, L. Kong, C. Chen, J. Gou, S. Sheng, W. Zhang, H. Li, L. Chen, P. Cheng, and K. Wu, Science Bulletin, vol. 63, p. 282, 2018.
- [64] B. Kiraly, X. Liu, L. Wang, Z. Zhang, A. J. Mannix, B. L. Fisher, B. I. Yakobson, M. C. Hersam, and N. P. Guisinger, ACS Nano, vol. 13, p. 3816, 2019.
- [65] N. A. Vinogradov, A. Lyalin, T. Taketsugu, A. S. Vinogradov, and A. Preobrajenski, ACS Nano, vol. 13, p. 14511, 2019.
- [66] B. Feng, O. Sugino, R.-Y. Liu, J. Zhang, R. Yukawa, M. Kawamura, T. Iimori, H. Kim, Y. Hasegawa, H. Li, L. Chen, K. Wu, H. Kumigashira, F. Komori, T.-C. Chiang, S. Meng, and I. Matsuda, *Phys. Rev. Lett.*, vol. 118, p. 096401, 2017.
- [67] H. Tang and S. Ismail-Beigi, Phys. Rev. Lett., vol. 99, p. 115501, 2007.
- [68] J. Kunstmann and A. Quandt, Phys. Rev. B, vol. 74, p. 035413, 2006.
- [69] X. Wu, J. Dai, Y. Zhao, Z. Zhuo, J. Yang, and X. C. Zeng, ACS Nano, vol. 6, p. 7443, 2012.
- [70] J. Yuan, N. Yu, K. Xue, and X. Miao, *Applied Surface Science*, vol. 409, p. 85, 2017.
- [71] K. H. Yeoh, T. L. Yoon, Rusi, D. S. Ong, and T. L. Lim, *Applied Surface Science*, vol. 445, p. 161, 2018.
- [72] B. A. Khalil and N. Gaston, Journal of Physics: Condensed Matter, vol. 33, p. 125901, 2021.
- [73] S. Kansara, S. K. Gupta, Y. Sonvane, T. Hussain, and R. Ahuja, ACS Applied Energy Materials, vol. 1, p. 3428, 2018.
- [74] I. Lukaevi, M. Varga Pajtler, M. Muevi, and S. K. Gupta, J. Mater. Chem. C, vol. 7, p. 2666, 2019.
- [75] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proceedings of the National Academy of Sciences, vol. 102, p. 10451, 2005.
- [76] Y. Wang, X. Fan, and J. Sun, *Materials Letters*, vol. 63, p. 350, 2009.
- [77] E. Bekaroglu, M. Topsakal, S. Cahangirov, and S. Ciraci, Phys. Rev. B, vol. 81, p. 075433, 2010.
- [78] M. Wu and X. C. Zeng, Nano Letters, vol. 16, p. 3236, 2016.

- [79] B. Ozdamar, G. Ozbal, M. N. m. c. Ç mar, K. Sevim, G. Kurt, B. Kaya, and H. Sevinçli, *Phys. Rev. B*, vol. 98, p. 045431, 2018.
- [80] S. Guo, Y. Zhang, Y. Ge, S. Zhang, H. Zeng, and H. Zhang, Advanced Materials, vol. 31, p. 1902352, 2019.
- [81] J. Li, H. Lv, W. Lu, D. Shao, R. Xiao, and Y. Sun, *Physics Letters A*, vol. 380, p. 3928, 2016.
- [82] X. Sui, C. Si, B. Shao, X. Zou, J. Wu, B.-L. Gu, and W. Duan, The Journal of Physical Chemistry C, vol. 119, p. 10059, 2015.
- [83] H. Sahin and F. M. Peeters, *Phys. Rev. B*, vol. 87, p. 085423, 2013.
- [84] J. Zhang, B. Zhao, and Z. Yang, *Phys. Rev. B*, vol. 88, p. 165422, 2013.
- [85] X. Lin and J. Ni, Phys. Rev. B, vol. 86, p. 075440, 2012.
- [86] V. Q. Bui, T.-T. Pham, H.-V. S. Nguyen, and H. M. Le, *The Journal of Physical Chemistry C*, vol. 117, p. 23364, 2013.
- [87] M. Luo, Y. H. Shen, and T. L. Yin, Journal of Superconductivity and Novel Magnetism, vol. 30, p. 1019, 2017.
- [88] T. P. Kaloni, The Journal of Physical Chemistry C, vol. 118, p. 25200, 2014.
- [89] D.-X. Xing, C.-C. Ren, S.-F. Zhang, Y. Feng, X.-L. Chen, C.-W. Zhang, and P.-J. Wang, Superlattices and Microstructures, vol. 103, p. 139, 2017.
- [90] G. Li, Y. Zhao, S. Zeng, and J. Ni, Applied Surface Science, vol. 390, p. 60, 2016.
- [91] M. Luo, Y. H. Shen, and T. L. Yin, JETP Letters, vol. 104, p. 557, 2016.
- [92] J. Du, C. Xia, Y. An, T. Wang, and Y. Jia, Journal of Materials Science, vol. 51, p. 9504, 2016.
- [93] Y. Mao, J. Yuan, and J. Zhong, Journal of Physics: Condensed Matter, vol. 20, p. 115209, 2008.
- [94] H. Valencia, A. Gil, and G. Frapper, The Journal of Physical Chemistry C, vol. 114, p. 14141, 2010.
- [95] J. Ding, Z. Qiao, W. Feng, Y. Yao, and Q. Niu, Phys. Rev. B, vol. 84, p. 195444, 2011.
- [96] P. Koskinen, S. Malola, and H. Häkkinen, *Phys. Rev. Lett.*, vol. 101, p. 115502, 2008.
- [97] S. Cahangirov, H. Sahin, G. Lay, and A. Rubio, ser. Lecture Notes in Physics. Springer International Publishing, 2016.
- [98] M. Sharma, A. Kumar, P. K. Ahluwalia, and R. Pandey, Journal of Applied Physics, vol. 116, p. 063711, 2014.
- [99] B. Huang, J. Yu, and S.-H. Wei, Phys. Rev. B, vol. 84, p. 075415, 2011.
- [100] R. Zheng, Y. Chen, and J. Ni, *Applied Physics Letters*, vol. 107, p. 263104, 2015.
- [101] P. Tao, H. Guo, T. Yang, and Z. Zhang, Journal of Applied Physics, vol. 115, p. 054305, 2014.
- [102] J. Thakur, M. K. Kashyap, H. S. Saini, and A. H. Reshak, Journal of Alloys and Compounds, vol. 663, p. 100, 2016.
- [103] S. Dutta and K. Wakabayashi, Phys. Rev. B, vol. 91, p. 201410, 2015.
- [104] E. Noguchi, K. Sugawara, R. Yaokawa, T. Hitosugi, H. Nakano, and T. Takahashi, Advanced Materials, vol. 27, p. 856, 2015.
- [105] S. Ichinokura, K. Sugawara, A. Takayama, T. Takahashi, and S. Hasegawa, ACS Nano, vol. 10, p. 2761, 2016.
- [106] T. P. Kaloni, M. U. Kahaly, and U. Schwingenschlgl, J. Mater. Chem., vol. 21, p. 18681, 2011.
- [107] X. Sun, L. Wang, H. Lin, T. Hou, and Y. Li, *Applied Physics Letters*, vol. 106, p. 222401, 2015.

