

**FIRST PRINCIPLE INVESTIGATION OF ELECTRONIC
STRUCTURE AND THERMOELECTRIC PROPERTIES OF
LAYERED TRANSITION METAL DICHALCOGENIDES**



By

FAWAD KHAN

**DEPARTMENT OF PHYSICS
UNIVERSITY OF MALAKAND**

2020

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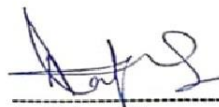
**DEPARTMENT OF PHYSICS
UNIVERSITY OF MALAKAND,**

2020

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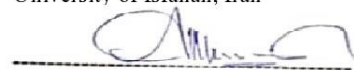


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Abstract

In this thesis, van der Waals heterostructures (vdW-h) consisting of MX_2 ($\text{M} = \text{Zr}, \text{Hf}$ and $\text{X} = \text{S}, \text{Se}$) monolayers are modeled and their physical properties are explored. The favorable stacking and stability of the modeled monolayer heterostructures are confirmed through binding energy and phonon dispersion calculations. After confirming stability, the electronic and thermoelectric properties of these compounds are explored using the first-principles calculations combined with semi-classical Boltzmann transport theory. It is found that type-II band alignment in $\text{ZrS}_2\text{-HfSe}_2$ facilitates charge separation for optoelectronics and solar energy conversion. All studied heterostructures show remarkably higher electrical conductivity than corresponding monolayers, responsible for large power factor values, especially at 1200 K. These findings indicate that the creation of vdW-h from MX_2 may be promising for efficient optoelectronic and thermoelectric devices.

The modeled vdW-h of monolayer TMDCs MX_2 ($\text{M} = \text{Zr}, \text{Hf}$ and $\text{X} = \text{S}, \text{Se}$), and their Janus materials with heterostructure are further investigated. Through binding energy the stacking and stability of modeled Janus monolayers and Janus heterostructures are confirmed. Using first-principles calculations the electronic properties of the stable materials were calculated. Mulliken electronegativity is used to find the band edge energies to determine the photocatalytic properties. It is concluded that the band edges of mono-layer ZrS_2 , HfS_2 , ZrSSe and HfSSe straddle the redox potentials of water at pH 0,

in case of heterostructure only in $\text{ZrS}_2\text{-HfS}_2$ the band edges straddles, which make these five materials promising for photocatalytic water splitting.

Even better functionalities can be achieved in transition metal dichalcogenides heterostructure than their individual monolayers. The electronic structure and band alignment controls the different device designs. For example type I band alignment is beneficial for high emission efficiency in light-emitting diodes, type II band alignment is required in light harvesting photovoltaic cells and the broken-gap alignment to boost the performance of next generation electronics like vertical tunneling field-effect transistors. For possible future electronic applications the understanding of band alignment in these tailored TMDCs heterostructure is very important. Novel vdW-h of monolayer TMDCs MX_2 ($\text{M} = \text{Zr, Hf, Pt}$ and $\text{X} = \text{S, Se}$) are modeled. Different stacking were theoretically investigated, from the binding energies most stable stacking were checked out for all the heterostructures through PBE and HSE06 and the electronic nature of these heterostructure are calculated. Type-II band alignment in these heterostructures was confirmed which facilitates charge separation for optoelectronics and solar energy conversion.

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Fawad Khan

Dedicated to my Family

List of Publications

This thesis consists the following published and under-review articles

- 1) **Fawad Khan**, H. Ud Din, S. A. Khan, G. Rehman, M. Bilal Iftikhar Ahmad, Li-Yong Gan, B. Amin. Theoretical investigation of electronic structure and thermoelectric properties of MX_2 (M=Zr, Hf; X=S, Se) van der Waals heterostructures.
- 2) **Fawad Khan**, Gul Rehman, Iftikhar Ahmad, Bin Amin “Photocatalytic Response of MX_2 and MXY (M=Zr, Hf X=Y=S, Se) Monolayer and Heterostructures”
(In preparation)
- 3) **Fawad Khan**, Gul Rehman, Iftikhar Ahmad, Bin Amin “Investigation of Band Alignment in Novel Zr/Hf X_2 -Pt X_2 (X=S, Se) vdW Heterostructure”
(In preparation)

List of Abbreviations

vdW:	van der Waals
FETs:	field-effect transistors
hBN:	Hexagonal boron nitride
vdW-h:	van der Waals heterostructures
DFT:	Density Functional Theory
TMDCs:	Transition Metal Dichalcogenides
CBM:	conduction band minimum
VBM:	valance band maximum
SC:	Seebeck coefficient
PF:	power factor
HER:	hydrogen evolution reaction
PCE:	power conversion efficiency
K.E:	kinetic energy
P.E:	potential energy
HF:	Hartree-Fock
VP:	Variational Principle
HK:	Hohenberg-Kohn
GSE:	ground state energy
SDFT:	Spin density functional theory
EDFT:	Ensemble density functional theory
CDFT:	Current density functional theory

RDFT:	Relativistic Density Functional Theory
TDDFT:	Time dependent density functional theory
KS:	Kohn-Sham
LDA:	Local density approximation
GGA:	Generalized gradient approximation
LSDA:	local spin-density approximation
HSE:	Heyd-Scuseria-Ernzerhof
FMM:	Fast multipole method
APW:	Augmented Plane Wave
QE:	Quantum espresso
VASP:	Vienna Ab-initio Simulation Package

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Chapter 1

Introduction

The ever-increasing demand of energy for human activities is a pressing concern in the world; invoking to adopt more advance techniques for the exploration and development of sustainable and environment friendly energy resources. The importance of an ideal renewable energy resource for practical realization of designing viable products to overcome the negative impact of anthropogenic carbon on global climate is curious among the scientific and industrial communities. Thermoelectric phenomenon, converting the waste heat energy into electrical energy, is an ideal renewable energy resource for cheaper power supply to meet the challenges of the future energy needs. Additionally, the photocatalytic water splitting under the solar irradiation, being the most abundant, cheap and environment friendly approach, is also gaining extraordinary attention. In view of these facts, the search of advance and efficient thermoelectric and photocatalytic materials is highly emphasized for emerging renewable energy device applications in materials science and technology.

The bulk form of many layered materials is formed from the stacks of layers which are strongly bonded with weak van der Waals (vdW) interaction, where this weak attraction between the layers allows the exfoliation into atomically thin individual layers [1]. Materials with a large ratio of their lateral size to thickness are classified as two-

dimensional (2D) materials [2]. The strong intralayer covalent bonding and the weak interlayer vdW interaction with binding energy of 40-70meV facilitate the exfoliation of 2D layer from their bulk crystals [3]. An effective method to control the electrostatic conductivity is offered by utilization of high quality of atomically thin and sub-nanometer thickness of 2D materials in electronic circuits. In electrochemistry, for layered material the high surface-to-volume ratio can be utilized [4] which results in extreme sensitivity in molecular sensors [5]. The 2D materials in many applications like conductive displays transport solar cells or protective light absorbing layers reduces the cost of the devices due to small thickness and reduction in mass and volume. In 2D materials, exotic properties for different applications like photonics, spintronics, plasmonics or valleytronics are also proposed [6-10].

In layered materials heat and charge carriers are confined to a single plane which causes unusual physical phenomena's like charge density waves and superconductivity at high temperature [11-13]. Layered materials with reduced dimensions, where the quantum confinement effect modifies the electronic, thermoelectric and photocatalytic response of free carriers are expected as promising candidates in resolving the renewable energy issues. A deep insight is taken into account to demonstrate the quantum confined materials and their hybrid structures with enhanced functionalities for thermoelectrics and photovoltaics. To compete the existing technologies developed from compound semiconductors, further studies and optimization of 2D materials is needed because of their reduced stability, higher contact resistance and lower mobility [14-16].

The first experimentally identified 2D material was graphene. It is derived from graphite which is present in nature abundantly. It comprises of a single layer of sp^2 hybridized carbon atom, having good electronic properties, like quantum Hall effect at room temperature [17] and ultrahigh carrier mobilities [18] which enables graphene field-effect transistors (FETs) for switching rate in tetra hertz [19]. The thickness of graphene is of the size of an atom, and it is flexible having great strength and optically transparent [20]. The charge carriers in graphene behaving like massless particles and its 2D hexagonal crystal structure makes it outstanding for electron transport while its high in-plane stiffness, superior strength and Young modulus makes graphene promising for mechanical properties. Due to these properties, graphene has a lot of applications in many fields like in electronics and energy storage due to its controllable durability and for structural applications due to plastically curved form. In spite of exciting photonic and electronic phenomena's the absence of band gap in graphene the 'original' 2D material, limits its applications in light emitting devices. Its applications are limited to radio frequency electronics, but in digital electronics, where not only high ON state current is required but also low OFF state currents are needed, graphene is unstable [21-24].

Hexagonal boron nitride (hBN) having band gap of 6eV makes it promising 2D material as dielectric which can be incorporated in heterostructure for electrostatic gating of other layered materials. 2D transition metal dichalcogenides (TMDCs) is an evolving class of crystals, having formula MX_2 (M= transition metals and X=S, Se and Te). There is a strong covalent or ionic bonding in the in-plane direction, however a weak van der

Waals heterostructures (vdW-h) forces hold the individual atomic layer together in the out of plane direction of these materials. Therefore, the individual layers are easily separated by liquid or mechanical exfoliation due to weak forces along the c-axis. These materials are sensitive to interlayer coupling and so the properties of these materials are qualitatively changed as their thickness is reduced from bulk to monolayer.

The absence of electronic band gap in graphene stimulated the researcher for search of other 2D materials having semiconducting nature. Because of large surface-to-volume ratio and quantum confinement effect, the physical behavior of TMDCs and Janus-TMDCs monolayers has shown great importance for optoelectronic applications. The dynamical stability, satisfactory lattice mismatching and semiconducting band nature have shown strong motivation to design vdW-h of TMDCs-TMDCs and Janus-TMDCs-Janus-TMDCs. Furthermore, in these vdW heterostructures the band alignment is also expected to be type-II which is crucial for light harvesting and photocatalytic purposes. In addition, the suitable band gap character of the vdW-h will encourage to focus on the demonstration of thermoelectric performance useful for exploration and development of sustainable and environmentally friendly energy resources. In this dissertation we report first-principle investigation of layered TMDCs, after confirming their dynamical stability, we have calculated the electronic, thermoelectric and photocatalytic properties of layered TMDCs along with their out of plane heterostructure. Janus-TMDCs and heterostructure were also investigated for electronic and photocatalytic properties. Band alignment in heterostructure is also confirmed using first-principle investigation.

This dissertation includes five chapters. In chapter 1, the problem is briefly introduced. In 2nd chapter different physical properties of TMDCs monolayer and their heterojunctions along with various applications are reviewed. In 3rd chapter introduction to Density Functional Theory (DFT) and different methodologies adopted are briefly demonstrated. The chapter 4 includes calculated results along with detail discussion of structural, electronic, thermoelectric and photocatalytic properties of the under study mono- and heterobilayers. Chapter 5; the summary of thesis is presented.

Chapter 2

Literature Review

2.1 Transition Metal Dichalcogenides (TMDCs)

TMDCs are extensively studied both theoretically and experimentally [25-27]. A single layer of TMDCs is composed of X-M-X sheets, stacked on one another, held by weak vdW forces. Even at high pressure shearing takes place easily due to weak forces between the sheets which make these materials efficient in lubricants applications [28]. The generic formula of layered TMDCs is MX_2 , where the transition metal is represented by M and the chalcogen atoms (S, Se and Te) by X. While within a layer the nature of interatomic interaction is covalent,

2.1.1 Structural Properties of TMDCs

Transition Metal Dichalcogenides exist in two different point-group symmetries, the D_{6h} point-group and D_{3d} point- group symmetry. The bulk state of TMDCs is formed from the stacking of many layers. The D_{6h} point-group compounds are known as 2H- MX_2 and the D_{3d} point-group are specified as 1T- MX_2 compounds. The IVB-VIA TMDCs are isostructural. These materials crystallize in 1T- CdI_2 like structure, $P\bar{3}m1$ space group. In bulk state of TMDCs, the chalcogen (X) atoms sandwich the transition metal (M)

forming X-M-X compounds. The M atom attached to X atoms is held by strong ionic bonds. The Brillouin zone of the bulk structure is different from the corresponding monolayer. Bulk MX_2 compounds ($\text{M}=\text{Zr}, \text{Hf}$ and $\text{X}=\text{S}$ and Se) are reported as indirect band gap semiconductors, where conduction band minimum (CBM) lies at M and valance band maximum (VBM) at G of Brillouin zone [29]. Numerous studies have reported nature of band gap to be indirect in these materials in the bulk phase [30-37].

Several structural phases of TMDCs monolayer are due to the different coordination sphere of transition metal atoms and stacking order. The most common phase of TMDCs monolayer is trigonal prismatic (2H) and octahedral (1T), where 1 and 2 shows the number of trilayer to form the bulk primitive unit cell. The individual layer of these materials is a combination of three atomic planes (chalcogen-transition metal-chalcogen) in different stacking and combination. In 1T phase the chalcogen atoms of different layers are shifted from one another forming ABC stacking (with tetragonal symmetry D_{3d} group) depending on the position of transition metals and chalcogen atoms in their corresponding layers, as displayed in Figure 2.1a (left) and 1b. In 2H or 3R phase, the chalcogen atoms are referred as trigonal prismatic coordination of the metal atom and described by D_{3h} group (hexagonal symmetry). That is, the chalcogen atoms in the top layer are located directly above the chalcogen atoms in the bottom layer in a perpendicular direction to the layers forming ABA stacking, shown in Figure 2.1. The 2H and 1T phase are considered as thermodynamically stable phase while meta stable phase can also be obtained.

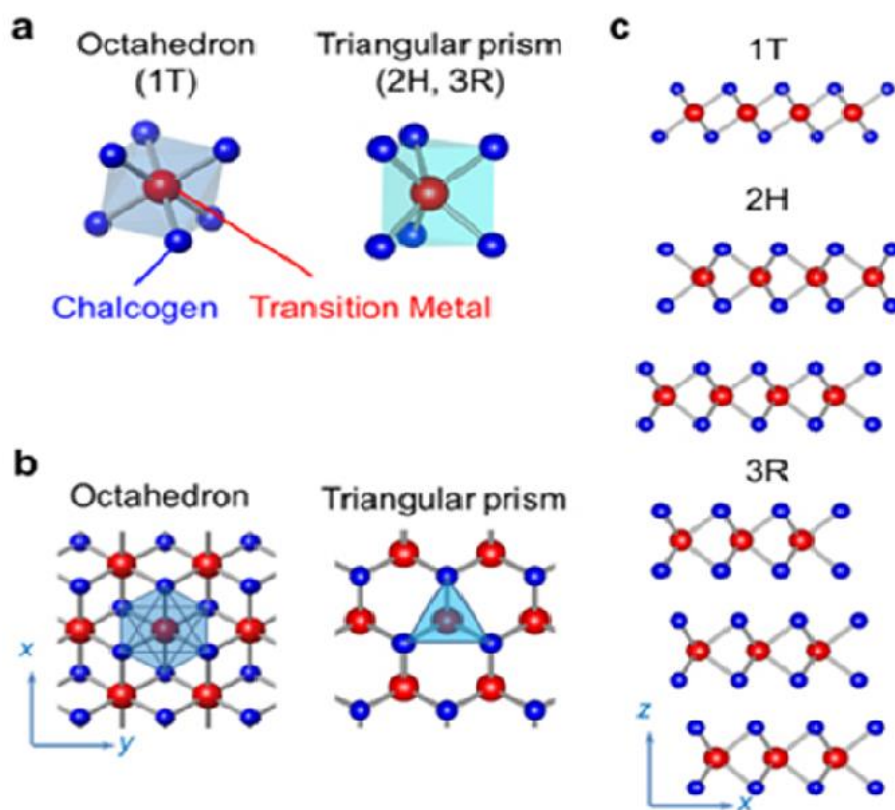


Figure 2.1: Structures of TMDCs. (a) Coordination in TMDCs. 1T structure is formed by Octahedral coordination (left) and 2H or 3R structure are formed by triangular prismatic coordination (right), (b) Octahedrally coordinated monolayers top view (left) and triangular prismatic coordinated monolayer top view (right). (c) Side views [24].

2.1.2 Electronic Properties of TMDCs

Metals are classified in semimetals and metals with small and large overlap between their valance bands and conduction bands, semiconductors are solids with band gap of 0.1-4eV and insulators are having band gap of $>4\text{eV}$. Near K and K' points of brillouin zone, the linear dispersion of charge carriers and due to zero band gap semiconducting nature among 2D materials, graphene has a unique position. Graphene has interesting physical properties like Klein tunneling, wave length-independent light absorption and relativistic charge carriers [38, 39]. In graphene the high charge carriers mobility (μ) is responsible for its high intrinsical conductivity (σ) which is tunable through charge carrier density (n).

Black phosphorous (BP) having wrinkled structure (Figure 2.2) at atmospheric pressure is the most stable allotrope of phosphorous with a band gap of 0.3 to 2eV. The band gap of BP can be modulated by number of layers. BP can absorb from visible light to nearly infrared light. In few layer BP the carrier mobility can reach to $10000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [41]. Furthermore the behavior of BP is ambipolar with high on-off ratio up to 10^5 , which provides opportunity to 2D complementary semiconductor electronics. Multilayer BP detector was implemented by Engel et al. [42] having stable performance, where in the data acquisition signal fluctuation is not noticed. Along with this the image quality is improved when there is increase in the gain of detector.

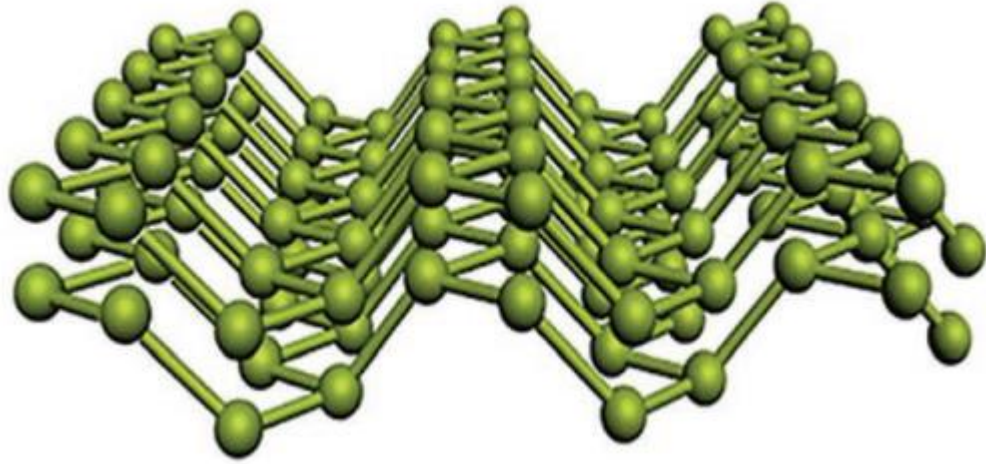


Figure 2.2: Two-dimensional structure of Black Phosphorous [40]

The lack of inversion symmetry leads to the electronic bands spin splitting driven by the spin orbit interaction. In 2H-TMDCs this is very important peculiarity. The spin degeneracy of the conduction band and the valence band maxima at K and K' are lifted because these points do not correspond to the time-reversal invariant momenta. In monolayer 2H-MoS₂ and WSe₂, where the spin splitting values ranges from 0.15eV to 0.46eV, where this effect is observed to be strong in the valence band [43]. To understand this trend the spin orbit interaction should be considered as a relativistic effect and this effect will be stronger for heavy elements. The conduction band spin splitting is even though an order of magnitude weaker but not negligible [44]. The spin splitting of bands at K and K' is opposite because of time reversal symmetry. This property of a material is referred as spin-valley coupling [45] and implies that the valley polarization of charge

carriers is automatically translated in to their spin polarization. In designing spintronic devices this intrinsic property may be used without involving magnetic material.

