CHAPTER 7
Summary and Future scope

Summary

The present thesis describes the electronic, mechanical and dynamical properties of various two-dimensional (2D) materials within density functional theory (DFT) based first-principles approach. Owing to the large surface to volume ratio and wide range of tuneable properties the 2D materials like arsenene, silicene and transition metal di-chalcogenides (TMDs) are considered for the study in present work. Their properties are tuned for various energy applications like solar cells for photovoltaics applications and electro/photo-catalysts for the generation of clean energy through water-splitting mechanism. The density functional theory has emerged as a novel quantum mechanical approach due to its markable prediction power of ground state properties for materials ranging from insulators to semi-conductors, and, to the highly correlated metals. Further, the enhancement in computational facilities, effective advanced numerical methods and emergence of various new exchange-correlation functionals that provide accurate predictions have rose DFT to the peak position in theoretical approaches. The present thesis contains seven chapters. **CHAPTER 1** describes the importance of 2D materials by means of connecting the early stage research and developments made on nanomaterials with the present advancements and progress. The uniqueness of 2D materials has been emphasized by means of tuning their electronic, optical and catalytic properties by imposing various conditions such as chemical doping or introducing defects in the material by applying strain or pressure and by applying external electric field. These distinct methods have been proven suitable to modulate the materials properties according to the application by limiting the structural/geometric distortions/modifications within a feasible range. Inspired from the signature benchmarks attained in the field of 2D materials, we have performed DFT based

computations covering various aspects to tailor energetics of the considered systems for diverse energy applications.

CHAPTER 2 covers the *first-principles* approach and formalism of DFT utilized for studying the ground state properties of the considered 2D systems. Starting from the conventional Born-Oppenheimer approach to the Kohn-Sham formulated density based approximations that are the foundation of DFT to the latest advancements made in the basic DFT are elaborated. The pseudopotential approach utilizing the plane-wave basis sets and implemented in QUANTUM ESPRESSO simulation package is discussed including the long-range van der Waals dispersion correction.

CHAPTER 3 is dedicated to the newly predicted two-dimensional form of arsenic known as arsenene. We describing its structural, electronic and catalytic activities of pristine

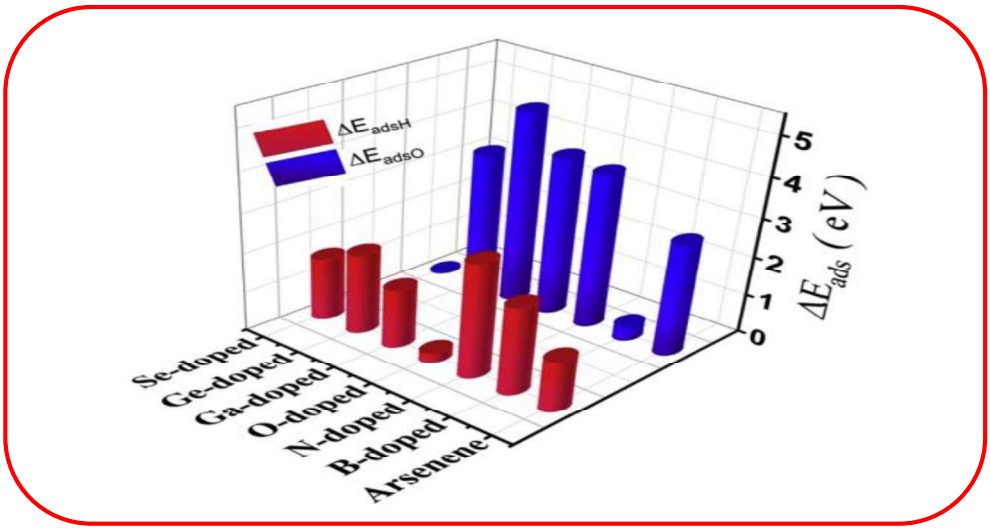

Figure 7.1: Adsorption energy of hydrogen and oxygen on pristine and B, N, O, Ga, Ge and Se doped arsenene.

and doped arsenene. The results on hydrogen evolution and oxygen evolution reactions precisely known as HER and OER activities for pristine and doped conditions show that the oxygen doped

arsenene is a potential HER catalyst owing to its prominent magnitude of adsorption energy (0.24 eV) whereas boron doped arsenene stands out to be most promising candidate for OER catalyst (see Fig. 7.1). Further, we have analyzed the catalytic activity of zirconium chalcogenides (ZrX; X=S_2, SSe and Se_2) as they exhibit semiconducting nature with band gap of 1.58 eV, 1.08 eV and 0.58 eV respectively. We observe among all three systems that the Janus ZrSSe is a better photocatalyst for HER at edge side. However, the edge is hindrance for the hydrogen production. We sieved arsenene with Nb, W and Pt dopants and found increased basal activity. These doped systems show metallic nature. Nb-$ZrSe_2$ shows better catalytic activity compared to other doped systems as its Gibb's free energy is close to zero and positive indicating easy hydrogen desorption.