- [108] O. V. Mykhailenko, Y. I. Prylutskyy, I. V. Komarov, and A. V. Strungar, Nanoscale Research Letters, vol. 12, p. 110, 2017.
- [109] X. Zhang, Y. Sun, L. Ma, X. Zhao, and X. Yao, Nanotechnology, vol. 29, p. 305706, 2018.
- [110] B. Ghosh, S. Nahas, S. Bhowmick, and A. Agarwal, *Phys. Rev. B*, vol. 91, p. 115433, 2015.
- [111] K. Kanayama and K. Nagashio, Scientific Reports, vol. 5, p. 15789, 2015.
- [112] D. Zhang, Z. Zhou, H. Wang, Z. Yang, and C. Liu, Nanoscale Research Letters, vol. 13, p. 400, 2018.
- [113] S. Ghosal, A. Bandyopadhyay, and D. Jana, Phys. Chem. Chem. Phys., vol. 22, p. 27458, 2020.
- [114] X. Du, I. Skachko, A. Barker, and E. Y. Andrei, Nature Nanotechnology, vol. 3, p. 491, 2008.
- [115] C. Rao, K. Gopalakrishnan, and A. Govindaraj, Nano Today, vol. 9, p. 324, 2014.
- [116] P. Vishnoi, K. Pramoda, and C. N. R. Rao, *ChemNanoMat*, vol. 5, p. 1062, 2019.
- [117] R. Balog, B. Jrgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Laegsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann, and L. Hornekaer, *Nature materials*, vol. 9, p. 315, 2010.
- [118] T. Niu, J. Zhang, and W. Chen, *ChemNanoMat*, vol. 5, p. 6, 2019.
- [119] W. Lei, G. Liu, J. Zhang, and M. Liu, Chem. Soc. Rev., vol. 46, p. 3492, 2017.
- [120] N. Honari, S. M. Tabatabaei, M. Pourfath, and M. Fathipour, The Journal of Physical Chemistry C, vol. 124, p. 5807, 2020.
- [121] L. Shi, X. Ren, Q. Wang, Y. Li, F. Ichihara, H. Zhang, Y. Izumi, L. Ren, W. Zhou, Y. Yang, and J. Ye, *Small*, vol. 16, p. 2002356, 2020.
- [122] J. C. Alvarez-Quiceno, G. R. Schleder, E. Marinho, and A. Fazzio, Journal of Physics: Condensed Matter, vol. 29, p. 305302, 2017.
- [123] A. Hashmi and J. Hong, The Journal of Physical Chemistry C, vol. 119, p. 9198, 2015.
- [124] V. Zlyomi, Rusznyk, J. Krti, and C. J. Lambert, The Journal of Physical Chemistry C, vol. 114, p. 18548, 2010.
- [125] X. Zhou, J. Yang, M. Zhong, Q. Xia, B. Li, X. Duan, and Z. Wei, Chemical Research in Chinese Universities, vol. 36, p. 584, 2020.
- [126] F. Lévy, ser. Physics and Chemistry of Materials with A. Springer, 1979.
- [127] W. Müller-Warmuth and R. Schöllhorn, ser. Physics and Chemistry of Materials with Low-Dimensional Structures. Springer Netherlands, 2012.
- [128] K. J. Koski, C. D. Wessells, B. W. Reed, J. J. Cha, D. Kong, and Y. Cui, *Journal of the American Chemical Society*, vol. 134, p. 13773, 2012.
- [129] K. P. Chen, F. R. Chung, M. Wang, and K. J. Koski, Journal of the American Chemical Society, vol. 137, p. 5431, 2015.
- [130] M. S. Stark, K. L. Kuntz, S. J. Martens, and S. C. Warren, Advanced Materials, vol. 31, p. 1808213, 2019.
- [131] V. Q. Bui, H. M. Le, Y. Kawazoe, and D. Nguyen-Manh, The Journal of Physical Chemistry C, vol. 117, p. 3605, 2013.
- [132] S. Pakhira, K. P. Lucht, and J. L. Mendoza-Cortes, The Journal of Chemical Physics, vol. 148, p. 064707, 2018.
- [133] Z. Huang, Y. Wu, X. Qi, C. He, X. Ren, and J. Zhong, physica status solidi (b), vol. 255, p. 1700370, 2018.