The covalent bond is facilitated by d orbitals of transition metals and the p orbitals of the chalcogen atoms in TMDCs monolayer. The pattern of atoms is hexagonal in c-axis, and weak vdW has held the individual layers. At the basal surface accessible orbitals of transition metal atoms and chalcogen atoms are involved in the intralayer bonding whereas for external or interlayer bonding high-energy antibonding orbitals are left, which results the absence of dangling bonds [45].

Interesting d-orbital physics arises due to the crystal field splitting of transition metal d-orbitals in TMDCs due to different stacking order [46]. The crystal field which splits the d-orbital of transition metal is based on their coordination environment with respect to the chalcogen atoms in TMDCs. In octahedrally coordinated transition metal atom, the d band splits to a e_g (d_{zz} , $d_{x^2-y^2}$) and t_{2g} (d_{yz} , d_{xy} , d_{xz}). And when the coordination with transition metal is trigonal prismatic, the d-band splits into three fold of A_1' (d_z^2), E' ($d_{x^2-y^2}$, d_{xy}) and E'' (d_{xz} , d_{yz}). A range of electronic properties that can be observed in different TMDCs can be qualitatively understood from this simple ionic picture. In the family of TMDCs, the different order of stacking and different positions of chalcogen atoms give rise to different phenomena based on electronic and vibrational properties.

2.1.3 Thermoelectric Properties of TMDCs

In search of renewable energy production, the direct conversion of unwanted heat to electricity has increased the importance of thermoelectric materials. Efficiency of a thermoelectric material depends on the voltage generated when a temperature gradient is maintained across the material. For efficient thermoelectric material the electrical conductivity is high and the thermal conductivity is low.

Nano structuring of material and quantum confinement effects in a material may be a good approach to improve the convergence capabilities and energy storage of a material. To overcome energy crisis, materials having good thermoelectric properties may provide partial solution to the problem. The electrostatic potential across a thermoelectric material is developed due to temperature gradient which is utilized for power. The Seebeck coefficient (SC) is defined by the conversion of heat to electric potential. In Bi_2Te_3 and Bi_2Se_3 , when the thickness was reduced from bulk to monolayer, improvement in their thermoelectric performance is observed [47, 48]. Theoretically large increase in ZT for monolayer Bi_2Te_3 has been predicted compared to their bulk [49-51]. In a single quintuple layer at the valence band edge, the density of modes has unique step-function shape which results in enhancement of ZT [50, 51]. The step-like shape and density of modes disappears in bilayer and trilayer, which leads to either slightly higher or slightly lower [51] value of ZT than that of the bulk.

To understand the variation of thermoelectric properties in TMDCs when it is reduced from bulk to layers, four TMDCs (Mo/WX_2 where $X=\text{S}$ and Se) were theoretically investigated. The improved degeneracy or near degeneracy of the band edges in these layers results an increase in ZT like Bi_2Te_3 . At room temperature, with energy differences of less than $k_B T$, different valleys become nearly degenerate. In these TMDCs the value of ZT is the largest, where the density of modes has the sharpest increase [52].

Thermoelectric properties of different TMDCs are investigated for search of efficient thermoelectric materials. To explore material having high thermoelectric performance theoretical investigation is an efficient method. Using first-principles method, Kai-Xuan Chen et al. [53] investigated the thermoelectric performance for series of TMDCs MX_2 ($M=\text{W}$ and Mo , $X=\text{S}$, Se) including monolayer, armchair (6, 6) and zigzag (10, 0) [53]. Each series is separately reported with consistent regularity. Large SC and ZT for monolayer are reported as compared to small nanotubes. Due to lower phononic thermal conductance, zigzag nano tube has larger ZT than the armchair nanotube. It is also reported that at room temperature the ZT for monolayer WSe_2 is 0.91 and for the Zigzag nanotube it is 0.47, which reveals the importance of layered materials. Hippalgaonkar et al. [54] reported a large power factor (PF) of $8.5 \text{ mWm}^{-1} \text{ K}^{-2}$ for MoS_2 at room temperature. This is one of the highest PF among the traditional thermoelectric materials. Thermoelectric properties of some TMDCs monolayers are reported [55-59]. For monolayer MoSe_2 at 1200 K a much low thermoelectric figure of merit of 0.1 is

reported by Kumar et al. [57]. In case of MoS₂ the value of ZT at 500 K is reported to be 0.11 by Jin et al. [55]. The value of ZT for monolayer WSe₂ is 0.7 at higher temperature which is better than the other reported materials. The reason behind such value of ZT is the high value of lattice thermal conductivity (K_l). The value of K_l at room temperature for monolayer MoS₂ is 100 Wm⁻¹K⁻¹ and for WSe₂ is 40 Wm⁻¹K⁻¹. Usually TMDCs have two different crystal structures, one is 2H-MoS₂ and the other is 1T-CdI₂ type [60]. In CdI₂, usually the transition metals are Ti, Zr and Hf etc. The lattice thermal conductivity is 15 times small for bulk Zr and Hf based TMDCs in comparison to Mo based TMDCs. The reason for this small value of K_l is that, the low lying optical modes strongly hybridize with acoustic mode [61]. For monolayer ZrS₂ in 1T phase similar behavior is also reported having a very small value of K_l equal to 3.29 Wm⁻¹K⁻¹ and ZT equal to 1.6 at 300K by Lv et al [59]. This reveals that these values are better than those of monolayer MoS₂. It is also observed that in monolayer TMDCs materials having 1T structure has small value of K_l than those of 2H-structure and hence has an enhanced ZT. Li et al. [62] theoretically investigated the thermoelectric properties of 1T-SnSe₂ monolayer semiconducting material. Results reveal that phonon thermal conductivity of the material is 3.27WmK⁻¹ at room temperature, which is much smaller than the 2H-TMDCs. The phonon calculations also reveal that the acoustics modes have lower frequency and couple with the optical mode which results the low phonon thermal conductivity. It is also reported that p-type doping enhance the thermoelectric performance and at 600 K the optimal ZT reaches to 0.94 which is higher than most of the 2H-TMDCs.

Effect of strain on the thermoelectric performance of ZrS_2 is theoretically reported by Lv et al. [59]. It is seen that applying the strain lead to increase the band gap and then it starts decreasing. Maximum band gap is achieved for ZrS_2 with 6% strain. Effective tuning of the SC is reported due to strain. Enhancement in SC compensates the drop in electrical conductivity, and hence maximum PF is obtained as the band gap increases. It is also reported that the simultaneous decrease in thermal conductivity and increase in SC enhance the thermoelectric performance of 6% strained ZrS_2 . H. Y. Lv et al. [63] also predicted the thermoelectric properties of HfS_2 and effect of strain on it. The maximum strain with which the material can withstand is 9%. It is also predicted that the thermoelectric performance of the material can be enhanced by applying strain. From the investigation of thermoelectric properties of 1T- ZrSe_2 and 1T- HfSe_2 by Guangqian Ding et al. [64] it is observed that PF of these materials are compatible with the MoS_2 monolayers. In these materials the high scattering rates and low group velocities are responsible for the low lattice thermal conductivity, which results high value of ZT in these materials. It is further suggested that n-type doping level of $\sim 10^{19} \text{ cm}^{-3}$ at moderate temperature will enhance the properties of these monolayers for thermoelectric applications. Dan Qin [65], using first principle calculation combined with Boltzmann equations have theoretically calculated the thermoelectric properties of single layer ZrSe_2 . The effect of tensile biaxial strain on thermoelectric performance was also investigated. Maximum PF is reported for monolayer with 7.5% strain. The ZT obtained for p and n-type doping is reported to be greater in strained than the unstrained monolayer. It is

effectively shown that in all of the cases the thermoelectric performance can be enhanced by applying strain.

2.1.4 Photocatalytic Properties of TMDCs

For hydrogen generation, photocatalytic water splitting is one of the most promising technologies. In 1970s the water splitting was demonstrated by Fujishima and Honda in the presence of UV light irradiation with TiO_2 photoanode and Pt cathode.

For promising material for water splitting some of the conditions may be fulfilled. Among these properties one is the band gap of the semiconductor must be such that it can drive the kinetics of oxygen and hydrogen evolution reactions, and the band edges must straddle the redox potential of water. In search of potential photocatalytic material, layered TMDCs were theoretically investigated. Among these monolayers TMDCs 13 are semi conducting in nature having four different types of band edges positions. MoS_2 , WS_2 , PtS_2 and PtSe_2 are confirmed as promising materials for water splitting. From the high enthalpies of solvation of these monolayers it is further confirmed that these monolayers are insoluble in water [66].

2.2 Tuning Properties of TMDCs

The properties of layered TMDCs can be tuned by doping [67], stacking [68], alloying [69], formation of superlattices [70] and strain engineering [71]. As band gap engineering plays vital role in the fabrication of devices used in optoelectronics, nanoelectronics and photonics. The band gap of 2D materials can possibly be tuned by alloying two different

materials having different band gap. Chen et al. [72] investigated the alloy of MoS₂ and WS₂ (Mo_{1-x}W_xS₂) for x=0-1. Experimentally it is investigated that the Mo and W atoms in monolayer Mo_{1-x}W_xS₂ are randomly arranged. The band gap was enhanced from 1.82eV to 1.99eV. The electronic structures of monolayer Mo_{1-x}W_xS₂ were further confirmed by DFT.

External electric field can be used to tune the band gap of layered materials like TMDCs. Using first principle investigations the band gap of layered materials MoS₂, MoSe₂, MoTe₂ and WS₂ were investigated [73]. It was observed that in contrast to graphene the band gap was decreasing by applying the electric field from 2-3V/nm in bilayers of these materials.

2.2.1 Strain Engineering in TMDCs

Strain changes the band gap, mobility of electrons and hence the effective mass, so it can be used as a useful tool to enhance performance of the devices. Layered TMDCs before breaking can with stand up to 10% strain [74]. This high enough strain make considerable changes in different properties of a material makes TMDCs promising for device applications. In case of lowering strain the three fold symmetry of these material is advantageous than the six fold symmetry of graphene [75, 76]. In semiconducting TMDCs the band gap is reduced by applying tensile strain [77-80] and also change the nature of band gap from direct to indirect [77,78, 81-87]. Strain also modulates thermal conductivity [88,89], spin orbit coupling [90, 91], dielectric properties [92] and on state

current in TMDCs transistors. Thus for the realization of various properties like electronic, electromechanical, optoelectronics, spintronics, strain engineering is a better approach.

In nanomechanical devices, for the application of strain a wide range of strategies have been applied. Among these are the fabrication of suspended devices polymer sacrificial layers [93] or wet-etching [94], trenches or pre-patterned holes for transfer on a substrate [95], pre-stretched or flexible [96-98] substrates, tailored nano-patterns [99] and piezoelectric [100] or thermal expansion [101]. To monitor the effect of strain on the vibrational modes and optical band gap of layered MoS₂ and other TMDCs [102,103], photoluminescence spectroscopy [96-100,104], absorption spectroscopy [97] and Raman spectroscopy [96, 98, 100, 105] are used. Theoretically predicted redshift of $\sim 70\text{meV}/\%$ of strain for direct gap transition and $\sim 110\text{ meV}/\%$ strain for the indirect gap transition and reduction of band gap [96] was confirmed by photoluminescence measurements [97] in MoS₂ bilayers. Furthermore the photoluminescence spectroscopy is only limited to mono and bilayer materials. Raman spectroscopy reveals that in MoS₂ monolayer and bilayer the doubly degenerate in-plane vibrational modes splits due to the Raman modes shift by strain induced symmetry breaking [96].

In TMDCs, tuning of band gap by strain and piezoelectric effect originates piezoresistive effects and piezotronics respectively which modulate strain induced modulation. Because of broken inversion symmetry, odd number layered 2H polymorphs of layered TMDCs are piezoelectric [106, 107]. For MoS₂ voltage to strain [96] and strain

to voltage [108] conversion has been reported. In a material the increase or decrease in height of Schottky barrier depends on the direction of polarization field or piezoelectric polarization which is due to piezotronic effect. In atomically thin TMDCs both in odd and even-layered, the piezoresistive effect appears unlike piezoelectric effect. Using atomic force microscope, piezoresistive effect can be quantified in locally strained, suspended MoS₂ by electromechanical experiment where in parallel with mechanical deformation, electrical conductivity is measured. In mono and bilayer MoS₂ the relative change in electrical resistance to strain (gauge factor) is greater than 100 [94], and have high piezoresistive coefficients which is two times greater than graphene [109, 110] and comparable with state of the art silicon strain sensor [111]. Furthermore the fracture strain in silicon is 0.7% [112] while in MoS₂ it is 11% [73]. So for highly deformable objects and curved surfaces MoS₂ flexible strain sensors will be more suitable. For ultra-power transduction logic devices, MoS₂ is a promising material due to the presence of piezoelectric and piezoresistive effect [113, 114]. The optical response in MoS₂ based flexible photodetectors can be modulated using piezophototronic effects [115].

2.2.2 Heterostructures of Transition Metal Dichalcogenides

The diversity in properties and functionalities of layered materials attracted the researchers to make heterostructures of these materials. For improvement in material application or for study of new phenomena different efforts are made [116-118]. The high defect density in traditionally alloyed material for electronic structure engineering is

much challenging. In MoS₂/MoSe₂ alloys, the PL peak energy tuning between 670nm and 795nm is an example of such an approach [119].

It has been experimentally proved that heterostructures are generally categorized into two types: in-plane stacking and out-of-plane stacking [120]. In-plane heterostructures are formed by lateral or side-by-side stitching of monolayers through covalent bonding. However, stacking of different monolayers via weak vdW interactions is termed as vdW or vertical heterostructures, shown in Figure 2.3 and Figure 2.4.

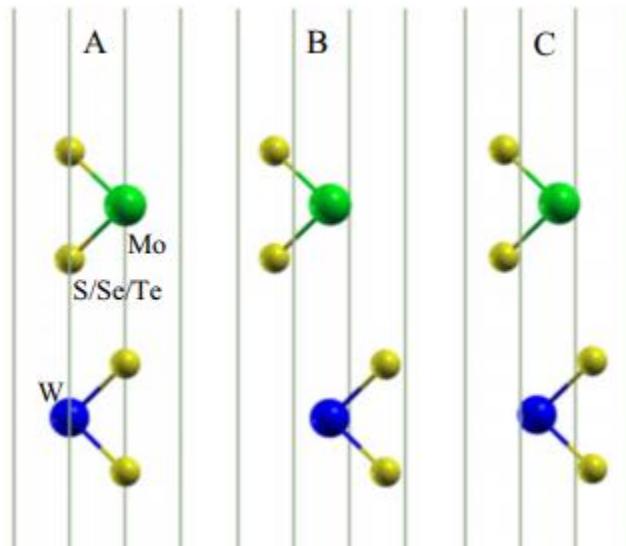


Figure 2.3: Out-of-plane heterostructures [121]

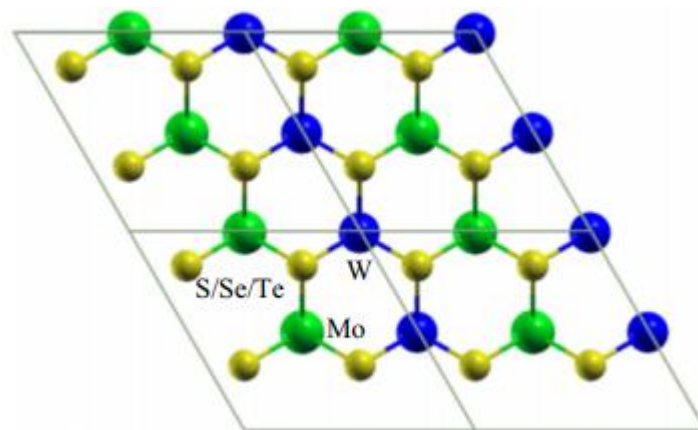


Figure 2.4: In-plane heterostructures [121].

To design electronic and optoelectronic devices suitable for generation of charge carriers, photons, excitons and their transportation vdW-h play important role due to their promising optical and electronic properties. Invention of flexible, low power and ultrathin devices are possible from assembling vdW heterostructure having atomically sharp interface and layered structure. For obtaining promising properties of materials, their heterostructures are the main focus of interest of researchers. Various heterostructures are experimentally developed from the junction of two semiconductors or from the metal-semiconductor contact [122]. These heterostructures enhance the electronic and optical properties due to their fascinating band structure [123-127]. Therefore in electronics, photonics and optoelectronics to design new devices semiconducting heterostructures are considered as efficient materials.

To form a vdW heterostructure, layered material are stacked one above the other, these stacked heterostructures are held by van der Waals forces, forming thin and smooth junctions. These materials play important role in devices having size of sub-nano meter. It has been observed that at van der Waals interface the transfer of charge and in interlayer excitons takes place. The uniqueness of these materials lie in the absence of material space along the c-axis. In vdW-h, the effective electronic band structures are dependent on the crystallographic orientation of the individual layers [128, 129].

In $\text{MoS}_2/\text{WSe}_2$ vdW heterostructures tunneling-mediated recombination is demonstrated at the vertical p-n junctions of the two materials [130]. Britnell et al. [131] constructed a photovoltaic device with 30% external quantum efficiency from a vdW-h of

Graphene/TMDCs/graphene. In search of efficient electroluminescence and photoluminescence, elastic polymer substrates in flexible optoelectronics are used to engineer light emitting device from TMDCs quantum wells by Withers et al. [132] where h-BN was used as a tunneling barrier and for charge extraction transparent conducting layer of graphene was used [132]. In MoSe₂/WSe₂ heterostructures, the photoexcited electron-hole pairs separation into inter-layer excitons with longer life time than in the individual layer observed [133]. From the proper alignment of the electronic band structure of the monolayers Hong et al. [68] demonstrated photoexcited MoS₂/WS₂ vdW heterostructures with very fast carrier separation of ~50 fs. PL tuning by mono and few-layer h-BN tunneling barriers are reported for MoS₂/WSe₂ [129]. MoS₂/graphene heterostructure was theoretically investigated for effective Schottky barrier and MoS₂/WS₂ heterostructure for excitonic-photovoltaic cells, having ~1% conversion efficiency which can be enhanced by increasing the stacking [134].

In-plane lateral heterostructures of TMDCs are synthesized [135, 136], due to defect-mediated recombination in a monolayer of MoSe₂-WSe₂, at heterostructure interface with maximum integrated intensity tuneable between 760 nm to 790 nm PL emission was realized [136]. Using a photocurrent spectral AFM in monolayer WSe₂/MoS₂ lateral heterostructures, characteristic diode behavior is reported [137].

This is also expected that strain will affect the heterostructures of TMDCs formed by different layers in vertical stacking [138, 139] due to interlayer interaction and lattice mismatch. Strain can be effectively used to modulate band gap in hybrid bilayers and

multilayers. Strain effect on anisotropic TMDCs like ReSe_2 and ReS_2 are theoretically investigated [140]. For these materials strong dependence of strain is observed on direction of applied strain in their 1T phase. In a direction perpendicular to the layers if strain is applied may significantly enhance the carrier mobility.