The next chapter of thesis, **CHAPTER 4** covers the study on the structural, electronic and dynamical properties of Bi, BiAs and BiSb monolayers under ambient and strained conditions. Here, the application of the external strain is utilized as a pathway for tuning and refining the system properties for desired applications. Furthermore, the stability and energetics of these systems are examined for validating the applicability of these systems under constrained environment. It is noteworthy that the signature *out-of-plane* phonon mode of 2D materials, also known as ZA mode show flexural behaviour and characteristic quadratic nature of frequency with reciprocal wave-vector **k**.

Our results show possibility of Bi, BiAs and BiSb monolayers for nano-electronic devices in wide range of extreme conditions. Followed by this, a novel approach of combining two monolayers made-up of silicene and $SnSe_2$ in form of a 2D hetero-structured configuration is presented in **CHAPTER 5**. The possibility of growing silicene over $SnSe_2$ is validated by

means of computing the lattice mismatch between the monolayers and the cohesive and formation energies of the heterostructure. As the results suggest 0.48% lattice mismatch with the energy of formation being -0.54 eV, the formation of the hetero-structure is possible under exothermic process. We have intercalated with phosphorous and chlorine atoms and ammonia (NH_3) molecule to weaken and manipulate the charge distribution between the Si/$SnSe_2$ hetero-structure. We found that the NH_3 shows inert nature towards silicene in Si/NH_3^b/$SnSe_2$ and a band opening of about of 0.23 eV is observed. The intercalation of phosphorous and chlorine atoms makes silicene metallic due to strong interaction between them.

The CHAPTER **6** comprises the DFT results of methylammonium lead iodide (MAPI) for validating its applicability in photovoltaic solar cells. The effect of external strain and dimensional confinement (one- and two-) is assessed to tailor the properties of MAPI. Furthermore, in case of 2D MAPI, we have performed layer dependent study to evaluate the optimum performance of MAPI for solar cell applications. The results on 2D MAPI show highest theoretical efficiency of 23.6% with reference to mesoporous (mp)-TiO_2 electrode.

Future scope

The prime goal of thesis is to understand and tune the fundamental properties of two-dimensional materials such as arsenene, silicene, transition metal-dichalcogenides such as ZrS_2, $ZrSe_2$, ZrSSe and $SnSe_2$, bismuthene and bismuthene alloys (BiSb and BiAS) and methyl ammonium lead iodide (MAPI) for desire applications. In the present studies, we have tuned the structural and electronic properties of arsenene and zirconium chalcogenides for the application of water splitting process. We have applied bi-axial strain to the bismuthene and its alloy to

understand the change in electronic, mechanical and dynamical properties. We observe that they can sustain high strain and their tunable band gap are suitable for optical electronic properties. Besides strain and doping, hetero-structuring of two-dimensional materials also tunes their fundamental properties. The semi-metallic nature of silicene provides hindrance for opto-electronic device, therefore we have considered $SnSe_2$ for tuning the electronic properties of silicene monolayer. We found that due to strong interaction between two monolayers leads to metallic nature which can be used for sensing purposes, Further, to make interaction weaker, we intercalated the hetero structure with P and Cl atoms and ammonium molecule. The ammonium molecule weakens interaction between these layers which opens the band gap. Lastly, we have seen that the two-dimensional materials are most suitable for solar-cell applications due to their tunable band gap.

As a future plan to extent these works, a possibility of finding the allotropes of these compounds that are will be checked. After confirming their stability, they will be explored for solar cell, photocatalyst and electro catalyst for water splitting and opto-electronic device point of view. These materials will also be explored for superconductivity, as cathode for Li-S batteries, field transistor and spintronic applications. A molecular dynamics simulation study will be performed to understand the interaction between hetero-structures with several layers. In brief the future plan is to explore new 2D materials for different applications such as sensing and energy.