- [134] X. Yao, D. Yi, and X. Zhang, J. Mater. Chem. C, vol. 7, p. 2068, 2019.
- [135] X. Zhang, B. Xi, Y. Liu, X. Yao, and X. Wu, The Journal of Physical Chemistry C, vol. 124, p. 4709, 2020.
- [136] L. Esaki and R. Tsu, IBM Journal of Research and Development, vol. 14, p. 61, 1970.
- [137] A. K. Geim and I. V. Grigorieva, Nature, vol. 499, p. 419, 2013.
- [138] J. E. Padilha, A. Fazzio, and A. J. R. da Silva, *Phys. Rev. Lett.*, vol. 114, p. 066803, 2015.
- [139] R. B. Pontes, R. H. Miwa, A. J. R. da Silva, A. Fazzio, and J. E. Padilha, *Phys. Rev. B*, vol. 97, p. 235419, 2018.
- [140] I. V. Sankar, J. Jeon, S. K. Jang, J. H. Cho, E. Hwang, and S. Lee, *Nano*, vol. 14, p. 1930009, 2019.
- [141] C.-J. Shih, Q. H. Wang, Y. Son, Z. Jin, D. Blankschtein, and M. S. Strano, ACS Nano, vol. 8, p. 5790, 2014.
- [142] Y. Deng, Z. Luo, N. J. Conrad, H. Liu, Y. Gong, S. Najmaei, P. M. Ajayan, J. Lou, X. Xu, and P. D. Ye, ACS Nano, vol. 8, p. 829, 2014.
- [143] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nature Nanotechnology, vol. 7, p. 699, 2012.
- [144] M. Bernardi, M. Palummo, and J. C. Grossman, Nano Letters, vol. 13, p. 3664, 2013.
- [145] M. M. Furchi, A. Pospischil, F. Libisch, J. Burgdrfer, and T. Mueller, Nano Letters, vol. 14, p. 4785, 2014.
- [146] T. Roy, M. Tosun, J. S. Kang, A. B. Sachid, S. B. Desai, M. Hettick, C. C. Hu, and A. Javey, ACS Nano, vol. 8, p. 6259, 2014.
- [147] G. W. King'ori, C. N. M. Ouma, A. K. Mishra, G. O. Amolo, and N. W. Makau, RSC Adv., vol. 10, p. 30127, 2020.
- [148] G. Wang, D. Li, Q. Sun, S. Dang, M. Zhong, S. Xiao, and G. Liu, Nanomaterials, vol. 8, 2018.
- [149] B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, and R. C. Ashoori, *Science*, vol. 340, p. 1427, 2013.
- [150] G. Giovannetti, P. A. Khomyakov, G. Brocks, P. J. Kelly, and J. van den Brink, *Phys. Rev. B*, vol. 76, p. 073103, 2007.
- [151] S. Y. Zhou, G.-H. Gweon, A. V. Fedorov, P. N. First, W. A. de Heer, D.-H. Lee, F. Guinea, A. H. Castro Neto, and A. Lanzara, *Nature Materials*, vol. 6, p. 770, 2007.
- [152] P. Shemella and S. K. Nayak, Applied Physics Letters, vol. 94, p. 032101, 2009.
- [153] K. F. Mak, C. H. Lui, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.*, vol. 102, p. 256405, 2009.
- [154] J. Sławińska, I. Zasada, and Z. Klusek, *Phys. Rev. B*, vol. 81, p. 155433, 2010.
- [155] A. Ramasubramaniam, D. Naveh, and E. Towe, Nano letters, vol. 11, p. 1070, 2011.
- [156] X. Zhong, Y. K. Yap, R. Pandey, and S. P. Karna, *Phys. Rev. B*, vol. 83, p. 193403, 2011.
- [157] X. Zhong, R. G. Amorim, R. H. Scheicher, R. Pandey, and S. P. Karna, Nanoscale, vol. 4, p. 5490, 2012.
- [158] P. P. Shinde and V. Kumar, *Phys. Rev. B*, vol. 84, p. 125401, 2011.
- [159] J. Park, W. C. Mitchel, G. J. Brown, S. Elhamri, L. Grazulis, H. E. Smith, S. D. Pacley, J. J. Boeckl, K. G. Eyink, S. Mou, D. H. Tomich, and J. E. Hoelscher, *Applied Physics Letters*, vol. 98, p. 203102, 2011.
- [160] G. Neri, *Chemosensors*, vol. 5, 2017.
- [161] Y. Zeng, S. Lin, D. Gu, and X. Li, Nanomaterials, vol. 8, p. 851, 2018.
- [162] O. Leenaerts, B. Partoens, and F. M. Peeters, *Phys. Rev. B*, vol. 77, p. 125416, 2008.
- [163] Y. Liu and J. Wilcox, Environmental Science & Technology, vol. 45, p. 809, 2011.
- [164] J.-W. Feng, Y.-J. Liu, H.-X. Wang, J.-X. Zhao, Q.-H. Cai, and X.-Z. Wang, Computational Materials Science, vol. 87, p. 218, 2014.
- [165] J. Prasongkit, R. G. Amorim, S. Chakraborty, R. Ahuja, R. H. Scheicher, and V. Amornkitbamrung, *The Journal of Physical Chemistry C*, vol. 119, p. 16934, 2015.
- [166] L. Kou, T. Frauenheim, and C. Chen, The Journal of Physical Chemistry Letters, vol. 5, p. 2675, 2014.
- [167] F. Yavari and N. Koratkar, The Journal of Physical Chemistry Letters, vol. 3, p. 1746, 2012.
- [168] A. Goldoni, R. Larciprete, L. Petaccia, and S. Lizzit, Journal of the American Chemical Society, vol. 125, p. 11329, 2003.
- [169] Y.-H. Zhang, Y.-B. Chen, K.-G. Zhou, C.-H. Liu, J. Zeng, H.-L. Zhang, and Y. Peng, *Nanotechnology*, vol. 20, p. 185504, 2009.
- [170] X. Chen, L. Xu, L.-L. Liu, L.-S. Zhao, C.-P. Chen, Y. Zhang, and X.-C. Wang, Applied Surface Science, vol. 396, p. 1020, 2017.
- [171] Z. Ao, S. Li, and Q. Jiang, Solid State Communications, vol. 150, p. 680, 2010.
- [172] T. Dasgupta, S. N. Punnathanam, and K. Ayappa, Chemical Engineering Science, vol. 121, p. 279, 2015.
- [173] A. Bhattacharya, S. Bhattacharya, C. Majumder, and G. P. Das, The Journal of Physical Chemistry C, vol. 114, p. 10297, 2010.
- [174] H. ping Zhang, X. gang Luo, X. yan Lin, Y. ping Zhang, P. ping Tang, X. Lu, and Y. Tang, Journal of Molecular Graphics and Modelling, vol. 61, p. 224, 2015.
- [175] T. Hussain, S. Chakraborty, and R. Ahuja, Chemphyschem : a European journal of chemical physics and physical chemistry, vol. 14, p. 3463, 2013.
- [176] S. Mehdi Aghaei, M. Monshi, I. Torres, M. Banakermani, and I. Calizo, *Physics Letters A*, vol. 382, p. 334, 2018.
- [177] M. Monshi, S. Aghaei, and I. Calizo, Surface Science, vol. 665, p. 96, 2017.
- [178] S.-Y. Cho, H.-J. Koh, H.-W. Yoo, and H.-T. Jung, Chemistry of Materials, vol. 29, p. 7197, 2017.
- [179] T. Hussain, D. Singh, S. K. Gupta, A. Karton, Y. Sonvane, and R. Ahuja, Applied Surface Science, vol. 469, p. 775, 2019.
- [180] V. Shukla, J. Wrn, N. K. Jena, A. Grigoriev, and R. Ahuja, The Journal of Physical Chemistry C, vol. 121, p. 26869, 2017.
- [181] V. Nagarajan and R. Chandiramouli, Materials Science and Engineering: B, vol. 229, p. 193, 2018.
- [182] A. Szabo and N. S. Ostlund. Mineola: Dover Publications, Inc., 1996.
- [183] L. H. Thomas, Mathematical Proceedings of the Cambridge Philosophical Society, vol. 23, p. 542, 1927.
- [184] E. Fermi, Rend. Accad. Naz. Lincei, p. 602, 1927.
- [185] R. Parr and Y. Weitao, ser. International Series of Monographs on Chemistry. Oxford University Press, 1994.
- [186] P. Hohenberg and W. Kohn, Phys. Rev., vol. 136, p. B864, 1964.
- [187] S. Cottenier, 2004.