The band structures alignment of the donors and acceptor play vital role in transfer of charge through the heterojunction, therefore different type of heterostructures are investigated. In type-I heterostructures, both electron and hole accumulates in one of the two components or in other words the narrow-band gap material is nestled entirely in the wider-band gap. As both holes and electrons are confined within the same material which leads to fast recombination. In type II and III heterostructures, the holes and electrons are separated into different layers of the semiconductors. Due to separate layers the electrons and holes will take long time for recombination in type II heterostructures. Type-II heterostructures allow larger offsets either on conduction or valance side and are much useful in unipolar electronics due to strong carrier confinement. Good examples of strong confinement in type-II heterostructures are InAs/AlSb based high electron mobility transistors [141]. Also in bipolar transistor as hot electron injector [142] and in tunneling bipolar transistor as quantum well resonant [143], the conduction band notches of type-II band can be used. For transition energy to be engineered from conduction to valance band the type-II and III heterojunctions are useful, particularly to enhance the current density in tunneling field effect transistors [144], wavelength photo detector [145]

and intersubband superlattice lasers [146]. Types of band alignments in heterostructure are shown in Figure 2.5.

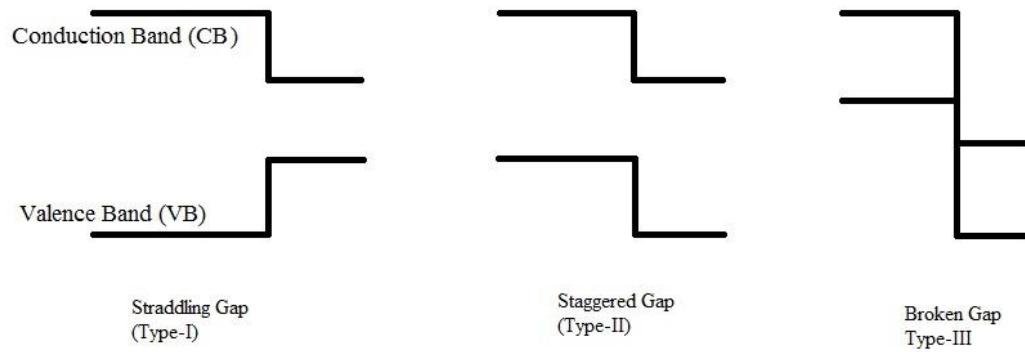


Figure 2.5: Types of band alignment in heterostructure [80].

In some of these heterostructures the observed band alignment is type II in which the recombination of charge is slow down causing the reduction of electron-hole wave function overlapping [147], which leads to an effectual way for the detection and harvesting of light [120, 148] .

2.3 Applications of 2D TMDCs

2D TMDCs have demonstrated physical properties, which make them potential candidates for novel device applications. In this section, we have briefly presented various TMDCs applications including, electronic, optoelectronic and thermoelectric.

2.3.1 Electronic Applications of TMDCs Heterostructures

Heterostructures comprised of out-of-plane stacking of layered materials possess metamaterial-like structure have interesting properties. Theoretically several heterojunction composed of TMDCs, TMDCs/BN and TMDCs/graphene are studied [68, 124, 149,150]. Indirect band gap in bilayer TMDCs heterostructure with same chalcogen atom is observed [151]. For example 1.58 eV indirect band gap in MoS_2/WS_2 , with VBM at K points and is in the one layer and the CBM is in the other layer [149]. Direct band gap is observed in the heterostructure composed of monolayers having different chalcogen atoms like $\text{WS}_2/\text{MoSe}_2$, $\text{MoS}_2/\text{MoSe}_2$ and WS_2/WSe_2 [149]. Direct band gap of constituents monolayers are greater than their heterostructure in TMDCs due to giant Stark effect. In WS_2/WSe_2 and $\text{MoS}_2/\text{WSe}_2$ heterostructures the band gaps are smaller than the constituents monolayers [72, 151,152]. The charge difference between net negative charge (S) and net positive charge (Se) creates intrinsic vertical electric field which helps in separation of holes and photogenerated electrons. A type II p-n junction having built-in electric field confined within 2 unit cell can be created in $\text{WSe}_2\text{-MoSe}_2$ and $\text{WSe}_2\text{-MoS}_2$ vdW-h. In these atomically thin junctions the quantum tunneling dominates charge transport instead of semiconductor depletion region [130]. In MoS_2/WS_2 and $\text{MoS}_2/\text{MoSe}_2$ vdW-h, within 50 fs ultrafast charge carrier has been demonstrated [68, 153]. Excitons have longer life (~ 1.8 ns) due to strong Coulomb attraction in vdW heterojunction than the isolated monolayer TMDCs [154], which

results the carrier diffusion length to be much longer and extract photo-induced charge carriers efficiently [155]. Between such junctions, to control the band alignment electrostatic gating can be used as a possible solution. Through Stark effect the externally perpendicular electric field can be used to tune the excitons effect [156], where the shifted excitons optical absorption resonance peak changes the absorption intensity. In self-electro-optic effect device, 2-D heterostructure lasers and in nonlinear optoelectronic devices (modulator) are potential applications of excitonic effects in vdW heterojunction of 2-D TMDCs [157,158].

2.3.2 Thermoelectric Applications

Due to promising engineering applications and extraordinary physical, mechanical and chemical properties TMDCs have attracted much attention [159]. The large flexibility, strong chemical stability and the semiconducting characteristics makes TMDCs interesting materials. In smart health diagnostics, flexible displays, wearable computing and in ubiquitous electronics TMDCs have are a promising materials [160]. For thermoelectric applications (heat and electricity conversion), due to low thermal and high electrical conductivity TMDCs are suitable materials. To evaluate the thermal to electrical energy conversion efficiency a dimensionless figure of merit ZT is used, which depends upon the SC, electrical and thermal conductivity [161]. The first ever 2D material graphene has high SC [162] but the ultrahigh thermal conductivity limits its advantages as an efficient thermoelectric material [163]. In comparison with inorganic thermoelectric

materials, organic thermoelectric devices are constructed using conjugated polymers and related processing techniques. These materials are advantageous due to low cost, low weight, elasticity, large area deposition and material abundance [164-166]. These materials have the value of ZT approaching to the best inorganic thermoelectric materials. For developing energy generation devices and integrated wearable heating/cooling, the alternative materials of organic thermoelectric materials are TMDCs. In comparison to graphene ultra high thermal conductivity, TMDCs have very low thermal conductivity. In comparison to black phosphorene the electrical conductivity and SC of TMDCs are relatively higher. These excellent properties increase the exciting expectation of high-performance thermoelectric applications in TMDCs. For the generation of electricity, using the temperature difference between ambient air and human body the TMDCs based self-powered wearable electronics are attractive on one hand while on the other hand thermal cooling is caused when electric current passes through TMDCs-based modules and heat is carried away [161]. Theoretical and experimental investigations have been carried out to study the thermoelectric response of TMDCs [167] and to enhance the thermoelectric efficiency of TMDCs many have been exploited [168].

2.3.3 Photocatalytic Hydrogen Evolution Reaction

Solar energy is used for the cheap production of hydrogen through hydrogen evolution reaction (HER) [169-172]. The dielectric constant of the photocatalyst determines the absorption rate of visible light, which is proportional to solar-to-fuel energy conversion.

The intra band transition is related to the imaginary part of dielectric constant functions which is associated with the capability of material for absorption of light [173]. Theoretical investigation of monolayer MoS₂, in visible region of light shows strong absorption peak. At pH 0, in monolayer MoS₂ the oxidizing and reducing powers are 0.06 and 0.41eV respectively [173], which is not ideal. To modify electronic band structure mechanical strain [174, 175] or extrinsic doping [173, 176-178] can be used. Oxidizing and reducing power of MoS₂ changes to 0.19 and 0.20eV when S atom is replaced by P and makes it ideal for HER. By adjusting the pH for water splitting, the redox potential can be adjusted to match the CBM and VBM.

On the basal surface, the catalytically active sites and metallic character of 1T phase shows better activity than the 2H phase for HER [179]. In 2H phase the active sites are located mainly at the edges, which are prone to oxidation and resulting reduced catalytic activity. Furthermore, in 2H polytypes the activity is limited because the charge transfer kinetics is hindered by high electrical resistance [180].

In monolayer TMDCs due to high exciton mobility have long diffusion length, thus the transfer of hole and electron, which are photogenerated are facilitated to the redox sites. The short transit distance in atomically thick monolayer TMDCs for the photo excited electron to move to the underlying conducting substrate and to the redox site from the TMDCs sheets is much advantageous in HER. The photocatalytic activity for natural TMDCs are investigated, which reveals that due to quantum confinement, the nanoparticles with 1.8eV indirect band gap show improved photocatalytic activity in

HER than their bulk counterpart [181, 182]. In the porous structure due to large surface area the number of active sites and optical absorption path length is enlarged in double-gyroid structure which creates interconnected network of porous sheets like that of graphene oxide porous hydrogel.

2.3.4 Solar Cells Applications of TMDCs

One nanometer thick solar cells composed of graphene and stacked monolayers of TMDCs are investigated. It is observed that TMDCs having thickness less than 1 nm can absorb from 5 to 10% of the incident sun light which is an order higher than that absorbed by Si and GaAs of the same size [133]. Calculation shows that sunlight absorbed by 50 nm of Si is equal to that of single TMDCs monolayer and the electric current produced by TMDCs is as high as $4.5\text{mA}/\text{cm}^2$, furthermore the comparison is attractive at nanometer level because the power conversion efficiency (PCE) of TMDCs (1-2%) is considerably less than Si and GaAs (20%). Stacked TMDCs form a 3-D structure, which will remove the constraints in ultrathin layers, of short optical absorption path. Another approach to remove these constraints is to use multi junction geometry, different TMDCs having energy from infrared to visible are interconnected like graphene as the interlayer in tandem solar cells [183]. Multiple p-n junctions are used in these cells. The junction in these cells are modified to a particular frequency and to generate a higher PCE, from each sub shell the current is combined to the graphene, where the theoretical limit of each component is exceeded. In addition to p-n junction made of p-type and n-

type TMDCs monolayer [130, 177, 184-187], p-n junction of TMDCs with semiconducting material like Si and GaAs are also used in solar cells. The PCE of type II heterostructure of p-type Si and n-type MoS₂ is up to 5.23% [188].

2.3.5 Piezoelectric Applications of TMDCs

In medical sensors and in environmental devices there is always need of devices which are self-powered. For micro or nano systems devices nanogenerators supply is required self-sustainable power [189]. Based on piezoelectric effect in layered materials nano generators are also developed [190, 191]. Electric polarization is produced in piezoelectric material when mechanical stress is applied on it and the originated piezoelectricity is due to structural non-centrosymmetry. Due to lack of center symmetry 21 out of 32 crystal classes are noncentrosymmetric, and among these 20 shows direct piezoelectricity. The presence of interlayer inversion center in bulk TMDCs make them non-suitable for piezoelectricity. In case of layered TMDCs as the thickness reduces the inversion center is lost due which layered TMDCs are distinct from the bulk one and are potential candidates for piezoelectricity when strain-induced lattice distortion is produced in the material. The piezoelectric coefficients are theoretically calculated by Duerloo et al. [106] for a series of monolayer TMDCs. In comparison to the traditional bulk wurtzite structures strong piezoelectric coupling were predicted in these monolayers. In atomically thin layered TMDCs the piezoelectric properties are experimentally measured [108].

In a free standing monolayer MoS₂ piezoelectricity are experimentally reported by Hanyu et al. [192]. Under isotropic mechanical deformation the theoretical prediction of piezoelectric effect was experimentally studied by Junjie et al. [193] in triangle monolayer MoS₂. In piezoelectric devices due to robust piezoelectricity, flexibility and stretchability layered piezoelectric materials have great potential applications. In low power logic circuits as mechanical resonator, piezoelectric-gated diodes and electromechanical sensors, TMDCs layered materials has a profound effect. Energy harvesting from the environment by self-powered wireless nanosystems and nanodevices in nanogenerators was possible due to conversion of mechanical energy in to electrical energy. Due to controlled number of layers and large area TMDCs meets the requirements of nanopiezoelectronics, and can be considered as efficient materials to be explored for nanopiezoelectronics applications.

Chapter 3

Theory and Computational Techniques

A brief discussion to the basic principles with mathematical subtleties where necessary are given to complete any discussion. The objective of this chapter in the thesis is how to use the theory for describing various properties of layered transition metal dichalcogenides structures and establish an origin for the explanation of the equations that will be used latter in all the applications. The basic theorems on which the theory is based will also be explained. A brief historical introduction to the basic theories are given in the first section, in the next section DFT is discussed, and in the last section the main computational details and the parameters being used are summarized.

3.1 Many Body Problem

In solid form, materials are composed of electrons having very small mass with negative charge and nuclei having heavy mass and positive charge as compared to electrons. For N number of nuclei there are $N+ZN$ numbers of interacting particles, these interacting particles interacts through electromagnetic forces. Due to very small size of these interacting particles, a system under study must be treated quantum mechanically. When a system have N numbers of nuclei having mass M_i and at $\vec{R}_i$ and at $\vec{r}_i$ electrons with mass m_e the Hamiltonian can be written as:

$$\begin{aligned}
\hat{H} = & \frac{-\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} \\
& + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}
\end{aligned} \tag{3.1}$$

For nuclei and electrons kinetic energy (K.E) operators are represented by the first and second terms respectively, while Columbic interaction between electron- nuclei is represented by the third term, the Columbic interaction between electron-electron by the fourth term and the Columbic interaction between nuclei-nuclei are respectively denoted last term. To find an exact solution to the problem which is under study different approximation are used.

3.1.1 The Born-Oppenheimer approximation

In solids, in comparison to electrons the nuclei are relatively slow and heavy, and are considered "frozen" at a fixed location, and electrons within the solids are considered to be momentarily balanced with these heavy nuclei. In many of these physical problems, to the electrons the nucleus acts as an external field and has positive charge, and the electrons are considered as key particles that affect the physical behavior of materials. By application of this approximation, the NZ electrons system interacts with the external potential of the fixed core. As the K.E of these fixed nuclei is zero so in equation 3.1 the first term disappears. The term left in Equation 3.1 is electrons cloud K.E and potential

energy (P.E) due to interaction between electrons and interaction between nuclei with electrons can be summarized as

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext} \quad 3.2$$

In equation 3.2 the first two terms are generic and involve only multi-electron systems, but are not applicable to attractive nuclear force systems such as multi-proton systems. The last term $\hat{V}_{ext}$ contain the specific information related to the system. Here nucleus external potential is represented by $\hat{V}_{ext}$.

3.1.2 Hartree-Fock (HF) Theory

After the approximation of Born-Oppenheimer, the HF theory is assumed to be able to achieve the exact solution of wave function of quantum multi-particle problem through a single Slater determinant of the N-spin orbit and to help determining the energy of the system under study at rest. The Slater determinant of the N electronic system is as follows

$$\psi = \begin{vmatrix} \psi_1(X_1) & \psi_1(X_2) & \dots & \psi_1(X_N) \\ \vdots & \vdots & & \vdots \\ \psi_i(X_1) & \psi_i(X_2) & \dots & \psi_i(X_N) \\ \vdots & \vdots & & \vdots \\ \psi_N(X_1) & \psi_N(X_2) & \dots & \psi_N(X_N) \end{vmatrix} \quad 3.3$$

The coordinate of space and spin are represented by “X”. By Pauli Exclusion Principle, the anti-symmetric wave function is written as

$$\psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) = -\psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) \quad 3.4$$

For N-electron system this leads to the full HF equation

$$\begin{aligned} \epsilon_i \psi_i(r) = & \left(-\frac{1}{2} \nabla^2 + V_{ion}(r) + \sum_j \int dr' \frac{|\psi_i(r')|^2}{|r - r'|} \right) \psi_i(r) \\ & - \sum_j \delta_{\sigma_i \sigma_j} \int dr' \frac{\psi_j^*(r') \psi_i(r')}{|r - r'|} \psi_j(r) \end{aligned} \quad 3.5$$

In the above equation on the right side, the first term and the second term, respectively represents the K.E contributions and ion electron potential. The electrostatic potential of the electron (Hartree-term) is represented by the third term, and the exchange term which is produced by determinant form of the wave function and Pauli principle are represented by the fourth term. In HF theory the major problem is that it ignores electronic correlations and it cannot explain electronic structures. Conversely, in several cases, the HF theory proposes a more precise qualitative prediction. Another method of HF theory is DFT, DFT deals with the exchange and associated energy of the corresponding system [194].

3.1.3 Variational Principle (VP)

The VP stresses that "the Schrödinger equation is considered to be stationary" or that the "wave function of stationary H is the Eigen function of energy". The time-independent

Schrodinger equation having Hamiltonian H , eigenvector ψ_n and energy eigenvalue E_n in Hilbert space is written

$$H|\psi_n\rangle = E_n|\psi_n\rangle \quad 3.6$$

The expectation value of H must be satisfied when ψ_n is normalized.

$$\langle H \rangle = E = \langle \psi_n | H | \psi_n \rangle / \langle \psi_n | \psi_n \rangle > E_0 \quad 3.7$$

Where the exact ground state energy is denoted by E_0 . The true ground state Eigen function will be represented by ψ_n if there is equality in above equation. Furthermore the best wave function is obtained when E is minimized.

3.2 Density Functional Theory (DFT)

Density functional theory (DFT) is a standard quantum mechanical approach to investigate different properties of solids like structure, electronic and polarization. DFT was proposed by Hohenberg and Kohn [195] which solve the complex system and reduced the $3N$ variable to three variables in terms of electronic density (x, y, z) hence become the mostly used methodology to study different properties accurately at a very low cost.

3.2.1 The Hohenberg-Kohn (HK) Theorem

The fundamental references of DFT is the work of Hohenberg and Kohn. It has been seen that for electronic system the ground state energy (GSE) is functional of electron density. Furthermore it is concluded that with respect to electron density, minimizing the energy functional, we can obtain the GSE. When the density is the true ground-state electron density, this minimizes the energy functional. These results can be summarized in two theorems as follows.

Theorem I: *The external potential $V_{\text{ext}}(r)$ is determined by electron density $n_0(r)$.*

As number of electrons can be determined from $n_0(r)$ for a system, so for other electronic properties the ground state wave function can also be determined from $n_0(r)$.

From this it is concluded that the electron density uniquely determines the Hamiltonian operator.

Theorem II: *The global minimum possible value of the functional $F_{\text{HK}}[n_0]$ gives the exact ground state energy $E[n_0]$ and the electronic density will be the exact ground state density.*

$$E_0 = \min_{n \rightarrow N} E[n] = E[n_0] \quad 3.8$$

The variational principle is shown by limit $n \rightarrow N$, from which the ground state densities can be determined. The energy of a system is defined as the functional of electronic density which proves that electron density at the ground state minimizes the energy

functional [196]. In comparison to the wave functional approach all of the terms in the above equation (3.8) are density dependent, which give poor results.

These theorems are proved for non-degenerate ground state system. To determine the exact functional Levy [197] extended the definition of functional in formally tractable and more clarified physical meaning. The HK theorems are extended to other formalism, such as for open shell molecule description (for transition metal complexes) Spin density functional theory (SDFT) [198], for the calculation of properties of the excited states Ensemble density functional theory (EDFT) [199,200], for systems interacting with magnetic fields Current density functional theory (CDFT) [201, 202], for systems with heavy atoms Relativistic Density Functional Theory (RDFT) [203, 204] and for the study of excited states and systems that interacts with time dependent potentials, Time dependent density functional theory (TDDFT) [205].

3.2.2 Kohn-Sham Equation

Kohn-Sham (KS) proposed an elegant method to solve many electrons system by considering no electron-electron repulsion. The density of such a non-interacting system is equal to ground state electron density. The electron behaves like charge less particles in such a non-interacting electron system having no interaction with each other. The field force produced by other electrons is experienced by each electron. Using single particle wave function (ϕ_i) the K.E of such system can be exactly calculated.

$$T_s = \sum_{i=1}^N \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_i \right\rangle \quad 3.9$$

The Kohn-Sham functional K.E is represented by T_s . The total GSE can be expressed as.

$$E[n_0] = T_s[n_0] + U[n_0] + E_{xc}[n_0] + \int V(r)n_0(r)d^3r \quad 3.10$$

Electrons classical electrostatic energy is represented by $U[n_0]$, the exchange correlation by $E_{xc}[n_0]$ and the external potential by $V(r)$. The E_{xc} term is used for the contribution of all the unknown spin-dependent energy. The $E_{xc}[n_0]$ is the sum of exchange and correlation energies and has no exact solution. So we can only approximate the exchange-correlation.

3.2.3 Exchange-Correlation Functionals

For charge density the unknown functional of exchange and correlation is introduced to replace the many electron problem by single electron problem. The main concern is that for exchange-correlation there is no detailed formalism in Kohn-Sham, to obtain exchange correlation energy exchange-correlation functional are approximated to solve the KS equation. Different exchange correlation are given below.

Local density approximation (LDA)

Generalized gradient approximation (GGA)

3.2.4 Local Density Approximation

In DFT the most widely used approximation to find E_{xc} is LDA. LDA is proposed for homogeneous electron gas system with interacting electron. This approximation will work for system with spatial variations in density. The approximation is mathematically expressed as

$$E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}^{heg}(n(r)) d^3r \quad 3.11$$

In the equation a homogeneous electron gas of density $n(r)$ the exchange-correlation per electron is denoted by $E_{xc}^{LDA}n(r)$. The high density limit is denoted by ϵ_{xc} which can accurately be computed at any density. To include the electronic spin this formalism can be generalized to the local spin-density approximation (LSDA) [206, 207].

$$E_{xc}^{LSDA}[n_{\uparrow}, n_{\downarrow}] = \int n(r) \epsilon_{xc}^{heg}(n_{\uparrow}(r), n_{\downarrow}(r)) d^3r \quad 3.12$$

Including spin in LDA, unexpectedly its domain of applicability extended beyond the nearly-free homogeneous electron gas and for inhomogeneous system correct results were obtained. In LDA the spin term was included by Perdew and Zunger [208] in 1981.

3.2.5 Generalized Gradient Approximation (GGA)

GGA is an improvement in the exchange-correlation functionals [209, 210]. GGA is still local formulation and depends on electron density $n_0(r)$ and electronic density. GGA is used to treat non-homogeneous systems where density is varying. GGA is described by

taking gradient of current density $\nabla n_0(r)$ which is better exchange-correlation functional for inhomogeneous system.

$$E_{xc}^{GGA}[n_0] = \int f_{xc}^{GGA}(n_0(r) \nabla n_0(r)) d^3r \quad 3.13$$

It is the well-known expression for GGA. Where the exchange-correlation energy per electron density is represented by f_{xc}^{GGA} . GGA depends on the density gradient $\nabla n_0(r)$. If spin term is included in GGA then

$$E_{xc}^{GGA}[n_0(r, \uparrow, \downarrow)] = \int f_{xc}^{GGA}(n_0 \uparrow, \downarrow) \nabla n_0(r, \uparrow, \downarrow) d^3r \quad 3.14$$

In comparison better results are provided by GGA than LDA. PBE96, B-88, PW-86 are the commonly used GGA potentials [211-217].

3.2.6 Heyd-Scuseria-Ernzerhof (HSE) exchange-correlation functional

After the use of LDA for quite some time in solid state physics, the DFT become a valuable tool in chemistry with the advent of functional based on GGA. The induction of Hartree-Fock (HF) in hybrid density functionals [218] has better results than the GGA. For large system linear scale DFT and HF [219-221] methods have reduced the calculation cost. Fast multipole method (FMM) [222-227] can efficiently calculate the long range Coulomb interaction. But for HF exchange interaction this method cannot be used. The range of exchange correlation interaction was shown by Kohn to decay exponentially as a function of band gap in insulators. For a system with sizable band gap

various attempt were made to exploit the exponential decay in the system [220,228,229]. These attempts were failed for small are no gaps. The failure of pure DFT calculations increased the demand of hybrid calculations.

An error function screened Coulomb Potential is used in HSE (Heyd-Scuseria-Ernzerhof) [230] exchange-correlation potential especially in system with no gap to calculate the exchange portion of the energy in order to improve the computational efficiency.

$$E_{xc}^{\omega PBEh} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE} \quad 3.15$$

Where ‘ a ’ and ‘ ω ’ are the mixing parameter and adjustable parameter respectively to control the short-rangeness of interaction. For most of the systems good results were obtained at $a = \frac{1}{4}$ and $\omega = 0.2$. For $\omega = 0$ the HSE exchange-correlation functional degenerates to PBE0 hybrid functional. The short range HF exact exchange functional is represented by $E_x^{HF,SR}(\omega)$, components of the PBE exchange functional for short range by $E_x^{PBE,SR}(\omega)$ and for long range by $E_x^{PBE,LR}(\omega)$. The last term $E_c^{PBE}(\omega)$ represents the PBE correlation functional [209].

3.2.7 The Augmented Plane Wave (APW)

The usefulness of Pseudopotential cannot be denied but for some reasons the alternatives are getting more attention. Pseudopotential method is not appropriate for information inherently contained in region near to the nucleus. The ideas for APW basis and

Pseudopotential are similar. As the electron far away from nuclei are more are less free, to describe free electrons plane waves are used, and electrons near to the nuclei behave like they are in a free atom. The space is divided in two regions due to far away and near to atom electrons. A *muffin tin sphere*, around each i.e. atom a sphere of radius R_α and the remaining space out side the *muffin tin sphere* is known as the *interstitial region*. For the expansion of $\psi_{\vec{k}}^n$, The APW can be expressed as:

$$\phi_{\vec{K}}^{\vec{k}}(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K})\cdot\vec{r}} & \vec{r} \in I \\ \sum_{l,m} A_{lm}^{\alpha, \vec{k}+\vec{K}} u_l^\alpha(r', E) Y_m^l(\vec{r}') & \vec{r} \in S_\alpha \end{cases} \quad 3.16$$

Here the unit cell volume is represented by V while $\vec{k}, \vec{K}$ and $\vec{r}$ have their common meaning. Like the plane wave basis set the APW basis set is $\vec{k}$ -dependent. With respect to center of each sphere, $\vec{r}'$ represents the position inside the sphere. r' represents the length of $\vec{r}'$, and for the direction of $\vec{r}'$ in spherical coordinates the angles θ and ϕ' are indicated by $\hat{r}'$. The Y_m^l represents the spherical harmonics. Like E , $A_{lm}^{\alpha, \vec{k}+\vec{K}}$ is the unknown parameter having the dimension of energy. For a free atom α having energy E the solution of radial part of the Schrodinger equation are given by u_l^α . For a free atom to find the solution u_l^α , the boundary condition $u_l^\alpha(r, E)$ must vanish for $r \rightarrow \infty$, which will limit the energies. In this case as the boundary condition can not be applied so for E we have to find numerical solution. The u_l^α are part the of the basis function and do not corresponds to something physical.

3.3 Boltzmann's Transport Theory

By the application of external field to a material the carriers (electron and phonons) start motion, the restriction to the motion of these particles is the scattering between them. Due to collision the interacting particles exchange momentum and energy and as a result the equilibrium of the carriers changes. These transport conditions are explained by two theories, the Green-Kubo theory [231] and the Boltzmann's Theory [232]. Transport parameters are related to the correlation function of electric current or heat flow by Kubo theory. While transport properties in terms of relaxation times as a result of various effects are treated by Boltzmann's theory. For a number of applications the Boltzmann's theory is valid and good agreement for the results obtained through the theory with experimental are achieved. In this section Boltzmann's theory is used to merge the electronic structure derived from first principle approach into electronic transport coefficient.

The electron system was described by Boltzmann theory by introducing a distribution function, where for electron in equilibrium state it is given by Fermi function. It is dependent on band index 'n' and the wave vector 'k' which represents the quantum number of electronic states. The distribution function for such an arrangement is given by $f_n(r, k, t)$. The distribution function in the neighborhood of spatial coordinates 'r' may be changed due to diffusion (some electron move to the neighborhood and some move in from the neighborhood), external field (electric field or temperature gradient) and

collision (interaction between electron-electron, electron-phonon and impurity-electron).

The total change of distribution due to diffusion, external field and collision is given by

$$\dot{f} = \dot{f}_{diff} + \dot{f}_{field} + \dot{f}_{coll} \quad 3.17$$

Here the time derivative is denoted by a dot on the function. When steady state is reached then the number of particles entering and leaving will be equal. So $\dot{f} = 0$ and in such case the Boltzmann equation can be written as

$$\dot{f}_{diff} + \dot{f}_{field} = -\frac{df}{dt_{coll}} \quad 3.18$$

To describe the scattering effect if one introduce the relaxation time $\tau(k)$ and assume that $f_n(r, k, t)$ approaches the equilibrium distribution $f^0(k)$, then

$$\frac{\partial f}{\partial t_{coll}} = \frac{f(k) - f^0(k)}{\tau(k)} \quad 3.19$$

as the function f is dependent on (r, k, t) , and due to diffusion and external field its distribution changes, so the rate of change of distribution is given by

$$-\dot{f}_{diff+field} = \frac{\partial f}{\partial r} \frac{r}{dt} + \frac{\partial f}{\partial k} \frac{e\mathcal{E}}{\hbar} \quad 3.20$$

Where

$$\frac{r}{dt} = v(k) \frac{1}{\hbar} \frac{\partial E}{\partial k} \quad 3.21$$

As there is very small deviation of f from f^0 , so in the above equation if we replace f by f^0 then from the definition of f^0 one can easily obtain the relation

$$\frac{\partial f}{\partial r} = -\frac{\partial f^0}{\partial E} \left(\nabla \mu + \frac{E - \mu}{T} \nabla T \right) \quad 3.22$$

Putting the value of $\frac{\partial f}{\partial r}$ from (3.22) in (3.20) and also substituting (3.19) and (3.20) into (3.18), then the distribution function is given by

$$f(k) = f^0(k) + \left(-\frac{\partial f^0}{\partial E} \right) v(k) \tau(k) \left\{ e\varepsilon - \left(\frac{\partial \mu}{\partial T} + \frac{E - \mu}{T} \right) \nabla T \right\} \quad 3.23$$

3.3.1 Transport Coefficients

Electric current is produced when charge move under the influence of electric field. The density is given by

$$\mathbf{J}_e = \frac{2e}{8\pi^3} \int v(k) f(k) dk \quad 3.24$$

The value of $f(k)$ is given in equation (3.23). Similarly the electrons produced heat current density is given by

$$\mathbf{J}_Q = \frac{2}{8\pi^3} \int v(k) [E - \mu] f(k) dk \quad 3.25$$

Here μ represents the chemical potential. Putting $f(k)$ from (3.23) in (3.24) and (3.25) and neglecting f^0 of (3.23) we have

$$\begin{aligned}
\mathbf{J}_e &= \frac{2e}{8\pi^3} \int v(k)v(k)\tau(k)\left(-\frac{\partial f^0}{\partial E}\right) \left[e\varepsilon - \nabla\mu + \frac{E-\mu}{T}(-\nabla T) \right] dk \\
&= \frac{e^2}{4\pi^3} \int v(k)v(k)\tau(k)\left(-\frac{\partial f^0}{\partial E}\right) \left[\varepsilon - \frac{1}{e}\nabla\mu \right] dk \\
&\quad + \frac{e}{4\pi^3\hbar} \int v(k)v(k)\tau(k) \left[\frac{E-\mu}{T} \right] (\nabla T) dk
\end{aligned} \tag{3.26}$$

$$\begin{aligned}
\mathbf{J}_Q &= \frac{2e}{8\pi^3} \int v(k)v(k)\tau(k) \left(-\frac{\partial f^0}{\partial E} \right) [e\varepsilon - \nabla\mu + \frac{E-\mu}{T}(-\nabla T)](E \\
&\quad - \mu) dk \\
&= \frac{e}{4\pi^3} \int v(k)v(k)\tau(k) \left[\varepsilon - \frac{1}{e}\nabla\mu \right] (E - \mu) \left(-\frac{\partial f^0}{\partial E} \right) dk \\
&\quad + \frac{1}{4\pi^3} \int v(k)v(k)\tau(k) \frac{E-\mu}{T} (-\nabla T) \left(-\frac{\partial f^0}{\partial E} \right) dk
\end{aligned} \tag{3.27}$$

Now defining the integral

$$K_n = \frac{1}{4\pi^3\hbar} \int v(k)v(k)\tau(k)(E - \mu)^n \left(-\frac{\partial f^0}{\partial E} \right) dk \tag{3.28}$$

In terms of K_n equation (3.26) and (3.27) can be expressed as

$$\mathbf{J}_e = e^2 K_0 \varepsilon + \frac{eK_1}{T} (-\nabla T) \tag{3.29}$$

$$\mathbf{J}_Q = eK_1 \varepsilon + \frac{K_2}{T} (-\nabla T) \tag{3.30}$$

When temperature gradient is zero, i.e $\nabla T = 0$ then equation (3.29) will become

$$\mathbf{J}_e = \sigma \varepsilon \tag{3.31}$$

Where electrical conductivity is represented by σ and is given by

$$\sigma = e^2 K_0 \quad 3.32$$

If only the temperature gradient exists and the electric field is absent then from equation (3.30) by taking coefficient of thermal gradient the thermal conductivity is obtained. It is to ensure that no electric current is passing through the sample. In such a case $j_e = 0$ the equation (3.29) is valid. Putting equation (3.29) in (3.30) the electric field is eliminated and we have

$$J_Q = \kappa(-\nabla T) \quad 3.33$$

Where κ represents the electronic thermal conductivity.

$$\kappa = \frac{1}{T} \left[K_2 - \frac{K_1^2}{K_0} \right] \quad 3.34$$

Considering the open circuit condition for which there is temperature gradient across the sample, then there will be no current but electric field then

$$\varepsilon = \frac{K_1}{eTK_0} \nabla T \quad 3.35$$

And from the definition of Seebeck coefficient one obtains,

$$S = \frac{K_1}{eTK_0} \quad 3.36$$

3.4 Computational Packages

3.4.1 Quantum Espresso

Quantum espresso (QE) is used for the investigation of electronic properties and modeling of materials. It is access free package and is distributed under the GNU General Public License. It is DFT based code, which includes ultrasoft pseudopotentials and plane-wave basis sets for electron and ion interactions. In Quantum espresso the word “espresso” is used for open-Source Package for optimization, simulation, and electronic structures. Both in series and parallel execution the performance of QE has reached to a maximum under standardized mathematical libraries (like FFTW, LAPLACK and BLAS). For large scale calculations, efficient programing technique and achieving better performance Fortran-95 is used for writing major part of QE. To solve the self-consistent Kohn-sham equations QE includes Plane-Wave Self-Consistent Field (PWscf) as a basic package. QE offers to calculate electronic band structure, perform the geometry optimization, study the electron-phonon interactions and spectroscopic and quantum transport properties [233].

3.4.2 VASP Package

In simulations and modeling of materials VASP (Vienna Ab-initio Simulation Package) is a distinguished computer program. In VASP either KS equation within the DFT or HF approach is solved to achieve Schrödinger equation or by solving the Roothaan equations. This package is implemented by many-body perturbation theory, Hybrid functional and Green's functions. To describe electronic charge density, local potentials and one-electron orbitals, plane-wave basis set is used. Ultrasoft pseudopotentials or

PAW or norm-conserving are used to demonstrate electron-ion interaction. By minimizing the force and full stress tensor, the geometry of the structure is relaxed to the instantaneous ground-state. Once the relaxation is completed all the other physical properties like magnetism, linear response to electric fields, optical properties can easily be computed in VASP [234].

Chapter 4

Results and Discussion

In first section of this chapter we will discussed the structure of single layer MX_2 ($\text{M}=\text{Zr}, \text{Hf}$; $\text{X}=\text{S}, \text{Se}$) TMDCs fallowed by their out-of-plane vdW heterostructures then the electronic properties and at last thermoelectric properties of these materials. In the second section we will focus on the photocatalytic properties of these materials along with their Janus compounds. In the last section we will discuss band alignment in TMDCs MX_2 - PtX_2 ($\text{M}=\text{Zr}, \text{Hf}$ $\text{X}=\text{S}, \text{Se}$) vdW heterostructures.

4.1 Electronic Structure and Thermoelectric Properties of MX_2 ($\text{M}=\text{Zr}, \text{Hf}$; $\text{X}=\text{S}, \text{Se}$) van der Waals Heterostructures

Controlling dimensions has proven to be effective method to manipulate the properties of solids, which can further be tuned by doping [67], alloying [69], strain engineering [71, 235], stacking [121, 236, 237], and the formation of superlattices [71]. Recently, the single-layer stacking to form vdW-h has become a new class of materials, and the quantum coupling between the stacked atomic-scale thin two-dimensional (2D) layers has produced fascinating phenomenon. These heterostructures play a significant role in modern semiconductor technologies and leading to innovative devices such as tunneling transistors, barristors, flexible electronics, and optoelectronic devices as well as double

heterostructure semiconductor lasers operational at room temperature and heterostructures bipolar transistors [238, 239]. In these heterostructures the band alignment is type-II which slow down the charge recombination and reduce the overlap between the electron and hole wave functions , which in fact is expected to be an effective way for light detection and harvesting [68, 240]. Band gap engineering and strong light-matter interaction facilitates the development of effective photovoltaic, optoelectronic and thermoelectric devices based on 2D TMDCs heterostructures [121, 131].

The most strikingly highlighted 2D graphene, exhibiting superior properties than graphite, has been extensively studied over the past few years. Rapid progress in graphene and methods used to prepare ultrathin layers, have inspired great enthusiasm to explore new 2D materials. Single layer TMDCs are emerging as efficient materials for a wide range of applications, e.g., in energy storage [241], gas sensors [242], catalysis [243], field-effect transistors [244], logic circuits [245], optoelectronic/photonic [246], memory devices [247] and potential thermoelectric applications [62, 64, 248]. Extremely strong light-matter interactions in TMDCs monolayers make them fascinating for constructing MX_2 heterostructure, which are exciting for novel photovoltaic and optoelectronic applications [249]. Very recently, an indirect band gap with an intrinsic type-I band alignment is observed in $\text{ZrS}_2/\text{HfS}_2$ vdW heterostructure, which can be modified to type-II band alignment by applying an electric field [250]. In fact similar lattice parameters allow the generation of various TMDCs heterostructures with few

structural defects, but lattice mismatch also produces strain at the interface, which plays a key role in the electronic properties of heterostructures and can improve device performance [238].