- [188] W. Kohn and L. J. Sham, Phys. Rev., vol. 140, p. A1133, 1965.
- [189] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., vol. 77, p. 3865, 1996.
- [190] Y. Zhao and D. G. Truhlar, The Journal of Chemical Physics, vol. 128, p. 184109, 2008.
- [191] L. J. Sham and M. Schlüter, Phys. Rev. Lett., vol. 51, p. 1888, 1983.
- [192] J. P. Perdew and M. Levy, Phys. Rev. Lett., vol. 51, p. 1884, 1983.
- [193] E. Engel, Springer, vol. 620, pp., chapter 2, 56, 2003.
- [194] J. Heyd, G. E. Scuseria, and M. Ernzerhof, The Journal of Chemical Physics, vol. 118, p. 8207, 2003.
- [195] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, The Journal of Chemical Physics, vol. 125, p. 224106, 2006.
- [196] G. Kresse and J. Furthmüller, *Phys. Rev. B*, vol. 54, p. 11169, 1996.
- [197] G. Kresse and D. Joubert, Phys. Rev. B, vol. 59, p. 1758, 1999.
- [198] P. E. Blöchl, *Phys. Rev. B*, vol. 50, p. 17953, 1994.
- [199] S. Grimme, Journal of Computational Chemistry, vol. 27, p. 1787, 2006.
- [200] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, The Journal of Chemical Physics, vol. 132, p. 154104, 2010.
- [201] S. Grimme, S. Ehrlich, and L. Goerigk, Journal of Computational Chemistry, vol. 32, p. 1456, 2011.
- [202] K. Momma and F. Izumi, Journal of Applied Crystallography, vol. 41, p. 653, 2008.
- [203] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett., vol. 78, p. 4063, 1997.
- [204] A. Togo and I. Tanaka, Scripta Materialia, vol. 108, p. 1, 2015.
- [205] A. Togo. [Online]. Available: https://phonopy.github.io/phonopy/
- [206] G. K. Madsen and D. J. Singh, Computer Physics Communications, vol. 175, p. 67, 2006.
- [207] N. W. Ashcroft. Holt, Rinehart Winston, 1976.
- [208] R. D'Souza and S. Mukherjee, Phys. Rev. B, vol. 95, p. 085435, 2017.
- [209] N. R. Glavin, R. Rao, V. Varshney, E. Bianco, A. Apte, A. Roy, E. Ringe, and P. M. Ajayan, Advanced Materials, vol. 32, p. 1904302, 2020.
- [210] T. Wehling, A. Black-Schaffer, and A. Balatsky, Advances in Physics, vol. 63, p. 1, 2014.
- [211] J. Wang, S. Deng, Z. Liu, and Z. Liu, National Science Review, vol. 2, p. 22, 2015.
- [212] B. Peng, H. Zhang, H. Shao, Z. Ning, Y. Xu, G. Ni, H. Lu, D. W. Zhang, and H. Zhu, Materials Research Letters, vol. 5, p. 399, 2017.
- [213] R. D. Shannon, Acta Crystallographica Section A, vol. 32, p. 751, 1976.
- [214] G. G. Guzmán-Verri and L. C. Lew Yan Voon, Phys. Rev. B, vol. 76, p. 075131, 2007.
- [215] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, and S. Ciraci, Phys. Rev. Lett., vol. 102, p. 236804, 2009.
- [216] B. van den Broek, M. Houssa, E. Scalise, G. Pourtois, V. V. Afanas'ev, and A. Stesmans, 2D Materials, vol. 1, p. 021004, 2014.
- [217] P. Rivero, J.-A. Yan, V. M. García-Suárez, J. Ferrer, and S. Barraza-Lopez, Phys. Rev. B, vol. 90, p. 241408, 2014.
- [218] H. Zhao, C.-W. Zhang, W.-X. Ji, R.-W. Zhang, S.-S. Li, S.-S. Yan, B.-M. Zhang, P. Li, and P.-J. Wang, *Scientific Reports*, vol. 6, p. 20152, 2016.