In this section a comprehensive insight is gained into the electronic structures of two types of heterostructures. One type includes $\text{ZrS}_2\text{-HfS}_2$ and $\text{ZrSe}_2\text{-HfSe}_2$, showing very small lattice mismatch ($<1\%$). While $\text{ZrS}_2\text{-HfSe}_2$ and $\text{ZrSe}_2\text{-HfS}_2$ heterostructures show lattice mismatch about 2%, which is experimentally achievable [251]. For comparison, we have also studied electronic structure of MX_2 ($\text{M} = \text{Zr, Hf}$ and $\text{X} = \text{S, Se}$) monolayers of the corresponding heterostructures. Thermoelectricity has also been proposed to be favorably controllable by reducing the dimensionality [252]. While these monolayers have shown to be of moderate gaps together with high S , σ and low κ , and thus are efficient materials for thermoelectric applications [253, 254]. Therefore, we have also investigated the thermoelectric performance in terms of the SC, electrical conductivity (σ) and PF of the corresponding heterostructures.

4.1.1 Structural Properties of MX_2 and Heterostructures

Bulk TMDCs (MX_2 where $\text{M} = \text{Zr, Hf}$ and $\text{X} = \text{S, Se}$) crystallize in 1T- CdI_2 structure [61], where 2D hexagonal close packed plane is formed by Zr/Hf atom and six chalcogen atoms has octahedrally coordinated each of them. Total energy difference of 1T and 2H phase ($\Delta E = E_{1T} - E_{2H}$) in Table 4.1 show that monolayers of these materials in 1T phase (Figure. 4.1.1 (i)) are more stable than in 2H phase. Atomic positions and lattice

constants of 1T-MX₂ monolayers are optimized and the results agree well with experiments and previous theoretical findings [246–258].

In heterostructures, one single layer is stacked on top of other single layer and re-optimized the lattice constants of the involved systems. Since, layer stacking is very sensitive to electronic structure [149], different choices are investigated, presented in Figure 4.1.1; (ii): Hf atom of HfS₂ monolayer is located on chalcogen atom (top-layer) of ZrS₂ monolayer; (iii): Hf atom of HfS₂ monolayer is located on chalcogen atom (bottom-layer) of ZrS₂ monolayer; (iv): Hf atom of HfS₂ monolayer is located on top of Zr atom of ZrS₂ monolayer; (v): to avoid on top position the two monolayers shifted laterally, is also analyzed.

The difference of total energy of heterostructure and corresponding two isolated monolayer systems gives the binding energy [70, 121, 259], $E = E_{\text{ZrX}_2\text{-HfX}_2} - E_{\text{ZrX}_2} - E_{\text{HfX}_2}$, show that the third stacking is most favorable; see Table 4.1 Therefore, this situation is studied in the following. Furthermore, the interlayer distance is approximately 3.0 Å, indicates there is no bonding between the chalcogen atoms and reveals the vdW interaction between two layers of the heterostructures. A small change in bond-length is because of mismatch of lattice constant between corresponding individual layers in heterostructures, presented in Table 4.1.

Change in bond-length of individual layers in heterostructures modifies the band structure and changes the phonon stiffness. Hence for further confirmation of the stability

of third stacking we have also investigated the phonon dispersion of the stacking, Figure 4.1.2. No imaginary frequency is observed in Phonon dispersion for all heterostructures which confirm their stability. Figure 4.1.2 also shows 15 optical modes and 3 acoustic modes at the Γ -point of the Brillouin zone due to the six atoms in the cell. The general behavior of all these systems is same. It is clear from Figure 4.1.2 that optical modes in the frequency range ($30\text{-}40\text{ cm}^{-1}$), above acoustic modes at Γ -point indicate weak vdW interaction between constituent single layers of these heterostructures. Similar low frequency optical modes are also experimentally observed in $\text{MoS}_2/\text{WSe}_2$ and $\text{MoSe}_2/\text{MoS}_2$ heterostructures [260] and theoretically demonstrated in $\text{MoSe}_2/\text{Zr}_2\text{CO}_2$, $\text{WSe}_2/\text{Zr}_2\text{CO}_2$, $\text{MoSe}_2/\text{Zr}_2\text{CF}_2$, $\text{WSe}_2/\text{Zr}_2\text{FO}_2$ and SiC-TMDCs heterobilayers [236, 261]. Moreover, the phonon spectra of these heterostructures, simply a sum of phonon vibrational modes of their parent monolayers, also indicate the weak vdW interaction across the interface. Changes in the frequencies of the optical modes from $\text{ZrS}_2\text{-HfS}_2$ and $\text{ZrSe}_2\text{-HfSe}_2$ to $\text{ZrS}_2\text{-HfS}_2$ and $\text{ZrS}_2\text{-HfSe}_2$ show considerable softening and hardening of the phonon frequencies due to the lattice mismatch.

Table 4.1: Difference of GSE (ΔE), lattice constant (a), bond length (M-X), band gap (E_{g-PBE} , E_{g-HSE}), binding energy (E_{ii} , E_{iii} , E_{iv} , E_v), interlayer distances (d) for monolayers and heterostructures.

Monolayer	ZrS ₂	HfS ₂	ZrSe ₂	HfSe ₂
ΔE (eV)	-0.55	-0.68	-0.45	-0.56
a (Å)	3.67	3.65	3.78	3.75
M-X (Å)	2.58	2.55	2.71	2.68
E_{g-PBE} (eV)	1.28	1.56	0.58	0.77
E_{g-HSE} (eV)	1.85	2.14	1.01	1.15

Hetero-bilayer	ZrS ₂ - HfS ₂	ZrSe ₂ - HfSe ₂	ZrSe ₂ - HfS ₂	ZrS ₂ - HfSe ₂
E_{ii} (eV)	-0.19	-0.257	-0.23	-0.21
E_{iii} (eV)	-0.187	-0.254	-0.22	-0.21
E_{iv} (eV)	-0.20	-0.272	-0.25	-0.23
E_v (eV)	-0.18	-0.24	-0.22	-0.20
a (Å)	3.66	3.75	3.71	3.70
d (Å)	2.90	2.98	2.93	2.95
Zr-X (Å)	2.57	2.70	2.69	2.59
Hf-X (Å)	2.56	2.69	2.57	2.67
E_{g-PBE} (eV)	1.26	0.52	0.38	0.53
E_{g-HSE} (eV)	1.80	0.85	0.58	0.76

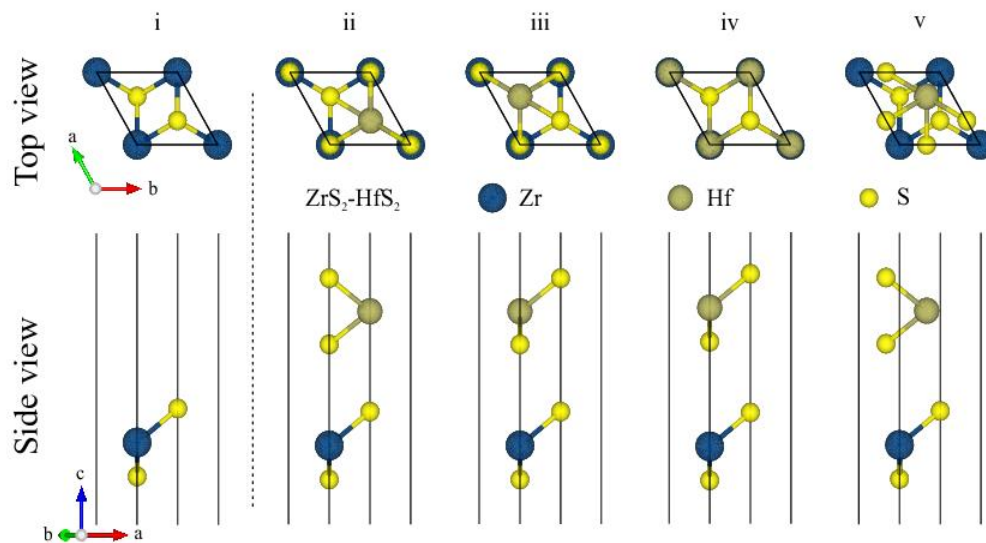


Figure 4.1.1:. (i): ZrS₂ monolayer; (ii): Hf atom of HfS₂ monolayer is located on chalcogen atom (top-layer) of ZrS₂ monolayer; (iii): Hf atom of HfS₂ monolayer is located on chalcogen atom (bottom-layer) of ZrS₂ monolayer; (iv): Hf atom of HfS₂ layer is located on top of Zr atom of ZrS₂ layer; (v): To avoid on top position two monolayers shifted laterally

4.1.2 Electronic Properties of MX_2 and Heterostructures

Band structures show that MX_2 (M= Zr, Hf and X= S, Se) monolayers are semiconductors with indirect band gap and VBM at Γ -point and CBM at M-point, Figure 4.1.3. VBM is mainly due to the chalcogen atom p state, while the transition metal d state contributes to CBM Figure 4.1.4. As the electronic configuration of $\text{Zr}:[\text{Kr}]4d^25s^2$ and $\text{Hf}:[\text{Xe}] 4f^{14}5d^26s^2$, where 4d,5s (Zr) and 5d,6s (Hf) states are the valence state located near the Fermi level and actively involved in physical behavior. However, the 4f orbital, as completely occupied in Hf, is not mainly involved to affect the electronic states in valence band or conduction band. The electronic structure and the band gap value depend upon the electronegativity and the distance apart the component atoms, in the crystal lattice. Large band gaps are associated with small interatomic spacing and large differences of electronegativity [262]. Moreover, 5d elements contain both d and f subshells, due to which it possesses poor shielding effect, making it less reactive than 4d elements. Hence, band gap value decreases (increases) in monolayer from S(Zr) to Se(Hf), presented in Table 4.1.

Magnitude of the monolayers band gap presented in Table 4.1 is better than other PBE calculations [29, 251]. The difference may be due to the pseudopotentials used in our calculations. Although, the band gap values are further improved by using HSE06 functional, presented in Figure 4.1.3 and the values are given in Table 4.1, but there is no experimental data for comparison. It is reported in DFT that with experiments the hybrid

functionals has better agreement than other semilocal functionals. But this approach depends upon the material's choice and is not generalized [74]. For MoS₂ monolayer, PBE(HSE06) band gap underestimates(overestimates) the experimental value by 0.12(0.45) eV [77, 263-265]. The above results and the qualitatively consistent nature of HSE06 and PBE band structures encourage us to choose PBE for the investigation of these materials.

Similar to corresponding monolayers, all heterostructures are semiconductors with indirect band gap having VBM at Γ -point and CBM at M-point, Figure 4.1.3. Here, we emphasize that intrinsic strain may result in different electronic properties of 2D TMDCs [266]. For instance, the heterobilayer ZrS₂-HfS₂ with a small intrinsic tensile strain in HfS₂ and compressive strain in ZrS₂, shows a comparatively smaller band gap than corresponding monolayers, presented in Table 4.1. This is due to the fact that compressive strain is more effective in band gap modulation than a tensile strain [267] because the P.E between atoms increases more rapidly when atoms are brought closer (compression) than in equilibrium rather than pulled further away (tension) from equilibrium [268]. In a similar fashion, the band gap of other heterostructures is also smaller than the corresponding monolayers.

Electronic nature in terms of partial density of states of heterostructures is presented in Figure 4.1.4. In case of ZrS₂-HfS₂, ZrSe₂-HfSe₂ and ZrSe₂-HfS₂ both the CBM and VBM are dominated by Zr-4d and chalcogen atom p states of ZrS₂ (ZrSe₂)

layer of heterostructure. This kind of localization of the VBM and CBM in similar regions of the heterostructure is known as type-I band alignment. Hence, these three heterostructures belong to type-I band alignment. Recently, intrinsic type-I band alignment with an indirect band gap in $\text{ZrS}_2\text{-HfS}_2$ has been reported [250], which is tuned to type-II by applying an external electric field. Surprisingly, the density of states (DOS) of $\text{ZrS}_2\text{-HfSe}_2$ show that VBM is due to the p state of Se with contribution of 5d state of Hf from the layer of HfSe_2 , while the 4d state of Zr atom of ZrS_2 layer contributes to CBM. This type of alignment is known as type-II band alignment (spatially separate electron-hole pairs) [267]. Type-II band alignment in $\text{ZrS}_2\text{-HfSe}_2$ heterostructure without external electric field may be due to the high electron affinity difference in corresponding monolayers [270]. To investigate band alignment, orbitally weighted band structures for $\text{ZrS}_2\text{-HfSe}_2$ heterostructure in Figure 4.1.5 show that CBM is mainly due to the Zr-d_{xz} and Zr-d_{z^2} states with small contribution of Zr-d_{xy} state at M-point of Brillouin zone, while $\text{Zr-d}_{x^2-y^2}$ and Zr-d_{xy} states are contributing mainly at Γ -point. Aforementioned all states of Hf are not contributing at the CBM. Similarly, VBM is mainly due to the Se-p state of HfSe_2 . In light detection and harvesting the localization of VBM and CBM in different layers of the stacked heterostructure is useful because of spatially separated electron-hole pairs (type-II band alignment), and no additional material is needed for this purpose.

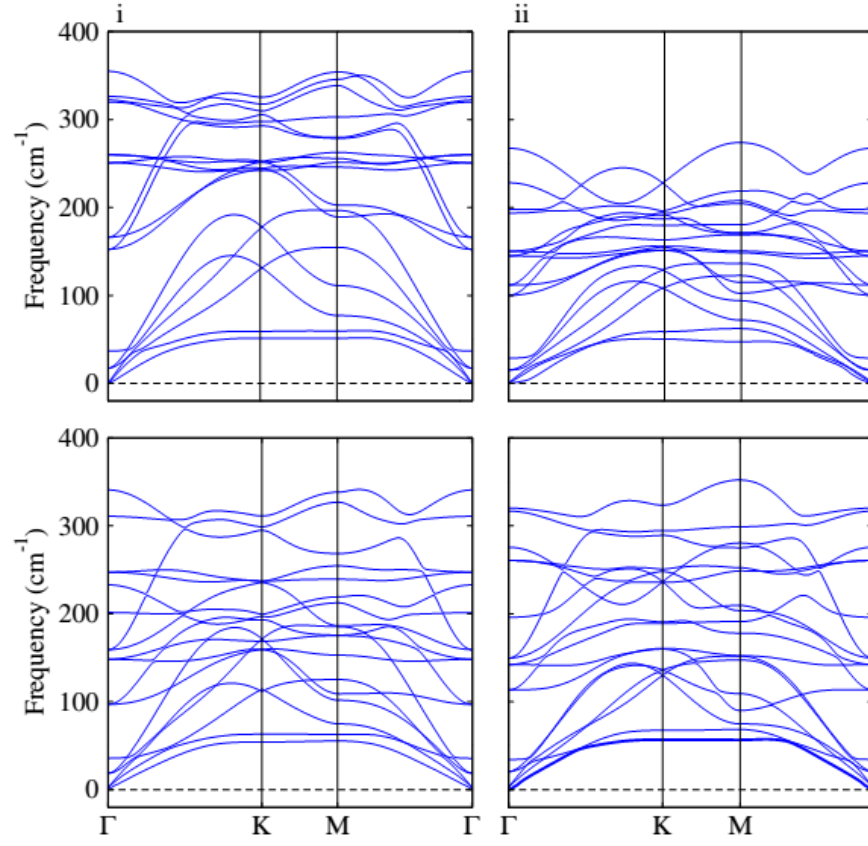


Figure 4.1.2: Phonon spectra of heterostructures, first row (i) $\text{ZrS}_2\text{-HfS}_2$, (ii) $\text{ZrSe}_2\text{-HfS}_2$, second row (i) $\text{ZrS}_2\text{-HfSe}_2$, (ii) $\text{ZrSe}_2\text{-HfSe}_2$.

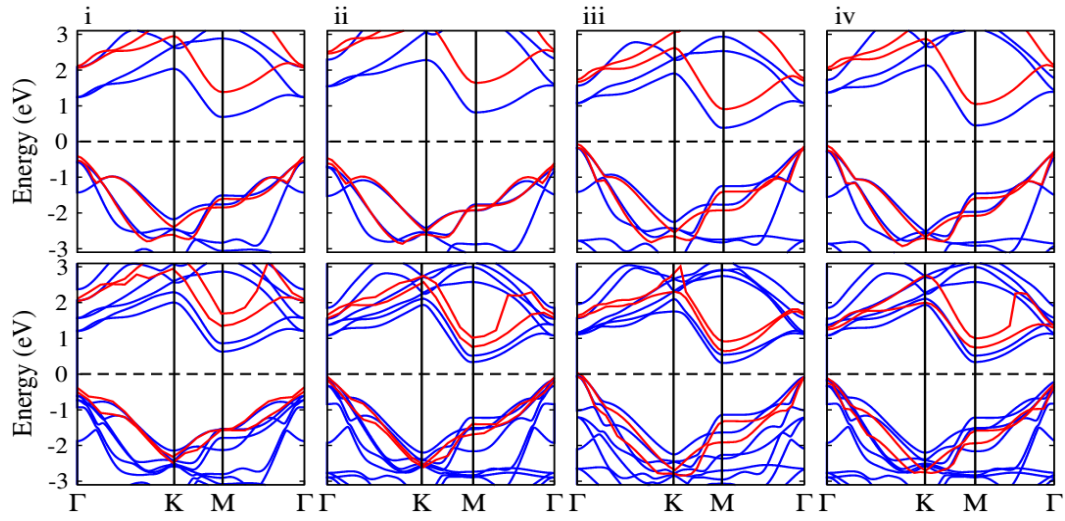


Figure 4.1.3: Band structures, first row i) ZrS_2 , ii) HfS_2 , iii) ZrSe_2 and iv) HfSe_2 monolayers and second row i) $\text{ZrS}_2\text{-HfS}_2$, ii) $\text{ZrSe}_2\text{-HfSe}_2$, iii) $\text{ZrSe}_2\text{-HfS}_2$ and iv) $\text{ZrS}_2\text{-HfSe}_2$, heterostructures of monolayers.

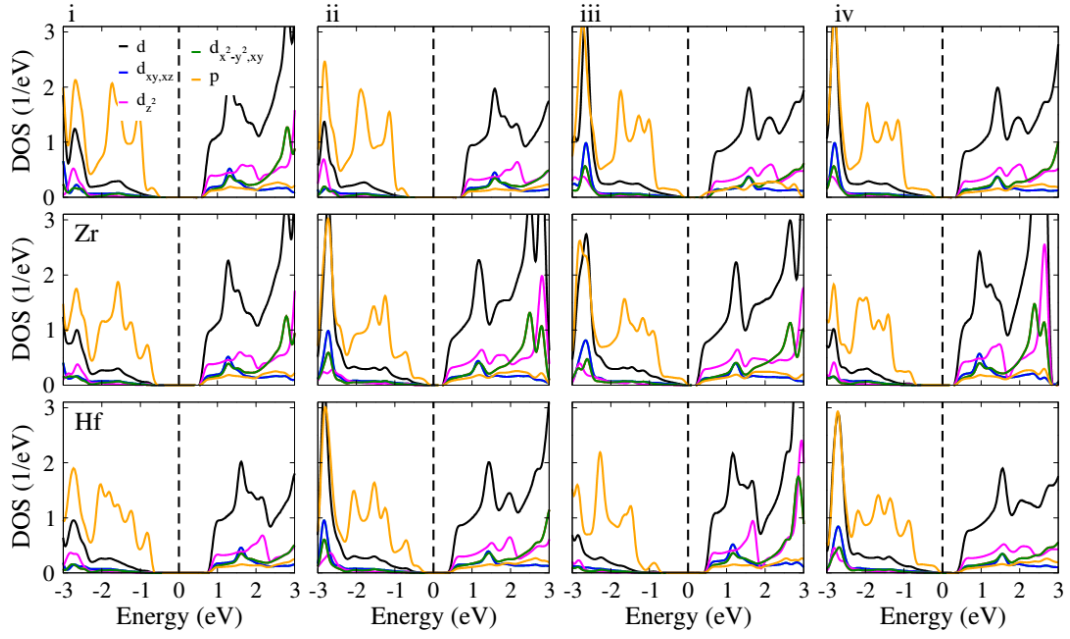


Figure 4.1.4: Partial density of states, first row i) ZrS₂, ii) HfS₂, iii) ZrSe₂ and iv) HfSe₂ monolayers and second and third row d and p states of corresponding layer in i) ZrS₂-HfS₂, ii) ZrSe₂-HfSe₂, iii) ZrSe₂-HfS₂ and iv) ZrS₂-HfSe₂, heterostructures.