- [219] D. Pandey, C. Kamal, and A. Chakrabarti, *Computational Condensed Matter*, vol. 16, p. e00319, 2018.
- [220] G. Henkelman, A. Arnaldsson, and H. Jónsson, Computational Materials Science, vol. 36, p. 354, 2006.
- [221] N. J. Roome and J. D. Carey, ACS Applied Materials & Interfaces, vol. 6, p. 7743, 2014.
- [222] C. Kamal, *Phys. Rev. B*, vol. 100, p. 205404, 2019.
- [223] H. ping Zhang, X. gang Luo, X. yang Lin, X. Lu, Y. Leng, and H. tao Song, Applied Surface Science, vol. 283, p. 559, 2013.
- [224] M. Sun, Q. Ren, S. Wang, Y. Zhang, Y. Du, J. Yu, and W. Tang, Computational Materials Science, vol. 118, p. 112, 2016.
- [225] M. Sun, S. Wang, Y. Du, J. Yu, and W. Tang, Applied Surface Science, vol. 389, p. 594, 2016.
- [226] W. Yu, Z. Zhu, C.-Y. Niu, C. Li, J.-H. Cho, and Y. Jia, Nanoscale Research Letters, vol. 11, p. 77, 2016.
- [227] B. Cordero, V. Gmez, A. E. Platero-Prats, M. Revs, J. Echeverra, E. Cremades, F. Barragn, and S. Alvarez, *Dalton Trans.*, p. 2832, 2008.
- [228] D. Pandey, C. Kamal, R. Dutt, and A. Chakrabarti, Applied Surface Science, vol. 531, p. 147364, 2020.
- [229] D. Pandey, C. Kamal, and A. Chakrabarti, AIP Conference Proceedings, vol. 2115, p. 030351, 2019.
- [230] A. D. Becke and K. E. Edgecombe, The Journal of Chemical Physics, vol. 92, p. 5397, 1990.
- [231] D. L. Duong, S. J. Yun, and Y. H. Lee, ACS Nano, vol. 11, p. 11803, 2017.
- [232] D. Pandey, C. Kamal, and A. Chakrabarti, The Journal of Chemical Physics, vol. 150, p. 194702, 2019.
- [233] D. Pandey, C. Kamal, and A. Chakrabarti, AIP Conference Proceedings, vol. 1942, p. 050096, 2018.
- [234] M. Wang, X. Huang, Z. Du, and Y. Li, *Chemical Physics Letters*, vol. 480, p. 258, 2009.
- [235] X. Zhang, X. Zhao, and Y. Liu, The Journal of Physical Chemistry C, vol. 120, p. 22710, 2016.
- [236] A. Kokalj, Journal of Molecular Graphics and Modelling, vol. 17, p. 176, 1999.
- [237] S. B. Dugdale, *Physica Scripta*, vol. 91, p. 053009, 2016.
- [238] M. P. Das and F. Green, Journal of Physics: Conference Series, vol. 726, p. 012001, 2016.
- [239] G. Grüner, Rev. Mod. Phys., vol. 60, p. 1129, 1988.
- [240] H.-M. Eiter, M. Lavagnini, R. Hackl, E. A. Nowadnick, A. F. Kemper, T. P. Devereaux, J.-H. Chu, J. G. Analytis, I. R. Fisher, and L. Degiorgi, *Proceedings of the National Academy of Sciences*, vol. 110, p. 64, 2013.
- [241] C.-W. Chen, J. Choe, and E. Morosan, Reports on Progress in Physics, vol. 79, p. 084505, 2016.
- [242] L. H. Li, Y. Chen, G. Behan, H. Zhang, M. Petravic, and A. M. Glushenkov, J. Mater. Chem., vol. 21, p. 11862, 2011.
- [243] D. Pandey, A. Kumar, A. Chakrabarti, and R. Pandey, Computational Materials Science, vol. 185, p. 109952, 2020.
- [244] C.-W. Zhang, Journal of Applied Physics, vol. 111, p. 043702, 2012.
- [245] J. Tersoff and D. R. Hamann, *Phys. Rev. B*, vol. 31, p. 805, 1985.
- [246] N. D. Lang, *Phys. Rev. B*, vol. 34, p. 5947, 1986.
- [247] Haiying He, R. Pati, R. Pandey, and S. P. Karna, vol. 2, 2005, p. 815.

- [248] S. K. Gupta, H. He, D. Banyai, A. K. Kandalam, and R. Pandey, The Journal of chemical physics, vol. 139, p. 244307, 2013.
- [249] P. Jamdagni, A. Kumar, A. Thakur, R. Pandey, and P. K. Ahluwalia, Journal of Physics: Condensed Matter, vol. 29, p. 395501, 2017.
- [250] S. K. Gupta, H. He, D. Banyai, M. Si, R. Pandey, and S. P. Karna, *Nanoscale*, vol. 6, p. 5526, 2014.
- [251] H. He, R. Pandey, and S. P. Karna, Chemical Physics Letters, vol. 428, p. 411, 2006.
- [252] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, *Nature Chemistry*, vol. 5, p. 263, 2013.
- [253] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, and W. Tang, Physica B: Condensed Matter, vol. 406, p. 2254, 2011.
- [254] S. Lebègue and O. Eriksson, Phys. Rev. B, vol. 79, p. 115409, 2009.
- [255] S. Bertolazzi, J. Brivio, and A. Kis, ACS Nano, vol. 5, p. 9703, 2011.
- [256] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, and M. C. Hersam, ACS Nano, vol. 8, p. 1102, 2014.
- [257] R. Ganatra and Q. Zhang, ACS Nano, vol. 8, p. 4074, 2014.
- [258] R. K. Defo, S. Fang, S. N. Shirodkar, G. A. Tritsaris, A. Dimoulas, and E. Kaxiras, *Phys. Rev. B*, vol. 94, p. 155310, 2016.
- [259] A. Ozden, F. Ay, C. Sevik, and N. K. Perkgoz, Japanese Journal of Applied Physics, vol. 56, p. 06GG05, 2017.
- [260] R. Gao and Y. Gao, physica status solidi (RRL) Rapid Research Letters, vol. 11, p. 1600412, 2017.
- [261] X. Li, Y. Dai, Y. Ma, W. Wei, L. Yu, and B. Huang, Nano Research, vol. 8, p. 2954, 2015.
- [262] F.-C. Chuang, L.-Z. Yao, Z.-Q. Huang, Y.-T. Liu, C.-H. Hsu, T. Das, H. Lin, and A. Bansil, Nano Letters, vol. 14, p. 2505, 2014.
- [263] M. Mehboudi, A. M. Dorio, W. Zhu, A. van der Zande, H. O. H. Churchill, A. A. Pacheco-Sanjuan, E. O. Harriss, P. Kumar, and S. Barraza-Lopez, *Nano Letters*, vol. 16, p. 1704, 2016.
- [264] S. Anand, K. Thekkepat, and U. V. Waghmare, Nano Letters, vol. 16, p. 126, 2016.
- [265] L. Xu, M. Yang, S. J. Wang, and Y. P. Feng, *Phys. Rev. B*, vol. 95, p. 235434, 2017.
- [266] A. K. Singh and R. G. Hennig, Applied Physics Letters, vol. 105, p. 042103, 2014.
- [267] F. Wang, L. Zhou, Z. Ma, M. He, F. Wu, and Y. Liu, Nanomaterials, vol. 8, 2018.
- [268] M. Yagmurcukardes, R. T. Senger, F. M. Peeters, and H. Sahin, *Phys. Rev. B*, vol. 94, p. 245407, 2016.
- [269] Z.-Q. Huang, W.-C. Chen, G. M. Macam, C. P. Crisostomo, S.-M. Huang, R.-B. Chen, M. A. Albao, D.-J. Jang, H. Lin, and F.-C. Chuang, *Nanoscale Research Letters*, vol. 13, p. 43, 2018.
- [270] B. P. Bahuguna, L. Saini, R. O. Sharma, and B. Tiwari, *Physica E: Low-dimensional Systems and Nanostructures*, vol. 99, p. 236, 2018.
- [271] A. Shafique and Y.-H. Shin, Scientific Reports, vol. 7, p. 506, 2017.
- [272] D. Pandey and A. Chakrabarti, *Physics Letters A*, vol. 383, p. 2914, 2019.
- [273] G. Grimvall, B. Magyari-Köpe, V. Ozoliņš, and K. A. Persson, Rev. Mod. Phys., vol. 84, p. 945, 2012.
- [274] M. Gmitra, S. Konschuh, C. Ertler, C. Ambrosch-Draxl, and J. Fabian, Phys. Rev. B, vol. 80, p. 235431, 2009.
- [275] M. Gmitra and J. Fabian, *Phys. Rev. B*, vol. 92, p. 155403, 2015.