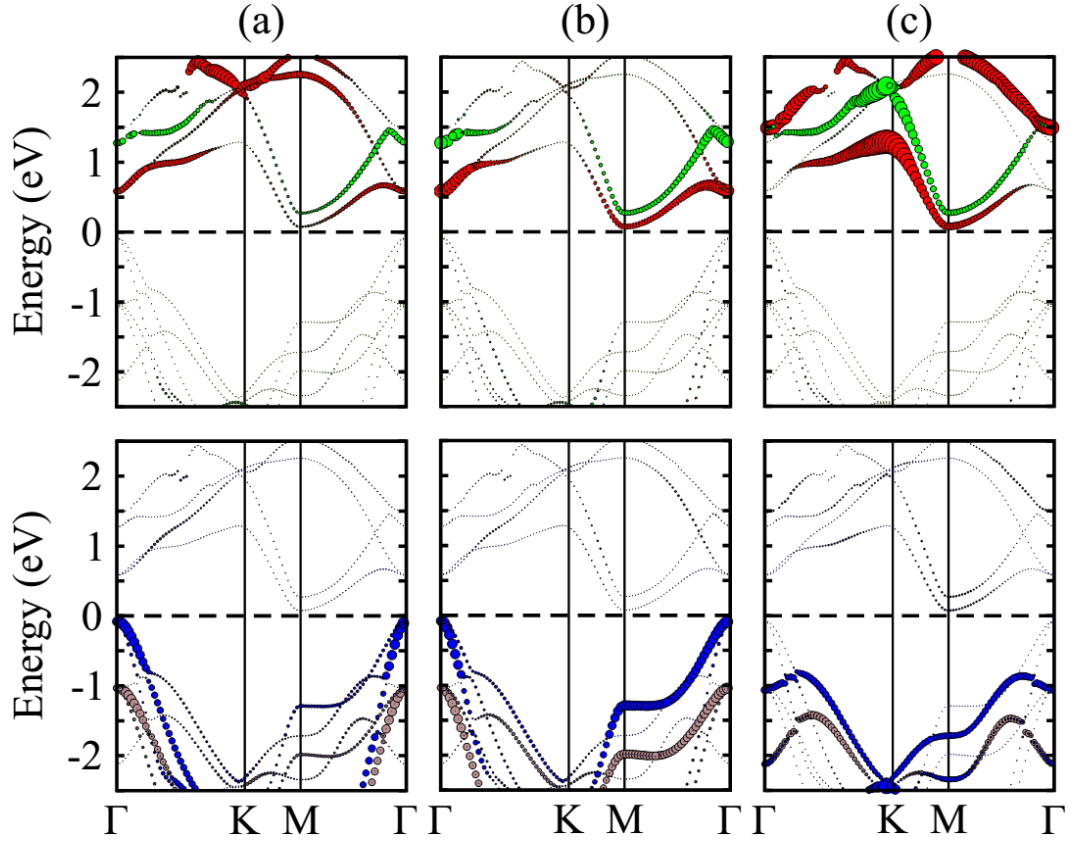


Figure 4.1.5: Orbitaly weighted band structures of the $\text{ZrS}_2\text{-HfSe}_2$ out-of-plane heterostructures for Zr (red), Hf (green), S(brown) and Se (blue). First row (a) Zr/Hf- d_{xy} (b) Zr/Hf- d_{xz} (c) Zr/Hf- d_{z^2} , second row (a) S/Se- p_x (b) S/Se- p_y (c) S/Se- p_z .

4.1.3 Thermoelectric Properties of MX_2 and Heterostructures

Transport coefficients as a function of chemical potential (μ) are investigated by solving the Boltzmann's transport equation using BoltzTraP code as implemented in PWSCF code [271], Figure 4.1.6. Chemical potential indicating doping level of a compound; for n-type doping, μ has positive which shifts up from Fermi level while for p-type doping, μ has negative value and shifts down from the Fermi level, which mainly influence the conductivity and SC.

A remarkable value of Seebeck (S) around $\mu = 0$ confirms that an enhanced S can be obtained through small p-type or n-type doping. An increase in band gap from $\text{ZrS}_2(\text{ZrSe}_2)$ to $\text{HfS}_2(\text{HfSe}_2)$ results in a significant shift of maximum S towards the gap edges. In thermoelectric materials for maximum value of ZT , the SC has usually larger value than $200\mu\text{V/K}$ [59, 65]. At 300K, the maximum measured value of SC for single layer of HfS_2 , HfSe_2 , ZrS_2 and ZrSe_2 , in p-type region is 2430, 1121, 1999, and $856\mu\text{V/K}$, and in n-type region, is 2513, 1210, 2070 and $934\mu\text{V/K}$, respectively. Large SC in n-type region for these monolayers is attributed to large contrast of DOS particularly near band gap edges (Figure 4.1.4) [272–274]. Similarly, large contrast of DOS in conduction band is responsible for large S values in n-type region of $\text{ZrS}_2\text{-HfS}_2$, $\text{ZrS}_2\text{-HfSe}_2$, $\text{ZrSe}_2\text{-HfS}_2$ and $\text{ZrSe}_2\text{-HfSe}_2$ heterostructures (Figure 4.1.4). Both $\text{ZrS}_2\text{-HfSe}_2$ and $\text{ZrSe}_2\text{-HfSe}_2$ heterobilayers have almost the same maximum S value attributed to the small difference in their energy gap. At 1200K, the S value decreases exponentially

and almost one-fourth of that obtained at 300 K for both monolayers and heterobilayers. The maximum S moves towards the band edges from $\text{ZrS}_2\text{-HfS}_2(\text{ZrSe}_2\text{-HfS}_2)$ to $\text{ZrS}_2\text{-HfSe}_2(\text{ZrSe}_2\text{-HfSe}_2)$ as confirmed by the decrease of their respective band gap values. The heterobilayer $\text{ZrS}_2\text{-HfS}_2$ attains larger S than the others hence, are promising for efficient thermoelectric applications. Smaller S in heterobilayer than that in monolayer is ascribed to the decreased band gap.

Electrical conductivity divided by constant relaxation time (σ/τ) demonstrates larger value in p-type region than n-type region at both 300 and 1200 K which may be attributed to the considerable difference in the dispersion of conduction and valence bands found along high symmetry directions. At 300 K, a larger (smaller) value of electrical conductivity observed for $\text{HfSe}_2(\text{HfS}_2)$ is due to smaller(greater) band gap nature. Further, a small decrease in electrical

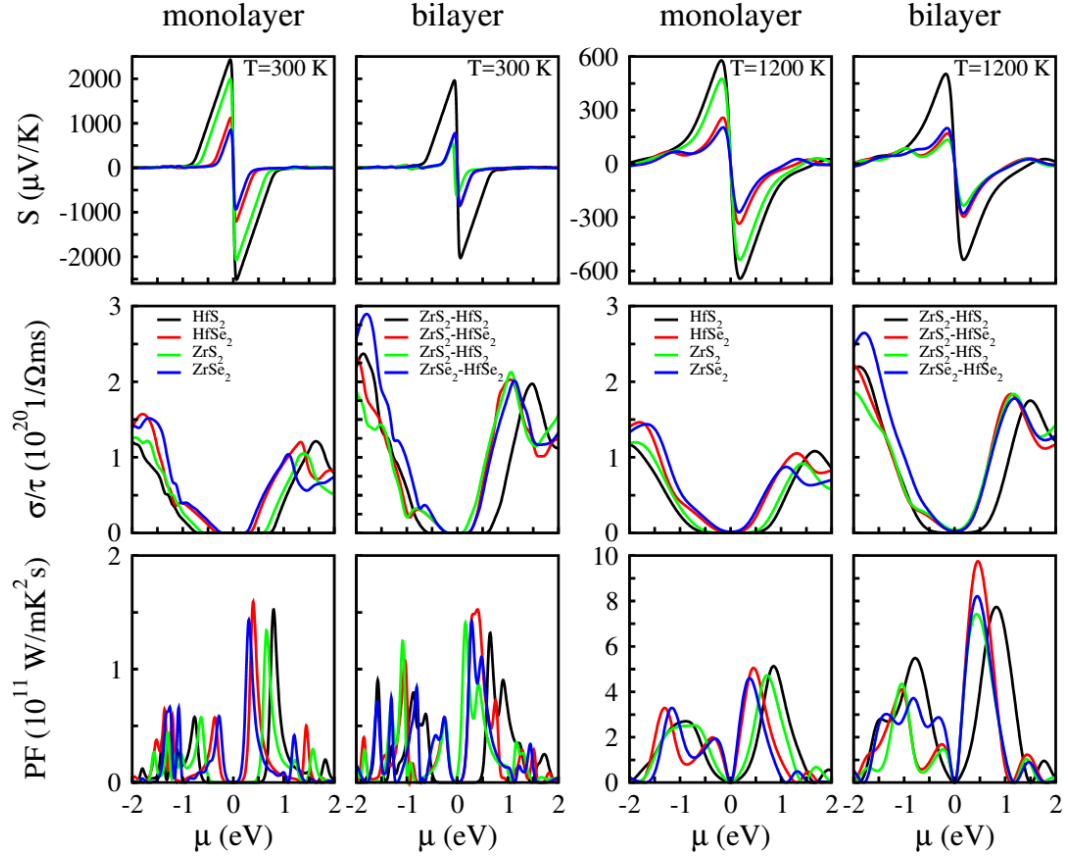


Figure 4.1.6: Transport coefficients as a function of chemical potential of single layer MX_2 and their corresponding heterostructures.

conductivity as compared to SC is found at 1200 K, indicating that the electrical conductivity is less sensitive to temperature. One can clearly observe almost the same trend in maximum σ/τ around chemical potential at both temperature 300 and 1200K. Moreover, the electrical conductivity (Seebeck coefficient) decreases (increases) as μ approach to 0. Sharp increase (decrease) in electrical conductivity (SC) is observed at higher chemical potential in both p and n-type regions. Similar mode is observed in electrical conductivity for all heterobilayers. At 300 K (1200K), the maximum value of electrical conductivity lying in p-type region is 2.37×10^{20} (2.20×10^{20}), 2.39×10^{20} (2.22×10^{20}), 2.01×10^{20} (1.87×10^{20}) and 2.89×10^{20} (2.65×10^{20}) ($1/\Omega.m.s$) for ZrS_2 - HfS_2 , ZrS_2 - $HfSe_2$, $ZrSe_2$ - HfS_2 and $ZrSe_2$ - $HfSe_2$ heterobilayers, respectively. It is noted that at both temperatures, σ/τ for heterobilayers attains considerable peak values as compared to that observed in monolayers which will affect the thermopower of the thermoelectric materials. This variation in σ/τ from monolayer to heterobilayer is due to the band gap engineering.

To optimize thermoelectric performance, PF as a function of chemical potential for individual layers and heterobilayers at temperature 300 and 1200 K are shown in Figure 4.1.6. Obviously, the peak values of PF at both 300 K and 1200 K in n-type region are greater than in p-type due to the larger S in n-type region. At 300 K, the optimized PF with maximum values of 1.525×10^{11} , 1.594×10^{11} , 1.340×10^{11} , and 1.433×10^{11} W/K²ms are found in n-type region, while at 1200 K in the same region these values are 5.126×10^{11} , 5.054×10^{11} , 4.726×10^{11} and 4.599×10^{11} W/K²ms for HfS_2 , $HfSe_2$, ZrS_2 and

ZrSe₂ respectively. More interestingly, the peak values of S for all monolayer and heterobilayer systems at 300 K are greater than at 1200 K, however, a higher value of PF at 1200 K is caused by the higher values of electrical conductivity. Further, it can be seen that HfS₂ has larger PF (at 1200 K) than HfSe₂, ZrS₂ and ZrSe₂, making it more suitable for thermoelectric applications. A similar behavior can be observed in heterobilayers. Among these heterobilayers, ZrS₂-HfSe₂ has comparatively greater PF in n-type region at 300 K devising better performance for TE materials. At 1200 K, highest PF values in n-type region for ZrS₂-HfS₂, ZrS₂-HfSe₂, ZrSe₂-HfS₂ and ZrSe₂-HfSe₂ are 7.737×10^{11} , 9.755×10^{11} , 7.419×10^{11} and 8.217×10^{11} W/K²ms, respectively. The optimized PF at 1200 K for ZrS₂-HfSe₂ is comparatively larger than other studied MX₂ heterobilayers/monolayers. Interestingly, remarkable larger values of PF calculated (at 300 and 1200 K) for both monolayers and heterobilayers is obtained as compared to other investigated low-dimensional materials [275], which indicate their potential applications in thermoelectric devices.

4.2 Photocatalytic Response of MX₂ and MXY (M=Zr, Hf X=Y=S, Se)

Monolayer and Heterostructures.

For environment protection and solar energy conversion, enormous photocatalysts have been developed after the photocatalytic water splitting on TiO₂ electrodes [276]. Electron-hole pairs are produced and separated when light falls on photoelectric material. These photogenerated holes and electrons are used as oxidant for pollutant degradation

and reductant for water reduction [277]. The unstable excited states of electron and holes and their easily recombination in semiconductor photocatalysts leads to a low photocatalytic activity (PA) [278]. To increase the efficiency of solar energy and its utilization different strategies have been employed in the past few decades. Among them the most important is designing of material with diverse properties like crystal structure [279], crystallinity [280] and particle size [281]. In these designed material the absorbing range of light are broader and the separation and migration of charge is efficient. To drive the kinetics of the oxygen and hydrogen evolution reactions for semiconductor to be an efficient candidate of water splitting the band gap must be at least 1.6-1.7eV, the redox potential must be straddled by the band edges and in aqueous solution the semiconductor will be insoluble [282].

The attractive electronic properties of layered transition metal dichalcogenides (TMDCs) received extensive attention [10]. Along with the investigation of electronic properties [283, 284], photochemical properties of TMDCs is a fast emerging field [269]. For solar water splitting and generation of hydrogen layered MoS_2 is theoretically reported as photocatalyst [269, 285]. WTe_2 and TiSe_2 are reported as semimetals [244], while single and few layered NbSe_2 and VSe_2 are true metals. These metals when combined with semiconductor a Schottky junction can be formed [244, 286].

TMDCs play important role in photocatalytic hydrogen evaluation and environmental remediation processes. It has outstanding electrical transport efficiency,

and its used in many advanced energy storage applications, e.g, lithium ion batteries [287], photodetectors [288] superconductors [289], and photocatalytic hydrogen production [173] in solar cells. The layered structure of TMDCs is an effective supports for anchor of semiconductor nanoparticles which reduce the mobility and provide more active sites. This also avoids amalgamation of the semiconductors which is useful in photocatalytic activity and stability [290-292]. Furthermore, Yanguang et al. [243] and Merki, Daniel et al. [293] reported experimentally and theoretically for the hydrogen evolution reaction of WSe₂ appears to be from active edge sites that play an essential role in hydrogen evolution reaction catalysis, although, due to the intrinsic interlayer vdW attraction, the layered TMDCs materials can be easily re-stacked as a result of affecting the active edge sites. And different properties in same TMDCs can be tuned by tailoring it with changing number or stacking sequence of their crystals [293].

The photocatalytic properties of monolayer MX₂ (M = Nb, Mo, Ta, W, Ti, V, Zr, Hf, and Pt; X = S, Se, and Te) are reported by Houlong and Hennig [66] to find conduction and valance band edge using G₀W₀ functional. The single-layer MoS₂, WS₂, PtS₂, and PtSe₂ were reported as potential photocatalyt for water splitting. In this we invistigate the photocatalytic properties of monolayer, heterostructures, Janus monolayers and Janus heterostructures of MX₂ (M= Zr, Hf and X= S, Se), using HSE06.

4.2.1 Photocatalytic Properties of MX_2 , MXY and Heterostructures

The electronic structure of four single-layer transition metal diachalcogenides (TMDCs) and their heterostructures are explored. Further we modeled Janus TMDCs MXY ($\text{M}=\text{Zr}, \text{Hf}$ and $\text{X}=\text{S}, \text{Se}$) and heterostructures. The optimized Janus heterostructure is shown in Figure 4.2.1 It is clear from the band plots that these materials are indirect band gap semiconductors. Both in monolayer and heterostructure the VBM is at the Γ point, while the CBM appears at the M point, Figure 4.2.2. The band plots are obtained both by PBE and HSE methods. In Table. 4.2 we summarize our calculated band gaps with HSE method. The PBE band gaps are smaller than our calculated band gaps and also underestimate the experimental ones [294]. In all the four monolayer TMDCs in each cation group a decrease in band gap is observed due to the decrease in ionicity. Mulliken electronegativity is used to find the energies of the VBM and CBM to determine the photocatalytic properties of mono-layer and hetrobilayer TMDCs and Janus TMDCs [295, 296].

$$E_{\text{VBM}} = \chi - E_{\text{elec}} + 0.5E_{\text{g}} \text{ and } E_{\text{CBM}} = E_{\text{VBM}} - E_{\text{g}}$$

The edge potentials are denoted by E_{VBM} and E_{CBM} , the geometric mean of electronegativities of the constituent atoms are represented by χ and the standard electrode potential on the hydrogen scale by $E_{\text{elec}}=4.5\text{eV}$.

For monolayer TMDCs ZrS_2 , ZrSe_2 , HfS_2 and HfSe_2 the values of χ are 5.15, 4.96, 5.09 and 4.91eV respectively. In case of hetrobilayer $\text{ZrS}_2\text{-HfS}_2$, $\text{ZrS}_2\text{-HfSe}_2$, $\text{ZrSe}_2\text{-}$

HfS₂ and ZrSe₂-HfSe₂ the value of χ are 5.12, 5.03, 5.03 and 4.94eV respectively. In case of Janus TMDCs ZrSSe and HfSSe the value of χ is 5.05 and 4.99 respectively and for heterostructure of Janus TMDCs ZrSSe-HfSSe the value of χ is 5.02.