- [276] Z. Wang, D. Ki, H. Chen, H. Berger, A. H. MacDonald, and A. F. Morpurgo, *Nature Communications*, vol. 6, p. 8339, 2015.
- [277] S. C. de la Barrera, M. R. Sinko, D. P. Gopalan, N. Sivadas, K. L. Seyler, K. Watanabe, T. Taniguchi, A. W. Tsen, X. Xu, D. Xiao, and B. M. Hunt, *Nature Communications*, vol. 9, p. 1427, 2018.
- [278] P. Lu, X. Wu, W. Guo, and X. C. Zeng, Phys. Chem. Chem. Phys., vol. 14, p. 13033, 2012.
- [279] W. Wang, C. Yang, L. Bai, M. Li, and W. Li, Nanomaterials, vol. 8, p. 74, 2018.
- [280] A. E. Maniadaki, G. Kopidakis, and I. N. Remediakis, Solid State Communications, vol. 227, p. 33, 2016.
- [281] X. Peng, Q. Wei, and A. Copple, *Phys. Rev. B*, vol. 90, p. 085402, 2014.
- [282] A. S. Rodin, A. Carvalho, and A. H. Castro Neto, Phys. Rev. Lett., vol. 112, p. 176801, 2014.
- [283] D. Pandey and A. Chakrabarti, AIP Conference Proceedings, vol. 2265, p. 030702, 2020.
- [284] B. Amorim and F. Guinea, *Phys. Rev. B*, vol. 88, p. 115418, 2013.
- [285] B. Sa, Y.-L. Li, J. Qi, R. Ahuja, and Z. Sun, The Journal of Physical Chemistry C, vol. 118, p. 26560, 2014.
- [286] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, *Science*, vol. 287, p. 622, 2000.
- [287] M. Donarelli and L. Ottaviano, Sensors, vol. 18, p. 3638, 2018.
- [288] Z. Yuan, R. Li, F. Meng, J. Zhang, K. Zuo, and E. Han, Sensors, vol. 19, p. 1495, 2019.
- [289] S. Yang, C. Jiang, and S.-h. Wei, Applied Physics Reviews, vol. 4, p. 021304, 2017.
- [290] N. R. Council. Washington, DC: The National Academies Press, 2008.
- [291] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, *Nature Materials*, vol. 6, p. 652, 2007.
- [292] A. R. Villagracia, H. L. Ong, D. S. Bayasen, H. Lin, M. David, and N. Arboleda, International Journal of Hydrogen Energy, 2020.
- [293] P. Reunchan and S.-H. Jhi, Applied Physics Letters, vol. 98, p. 093103, 2011.
- [294] H. ping Zhang, X. gang Luo, X. yang Lin, X. Lu, and Y. Leng, International Journal of Hydrogen Energy, vol. 38, p. 14269, 2013.
- [295] R. Lotfi and Y. Saboohi, Physica E: Low-dimensional Systems and Nanostructures, vol. 60, p. 104, 2014.
- [296] L. Li, H. Zhang, and X. Cheng, Computational Materials Science, vol. 137, p. 119, 2017.
- [297] H. ping Zhang, W. Hu, A. Du, X. Lu, Y. ping Zhang, J. Zhou, X. Lin, and Y. Tang, Applied Surface Science, vol. 433, p. 249, 2018.
- [298] Z. Yu, N. Wan, S. Lei, and H. Yu, Journal of Applied Physics, vol. 120, p. 024305, 2016.
- [299] G. J. Kubas, Journal of Organometallic Chemistry, vol. 635, p. 37, 2001.
- [300] M. Zhou, Y.-H. Lu, Y.-Q. Cai, C. Zhang, and Y.-P. Feng, Nanotechnology, vol. 22, p. 385502, 2011.
- [301] Y. Fan, J. Zhang, Y. Qiu, J. Zhu, Y. Zhang, and G. Hu, Computational Materials Science, vol. 138, p. 255, 2017.
- [302] G. Blyholder, The Journal of Physical Chemistry, vol. 68, p. 2772, 1964.
- [303] B. Hammer and J. Nrskov, Surface Science, vol. 343, p. 211, 1995.
- [304] S. S. Sung and R. Hoffmann, Journal of the American Chemical Society, vol. 107, p. 578, 1985.