In Figure 4.3.3 the band edge positions of individual layer, and heterobilayer TMDCs and in Figure 4.3.4, the band edge positions of individual layer of Janus TMDCs and Janus heterobilayer are compared at pH 0 with redox potential of oxygen evolution (O₂/H₂O) and hydrogen evolution (H⁺/H₂). From the edge energies of mono-layer ZrSe₂ and HfSe₂ and heterobilayer ZrSe₂-HfSe₂, ZrS₂-HfSe₂ and ZrSe₂-HfS₂ it is clear that without external bias potential these materials are not good for photocatalytic water splitting. ZrSe₂, HfSe₂ and ZrSSe-HfSSe can reduce H⁺ to H₂ but fails to oxidize H₂O to O₂. It is further observed that the band edges of monolayer ZrS₂, HfS₂, ZrSSe and HfSSe straddle the redox potentials of water at pH 0, in case of heterobilayer only in ZrS₂-HfS₂ the band edges straddles, which make these five materials promising for photocatalytic water splitting. This may be due to the fact that exciton splits into a hole in the valance band and an electron in the conduction band, which diffuse separately and react with water resulting water splitting. In such a case there is need to overcome the exciton binding energy and the CBM and VBM must be favorable with the water redox potentials.

Different techniques can be used to shift the band edges and enable a material for oxygen evolution reaction. One of those methods is applying an external bias voltage. The voltage applied depends on the difference between CBM and energy level of H⁺/H₂

and VBM and energy level of $\text{O}_2/\text{H}_2\text{O}$, the larger the energy difference and the larger will be the required bias voltage.

Another method is the dependence of the redox potentials on the pH values [297]. The energy levels of H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ can be shifted upward by increasing the pH value and can make a material a possible photocatalyst. The application of mechanical strain is the third possible method for the adjustment of bandgaps and band edge positions in semiconducting materials.

Table 4.2: Lattice constant (a), bond length ($b_{\text{Zr-X}}(\text{\AA})$ and $b_{\text{Hf-X}}(\text{\AA})$), interlayer distances ($d(\text{\AA})$) band gap ($E_{\text{g}}^{\text{HSE}}(\text{eV})$) and energy edges (E_{CBM} and E_{VBM}) of MX_2 monolayer, Janus monolayer and their heterostructures.

compound	$a_0 (\text{\AA})$	$b_{\text{Zr-X}}(\text{\AA})$	$b_{\text{Hf-X}}(\text{\AA})$	$d(\text{\AA})$	$E_{\text{g}}^{\text{HSE}}(\text{eV})$	E_{CBM}	E_{VBM}
ZrS_2	3.67	2.58	-	-	1.85	-0.277	1.573
ZrSe_2	3.78	2.71	-	-	1.01	-0.041	0.969
HfS_2	3.65	-	2.55	-	2.14	-0.480	1.660
HfSe_2	3.75	-	2.68	-	1.15	-0.167	0.983
$\text{ZrS}_2\text{-HfS}_2$	3.66	2.57	2.56	2.90	1.80	-0.241	1.479
$\text{ZrS}_2\text{-HfSe}_2$	3.70	2.59	2.67	2.95	0.76	0.242	0.812
$\text{ZrSe}_2\text{-HfS}_2$	3.71	2.69	2.57	2.93	0.58	0.247	0.807
$\text{ZrSe}_2\text{-HfSe}_2$	3.75	2.70	2.69	2.98	0.85	0.016	0.856
ZrSSe	3.70	2.562	-	-	1.333	-0.111	1.221
HfSSe	3.67	-	2.538	-	1.514	-0.259	1.255
ZrSSe-HfSSe	3.68	2.558	2.671	3.68	1.2585	-0.103	1.156

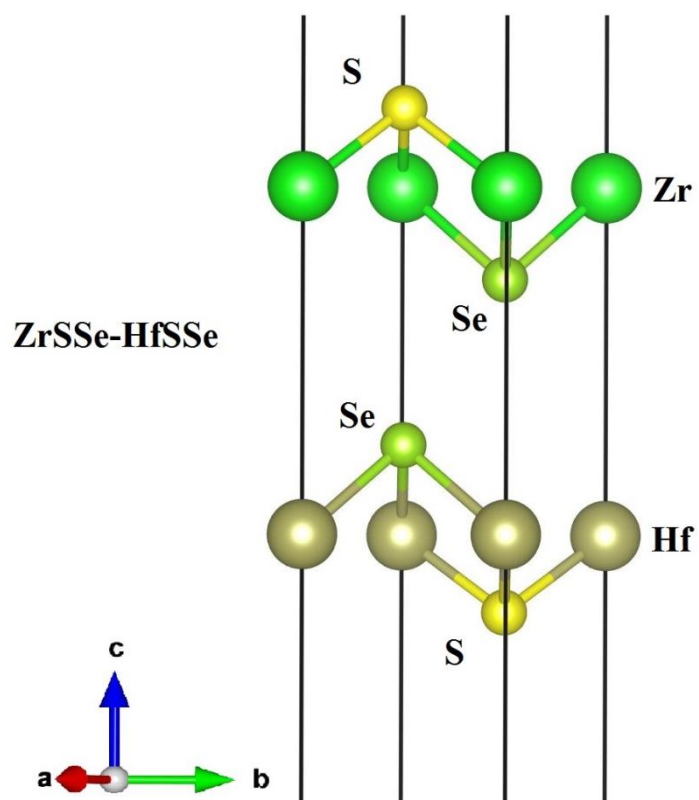


Figure 4.2.1: Heterostructure of Janus TMDCs.

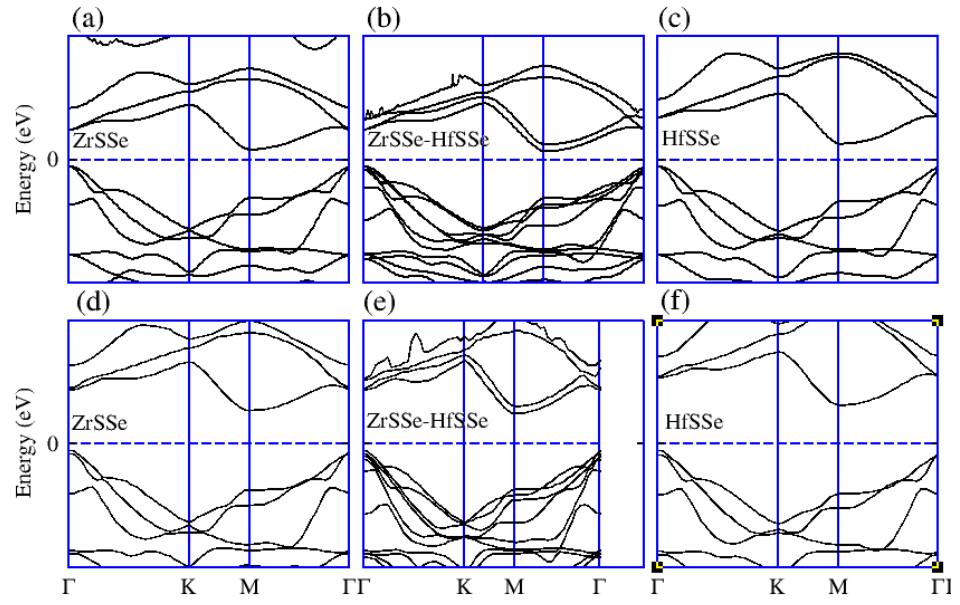


Figure 4.2.2: PBE (a, b and c) and HSE (d, e, and f) band plot of Janus TMDCs and heterostructure.

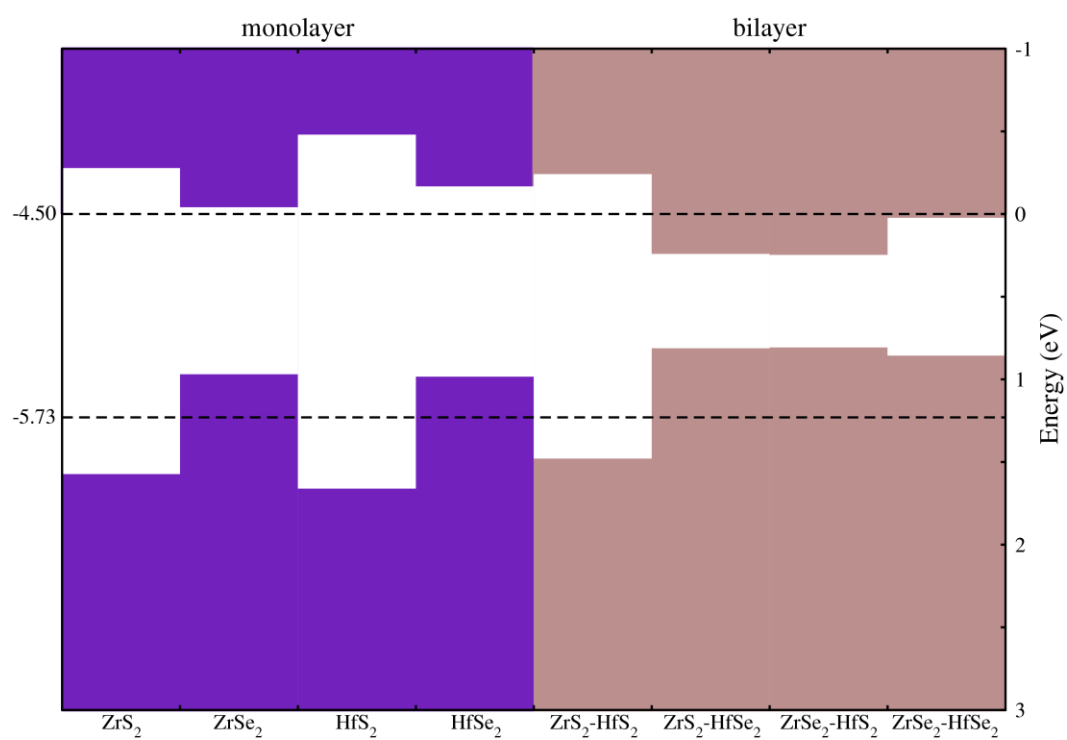


Figure 4.2.3: Valence band edge potential and conduction band edge potential of four monolayers MX₂ (M=Zr, Hf and X =S, Se) and their Heterostructures.

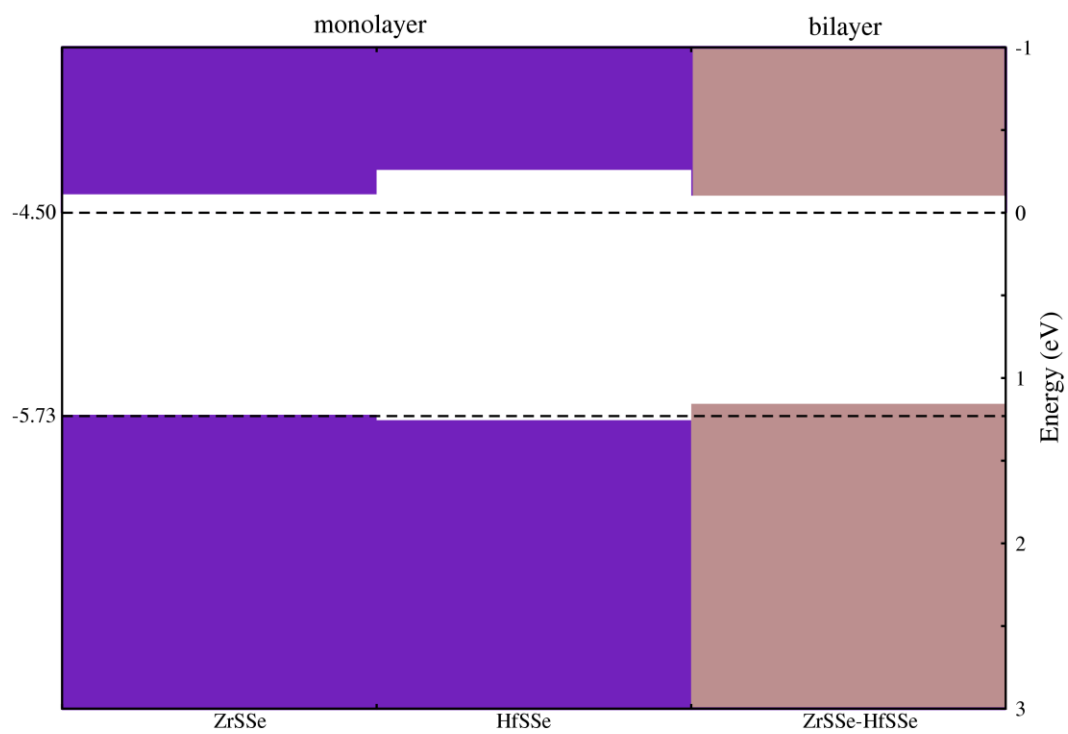


Figure 4.2.4: Valence band edge potential and conduction band edge potential of Janus TMDCs monolayers MXY (M=Zr, Hf and X=Y =S, Se) and their Heterostructure.

4.3 Band Alignment in Novel Zr/HfX₂-PtX₂ (X=S, Se) vdW

Heterostructure

In the technological revolution semiconductors are considered as the most innovative in transformative devices, and researcher are recently focused on 2D semiconducting material and specially on their heterostructures [112]. These heterostructures include, graphene [299, 300], silicene and germanene [301-303], boron nitride, oxygenated monolayers of silicene and graphene [265, 304] and transition-metal dichalcogenides [284, 305-307]. In nature there exist numerous 2D materials, and the arrangement of stacking of these materials in different stacking order and different combination forms several heterostructures. To identify promising stacked materials in device applications, theoretical as well as experimental studies of these heterostructures are required for their technological usage depending on their band alignment.

There are three types of heterostructures based on their band alignment, i.e., symmetric, staggered and broken which are commonly known as type I, type II and type III, respectively. These band alignments have different applications in different devices. In laser and light-emitting diodes (LEDs) which are optical devices, mostly type I band alignment materials are utilized [308]. In type I band alignment, efficient recombination of electron and holes occurs due to their spatial confinement electrons and holes. The performance of LEDs and laser devices are enhanced due to the fabrication of single and multiple quantum wells. The type II band alignments allow larger offsets either on

valance band or on conduction band allowing carrier confinement strongly, which makes these materials promising in unipolar electronic device applications. In type II heterostructures, InAs/AlSb based high electron mobility transistors (HEMTs) are good examples, where strong carrier confinement occurs [141]. In bipolar transistors as hot electron injectors, conduction band notches can be used [309]. To engineer transition energy from conduction to valence type II and III heterostructures are advantageous. In wavelength photodetectors [145], infrared intersubband superlattice lasers [146] and in tunneling field effect transistors (TFETs) [310] type II and III heterostructure are very important. The exhibition of current rectification and collection of photoexcited carriers are recently demonstrated in atomically thin pn-diodes of type II heterostructures [144]. Graphene/TMD/graphene heterostructures can also be used for collection of photoexcited carriers [130]. Recently, type II heterostructures have been investigated as platforms for the use of long-lived interlayer excitons [131, 133]. In addition, TMDCs lateral heterostructures and other types of single layer materials can be used in a variety of applications [120, 311-313].

Due to wide range of functions as specified above, the electronic band structures of layered materials and their band gap engineering have attracted great attention in th recent years. However, in addition to the more common 2D materials such as some TMDCs, BN and graphene, their relative band alignment has not been completely investigated. In the case of a heterostructure, the comparative band alignment of the semiconductor is one of the most significant parameters in the design because it

determines the nature of heterostructure. Additionally, in all of the discussed devices, as in their bulk counterparts, it is critical that the valence and/or conduction band edges of the constituent heterostructure materials are momentum matched. For example, due to the inherent possibility of some degree of misorientation in a layered stack, and the need to combine highly diverse material groups, layered materials having edges at the center of the region are particularly attractive because momentum space can largely eliminate matching problems by using these materials.

In this section, we have conducted a broad study of the Zr/HfX₂-PtX₂ semiconducting materials due to the emergence of two-dimensional heterostructures as the next generation of materials and their comparison of alignment and momentum matching in heterostructure design, their band edge characteristics and the possibility of forming momentum to match heterostructures.

4.3.1 Structure and Electronic Properties of Novel MX₂ (M=Zr, Hf and Pt X=S and Se) Heterostructures

In a heterostructure, a single layer is stacked on the top of another layer and the average in-plane lattice constant of the system involved is re-optimized. Different choices of stacking are investigated to obtain an optimize one because the layer stacking affects the electronic structure. The different choices of stacking are: i) Pt atom of PtS₂ layer is located on chalcogen atom (top-layer) of ZrS₂ monolayer; (ii): Pt atom of HfS₂

monolayer is located on chalcogen atom (bottom-layer) of ZrS₂ monolayer; (iii): Pt atom of HfS₂ monolayer is located on top of Zr atom of ZrS₂ monolayer; (iv): to avoid on top position the two monolayers shifted laterally. In addition, the distance between the layers is more than 3 (Å), indicating that there is no bond between the chalcogen atoms of the layers that reveals the vdW interaction between the two monolayers. The small change in bond length is due to lattice mismatch between the constituent individual layers in the heterostructure, as shown in Table 4.3. The calculated band structures through PBE and HSE in Figure 4.3.1 and Figure 4.3.2 indicate that the MX₂ (M = Zr, Hf, Pt and X = S, Se) heterostructures are indirect band gap semiconductors with VBM at the defect and CBM at the M site. VBM is mainly due to the p-state of the S/Se atom, while the CBM is occupied the transition metal d state, Figure 4.3.3

The electronic configuration of Zr is [Kr] 4d² 5s², Hf is [Xe] 4f¹⁴ 5d² 6s², and Pt is [Xe] 4f¹⁴ 5d⁹ 6s¹ where 4d and 5s of Zr as well as 5d and 6s of Hf are valence states that are located near the Fermi level. These states actively participate in physical behavior of the materials. However, the 4f orbital of Hf and Pt are completely occupied and does not affect the electronic state in the valence band or conduction band.

The electronic structure and band gap values depend on the electronegativity and the distance between the constituent atom in a crystal. The large band gap is related to the large difference in atomic spacing and electronegativity [263]. In addition, 5d elements contain d and f subshells, so they have poor shielding effect, making them less reactive

than 4d elements. Therefore, the band gap value is reduced (increased) from S(Zr) to Se(Hf/Pt) in a single layer, as shown in Table 4.3.

The electronic structures of the partial density of state of the heterostructures are shown in Figure 4.3.3. In the case of $\text{ZrS}_2\text{-PtS}_2$, $\text{ZrS}_2\text{-PtSe}_2$ and $\text{ZrSe}_2\text{-PtSe}_2$ CBM is dominated by Zr-4d state while the valance band is occupied by chalcogen atom of the other layer (PtX_2) except in $\text{ZrSe}_2\text{-PtS}_2$ in which conduction and valance bands are comprised by Zr-4d and Se-p of ZrSe_2 layer respectively. In the case of $\text{HfS}_2\text{-PtS}_2$, $\text{HfS}_2\text{-PtSe}_2$ and $\text{HfSe}_2\text{-PtSe}_2$ CBM is dominated by Hf-4d state while the valance band is occupied by chalcogen atom of the other layer (PtX_2) except in $\text{HfSe}_2\text{-PtS}_2$ where conduction and valance bands are comprised by Hf-4d and Se-p of HfSe_2 layer. This positioning of the VBM and CBM in different regions of the heterostructure is referred to type-II band alignment. Therefore, these six heterostructures belong to the II-type band alignment. The arrangement of the type II bands in these heterostructures may be due to the difference in high electron affinity in the corresponding monolayers [270]. In order to further study the type II energy band alignment, the orbital weighted band structure of $\text{Zr/HfX}_2\text{-PtX}_2$ heterostructure is shown in Figure 4.3.4. the figure reveals that CBM is mainly due to the Zr/Hf-d_z^2 of Zr/HfX_2 layer and the VBM is due to X-pz of PtX_2 layer. The $\text{ZrSe}_2\text{-PtS}_2$ and $\text{HfSe}_2\text{-PtS}_2$ show type I band alignment. The weighted band structure reveals that in these heterostructure the CBM is due to the Zr/Hf-d_z^2 and VBM is due to X-px of Zr/HfX_2 layer. This band alignment can be tuned to type II by applying external field. For light detection and harvesting the positioning of VBM and CBM in different layers of the heterostructure known as type-II band alignment is very important.