- [305] H. Kobayashi, M. Yamaguchi, S. Yoshida, and T. Yonezawa, Journal of Molecular Catalysis, vol. 22, p. 205, 1983.
- [306] J. Nie, R. J. Li, L. J. He, and J. Li, Materials Science Forum, Trans Tech Publications Ltd, vol. 804, p. 145, 2015.
- [307] Q. Ge and D. King, *Chemical Physics Letters*, vol. 285, p. 15, 1998.
- [308] J. Zhang, X. Liu, G. Neri, and N. Pinna, Advanced Materials, vol. 28, p. 795, 2016.
- [309] Y. Yong, H. Cui, Q. Zhou, X. Su, Y. Kuang, and X. Li, RSC Adv., vol. 7, p. 51027, 2017.
- [310] X. Tang, A. Du, and L. Kou, WIREs Computational Molecular Science, vol. 8, p. e1361, 2018.
- [311] Q. Yue, Z. Shao, S. Chang, and J. Li, Nanoscale Research Letters, vol. 8, p. 425, 2013.
- [312] M. Ganji, N. Sharifi, M. Ghorbanzadeh Ahangari, and A. Khosravi, *Physica E: Low-dimensional Systems and Nanostructures*, vol. 57, p. 28, 2014.
- [313] I. N. Yakovkin and N. V. Petrova, The Journal of Chemical Physics, vol. 130, p. 174714, 2009.
- [314] Z. Ji and J.-Q. Li, The Journal of Physical Chemistry B, vol. 110, p. 18363, 2006.
- [315] F. J. E. Scheijen, J. W. H. Niemantsverdriet, and D. Curulla-Ferr, The Journal of Physical Chemistry C, vol. 112, p. 7436, 2008.
- [316] A. Shokri and N. Salami, Sensors and Actuators B: Chemical, vol. 236, p. 378, 2016.
- [317] C. Zhou, W. Yang, and H. Zhu, The Journal of Chemical Physics, vol. 142, p. 214704, 2015.
- [318] F. Ersan, E. Aktrk, and S. Ciraci, The Journal of Physical Chemistry C, vol. 120, p. 14345, 2016.
- [319] C. Liu, C.-S. Liu, and X. Yan, *Physics Letters A*, vol. 381, p. 1092, 2017.
- [320] Y. Cai, Q. Ke, G. Zhang, and Y.-W. Zhang, The Journal of Physical Chemistry C, vol. 119, p. 3102, 2015.
- [321] S. Haldar, S. Mukherjee, and C. V. Singh, RSC Adv., vol. 8, p. 20748, 2018.
- [322] S. Kumar, M. Singh, D. K. Sharma, and S. Auluck, Computational Condensed Matter, vol. 22, p. e00436, 2020.
- [323] X. Zang, T. Wang, Z. Han, L. Li, and X. Wu, Nano, vol. 14, p. 1930001, 2019.
- [324] Y.-M. Chang, H.-W. Lin, L.-J. Li, and H.-Y. Chen, Materials Today Advances, vol. 6, p. 100054, 2020.
- [325] D. Li, Y. Gong, Y. Chen, J. Lin, Q. Khan, Y. Zhang, Y. Li, H. Zhang, and H. Xie, *Nano-Micro Letters*, vol. 12, p. 36, 2020.
- [326] F. Tesfaye and M. Moroz, Journal of Electronic Research and Application, vol. 2, p. 28, 2018.
- [327] Y. Yu, M. Cagnoni, O. Cojocaru-Mirdin, and M. Wuttig, Advanced Functional Materials, vol. 30, p. 1904862, 2020.

Thesis Highlight

Name of the Student: Dhanshree Pandey

Name of the CI/OCC: Raja Ramanna Centre for Advanced Technology

Enrolment No.: PHYS03201504002

Thesis Title: First-Principles Studies on Effect of Functionalization and Adsorption of Various Gases on Two-Dimensional Nanostructures

Discipline: Physical Sciences Sub-Area of Discipline: Two-Dimensional Nanostructures

Date of viva voce: 22.06.2021

Study on two-dimensional (2D) materials is an active area of research because of various fascinating properties and applications associated with this class of materials. The rich properties exhibited by the 2D systems are primarily due to specific atomic arrangements leading to a variety of electronic properties, covering from metals to insulators. Because of the metallic bonding exhibited by group-III 2D monoelemental systems, they exhibit a number of allotropes with interesting electronic properties, as has been observed for boron and aluminium atom based 2D monolayers: borophene and aluminene, respectively. Besides, new "post-graphene" 2D binary monolayer structures are also finding increasing research interest in the literature.

In this regard, successful predictions have been made about the possibility of (i) a new allotrope of group-III-based 2D aluminene monolayers, with interesting Dirac cones lying close to the Fermi level with Fermi velocity comparable to that of graphene, and (ii) new transition metal monochalcogenides with bandgaps. Such systems may hold promises as new members of "Dirac materials", and "2D bandgap materials", respectively, which



Figure 1. Prediction of novel 2D materials (aluminene and monochalcogenides), and suitable functionalization of different allotropes of aluminene in pursuit of gas sensing applications.

suggests their potential future applications in the field of nanoelectronics and energy materials. Further, from the literature, it has been seen that influence of defects/functionalization or formation of heterostructures of 2D materials have led to improved applications of 2D materials in the area of electronics, spintronics, batteries, and gas sensing etc. In this direction, various exciting properties like emergence and tuning of magnetic moments and the charge polarities, signature of Fermi surface nesting, bandgap opening in metallic planar aluminene via formation of the van der Waals (trilayer) heterostructures of planar aluminene with BN monolayers have been observed from the studies of functionalization of 2D aluminene lattice. Besides, these pristine (2D aluminene and monochalcogenides) and functionalized systems have been employed to utilize their properties for various applications, like gas sensing behavior of these 2D materials. A comparative analysis of gas adsorption predicts that in comparison with many of the well-known pristine 2D systems studied in the literature, the 2D surfaces probed in this thesis may serve better in terms of adsorption and sensing of these gas molecules.