Table 4.3: Structural parameters of Zr/HfX₂-PtX₂ heterostructure.

Compound	a ₀ (Å)	b _{Zr/Hf-X} (Å)	B _{Pt-X} (Å)	d (Å)	E _g ^{PBE} (eV)	E _g ^{HSE} (eV)
ZrS ₂ -PtS ₂	3.595	2.56	2.41	3.44	0.629	1.426
ZrS ₂ -PtSe ₂	3.68	2.578	2.52	3.56	0.302	0.91
ZrSe ₂ -PtS ₂	3.64	2.68	2.42	3.43	0	0.5341
ZrSe ₂ -PtSe ₂	3.72	2.69	2.53	3.55	0.214	1.2316
HfS ₂ -PtS ₂	3.61	2.53	2.40	3.385	0.746	1.5841
HfS ₂ -PtSe ₂	3.67	2.55	2.52	3.498	0.375	1.054
HfSe ₂ -PtS ₂	3.65	2.65	2.24	3.34	0.260	0.951
HfSe ₂ -PtSe ₂	3.72	2.66	2.53	3.49	0.317	0.9688

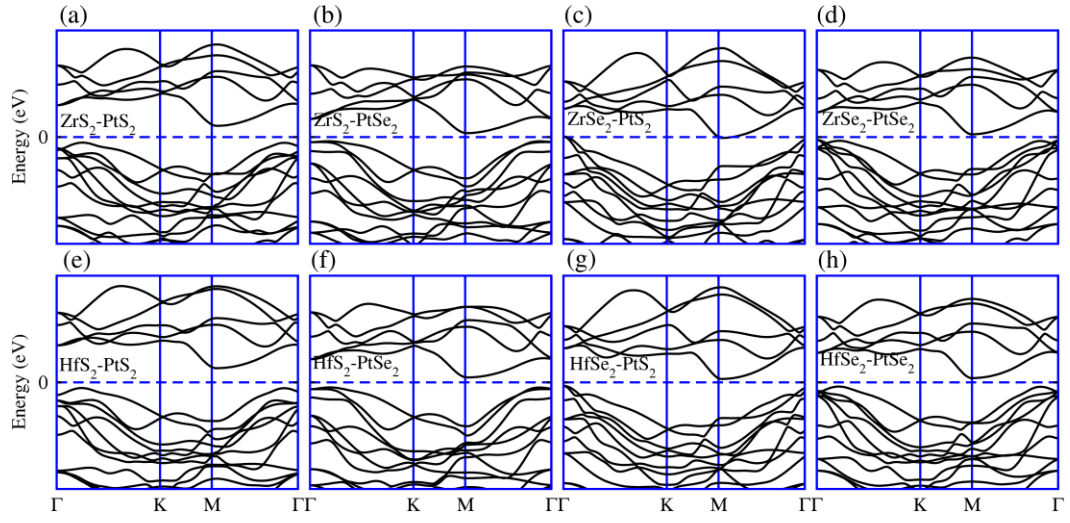


Figure 4.3.1: PBE band structure of Zr/Hf-Pt heterostructure

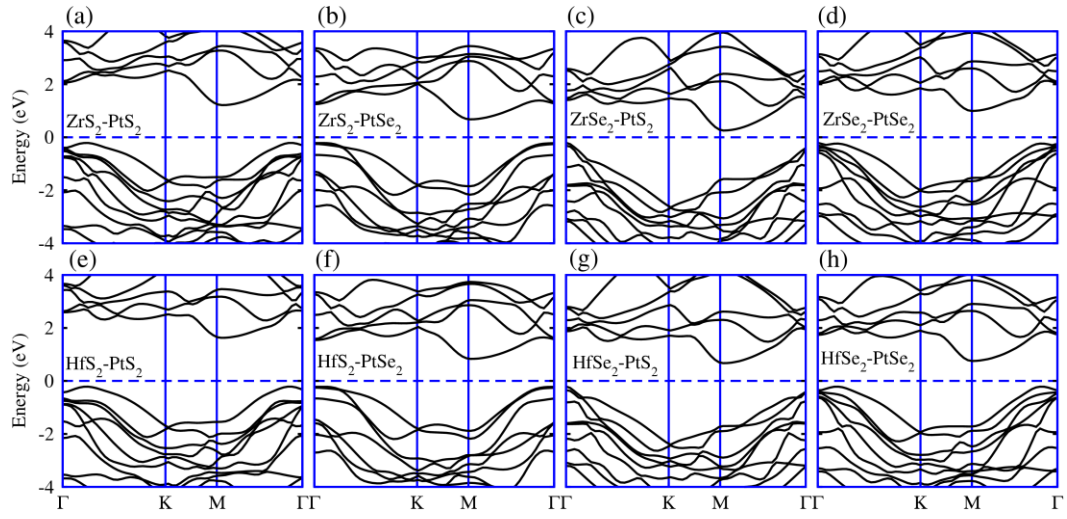


Figure 4.3.2: HSE band structure of Zr/Hf-Pt heterostructure.

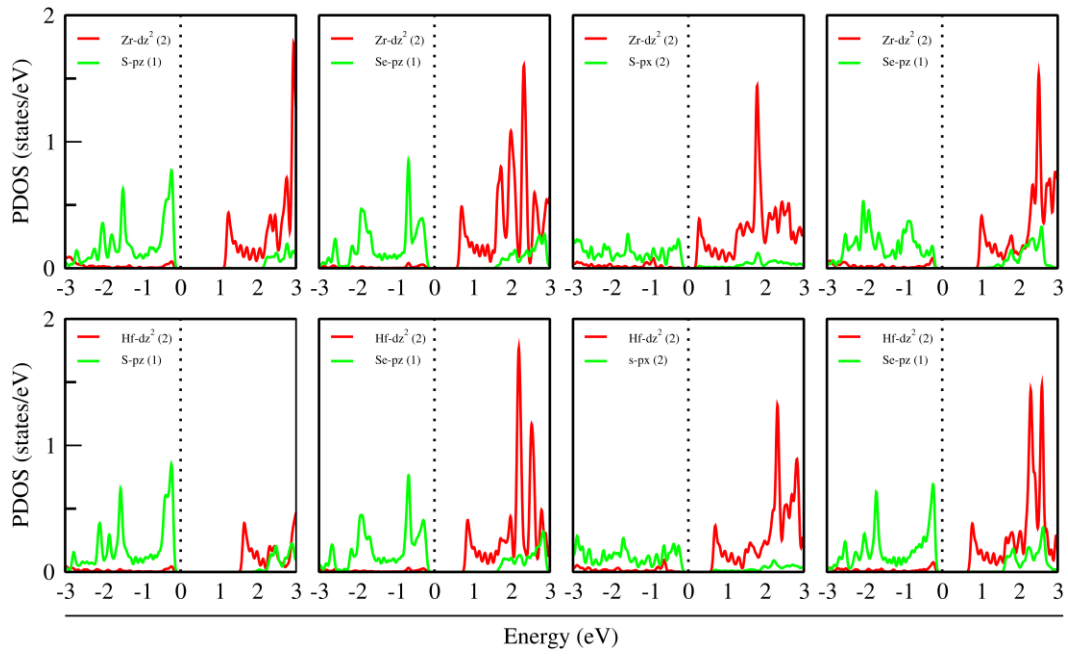


Figure 4.3.3: Partial density of states, first row i) $\text{ZrS}_2\text{-PtS}_2$, ii) $\text{ZrS}_2\text{-PtSe}_2$ iii) $\text{ZrSe}_2\text{-PtS}_2$ iv) $\text{ZrSe}_2\text{-PtSe}_2$ and second row i) $\text{HfS}_2\text{-PtS}_2$, ii) $\text{HfS}_2\text{-PtSe}_2$ iii) $\text{HfSe}_2\text{-PtS}_2$ iv) $\text{HfSe}_2\text{-PtSe}_2$ heterostructures.

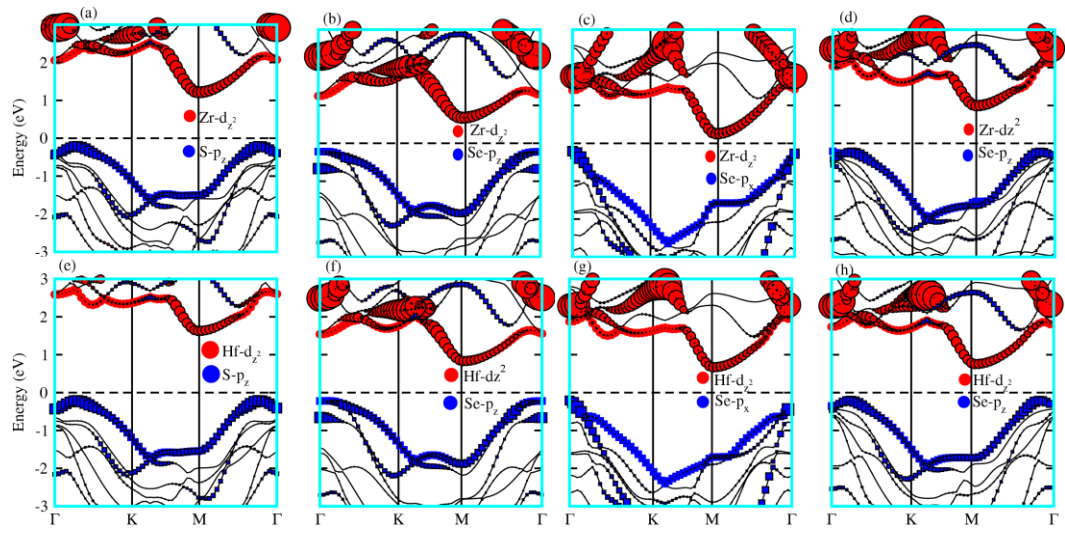


Figure 4.3.4: Orbitaly weighted band structures of Zr/HfX₂-PtX₂ heterostructures.

Chapter 5

Conclusions

Structural, vibrational, electronic and thermoelectric properties of MX_2 (M= Zr, Hf and X= S, Se) single layers and their out-of-plane heterostructures are explored by first principles density functional theory and Boltzmann transport calculations. The structural properties reveal that all MX_2 monolayers are stable in 1T-phase. The stacking order of minimum energy is determined for all heterostructures, which is further confirmed by calculations of phonon dispersion. Both monolayers and their heterostructures show indirect semiconducting band gap nature. It is concluded that type-II band alignment in $\text{ZrS}_2\text{-HfSe}_2$ without application of external electric field enhances its performance for light detection. Transport coefficients such as electrical conductivity, SC and PF at 300 K and 1200 K are investigated against chemical potential reveal that SC (electrical conductivity) attains large values in n-type(p-type) doping. The PF values in n-type region of all heterostructures are larger than their corresponding monolayers at high temperature 1200 K.

The structural and electronic properties of Janus TMDCs MXY (M=Zr, Hf and X=Y= S,Se) single layer and their out-of-plane heterostructure in 1T-phase are also theoretically investigated. These layered materials and their heterostructures are

confirmed as indirect band gap semiconducting materials. The photocatalytic properties of MX_2 ($\text{M} = \text{Zr}, \text{Hf}$ and $\text{X} = \text{S}, \text{Se}$) layers and their out-of-plane heterostructures along with MXY and their heterostructures were also explored. Among the monolayers ZrS_2 , HfS_2 , ZrSSe , and HfSSe are found to have good photocatalytic properties without applying any external potential. While in their heterostructures only $\text{ZrS}_2\text{-HfS}_2$ has the efficiency for hydrogen evaluation reaction.

The band alignment plays a vital role in device applications and to confirm the band alignment in vdW-h, the structure and electronic properties of novel $\text{Zr/HfX}_2\text{-PtX}_2$ ($\text{X} = \text{S}, \text{Se}$) vdW-h are investigated. It is confirmed that the band gap nature of these novel materials is indirect. Type-II band alignment is confirmed in $\text{ZrS}_2\text{-PtS}_2$, $\text{ZrSe}_2\text{-PtS}_2$, $\text{ZrSe}_2\text{-PtSe}_2$, $\text{HfS}_2\text{-PtS}_2$, $\text{HfSe}_2\text{-PtS}_2$ and $\text{HfSe}_2\text{-PtSe}_2$ heterostructures where conduction band is comprised by the transition metal d-state of one layer and valence band by chalcogen atom of the other layer. Type-I band alignment is observed in $\text{ZrSe}_2\text{-PtS}_2$ and $\text{HfSe}_2\text{-PtS}_2$ heterostructures, where CBM and VBM are comprised by transition metal atom and chalcogen atom of the same layer.

Bibliography

- [1] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim “Two-dimensional atomic crystals” *Proc. Natl Acad. Sci. USA*, 102, 10451–10453 (2005).
- [2] K.S. Novoselov, V.I. Fal’ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, “A roadmap for graphene” *Nature*, 490, 192–200 (2012).
- [3] S.Z. Butler, S.M. Hollen, L. Cao, Y. Cui, J.A. Gupta, H.R. Gutiérrez, T.F. Heinz, S.S. Hong, J. Huang, A.F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R.D. Robinson, R.S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M.G. Spencer, M. Terrones, W. Windl, J.E. Goldberger, “Progress, challenges, and opportunities in two-dimensional materials beyond graphene” *ACS Nano*, 7, 2898–2926 (2013).
- [4] M. Pumera, Z. Sofer, A. Ambrosi, “Layered transition metal dichalcogenides for electrochemical energy generation and storage” *J. Mater. Chem. A*, 2 8981–8987 (2014).
- [5] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D.W.H. Fam, A.I.Y. Tok, Q. Zhang, H. Zhang, “Fabrication of single- and multilayer MoS₂ film-based field-effect transistors for sensing NO at room temperature” *Small*, 8, 63–67 (2012).
- [6] P. Koskinen, I. Fampiou, A. Ramasubramaniam, “Density-functional tight-binding simulations of curvature-controlled layer decoupling and band-gap tuning in

- bilayer MoS₂” *Phys. Rev. Lett.* 112, 186802 (2014).
- [7] H.S. Lee, D.H. Luong, M.S. Kim, Y. Jin, H. Kim, S. Yun, Y.H. Lee, “Reconfigurable exciton-plasmon interconversion for nanophotonic circuits” *Nat. Commun.* 7, 13663 (2016).
- [8] K.F. Mak, K. He, J. Shan, T.F. Heinz, “Control of valley polarization in monolayer MoS₂ by optical helicity” *Nat. Nanotechnol.* 7, 494–498 (2012).
- [9] K.S. Novoselov, A. Mishchenko, A. Carvalho, A.H. Castro Neto, “2D material sand van der Waals heterostructures” *Science*, 353, aac9439 (2016).
- [10] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides” *Nat. Nanotechnol.* 7, 699–712 (2012).
- [11] J A. Wilson, A. D. Yoffe “Transition Metal Dichalcogenides Discussion and Interpretation of Observed Optical, Electrical, and Structural Properties” *Adv. Phys.* 18, 193–335 (1969).
- [12] J. G. Bednorz, K. A. Muller “Possible High-T_c Superconductivity in the Ba-La-Cu-O System” *Z. Phys. B*, 64, 189-193 (1986).
- [13] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, H. Hosono “Iron-Based Layered Superconductor: LaOFeP” *J. Am. Chem. Soc.* 128, 10012–10013 (2006).
- [14] I. S. Kim, V. K. Sangwan, D. Jariwala, J.D. Wood, S. Park, K.-S. Chen, F. Shi, F. Ruiz-Zepeda, A. Ponce, M. Jose-Yacamán, V. P. Dravid, T. J. Marks, M. C.

- Hersam, L. J. Lauhon, "Influence of Stoichiometry on the Optical and Electrical Properties of Chemical Vapor Deposition Derived MoS₂" *ACS Nano*, 8, 10551-10558 (2014).
- [15] J. D. Wood, S. A. Wells, D. Jariwala, K.-S. Chen, E. Cho, V. K. Sangwan, X. Liu, L. J. Lauhon, T. J. Marks, M. C. Hersam, "Effective Passivation of Exfoliated Black Phosphorus Transistors against Ambient Degradation" *Nano Lett.* 14, 6964-6970 (2014).
- [16] A. Allain, J. Kang, K. Banerjee, A. Kis, "Electrical contacts to two-dimensional semiconductors" *Nat Mater.* 14, 1195-1205 (2015).
- [17] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim and A. K. Geim, "Room-Temperature Quantum Hall Effect in Graphene" *Science*, 315, 1379 (2007).
- [18] K. Kim, J. Y. Choi, T. Kim, S. H. Cho, H. J. Chung "A role for graphene in silicon-based semiconductor devices" *Nature*, 479, 338 (2011).
- [19] A. Zak, M. A. Andersson, M. Bauer, J. Matukas, A. Lisauskas, H. G. Roskos, J. Stake "Antenna-Integrated 0.6 THz FET Direct Detectors Based on CVD Graphene" *Nano Lett.* 14, 5834 (2014).
- [20] A. K. Geim "Graphene: Status and Prospects" *Science*. 324, 1530-1534 (2009).
- [21] F. Schwierz, "Graphene transistors" *Nat. Nanotechnol.* 5, 487–496 (2010).

- [22] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill and P. Avouris “100-GHz Transistors from Wafer-Scale Epitaxial Graphene” *Science*, 327, 662 (2010)
- [23] L. Liao, Y.-C. Lin, M. Bao, R. Cheng, J. Bai, Y. Liu, Y. Qu, K. L. Wang, Y. Huang and X. Duan “High-speed graphene transistors with a self-aligned nanowire gate” *Nature*, 467, 305–308 (2010).
- [24] R. Cheng, J. Bai, L. Liao, H. Zhou, Y. Chen, L. Liu, Y.-C. Lin, S. Jiang, Y. Huang and X. Duan “High-frequency self-aligned graphene transistors with transferred gate stacks” *Proc. Natl. Acad. Sci. U.S.A.*, 109(29), 11588–11592 (2012).
- [25] J. A. Wilson, A. D. Yoffe “The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties” *Adv. Phys.* 18(73), 193-335 (1969).
- [26] H. S. S. Ramakrishna Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati, C. N. R. Rao “MoS₂ and WS₂ analogues of graphene” *Angew. chem. int. ed.* 49(24), 4059-4062 (2010).
- [27] B. Liu, Y. Han, C. Gao, Y. Ma, G. Peng, B. Wu, W. Ren “Pressure induced semiconductor-semimetal transition in WSe₂” *J. Phys. Chem. C*, 114(33), 14251-14254 (2010).

- [28] C. Drummond, N. Alcantar, J. Israelachvili, R. Tenne, Y. Golan, “Microtribology and Friction-Induced Material Transfer in WS₂ Nanoparticle Additives” *Adv. Funct. Mater.* 11(5), 348-354 (2001).
- [29] Q. Zhao, Y. Guo, K. Si, Z. Ren, J. Bai, X. Xu, “Elastic, electronic, and dielectric properties of bulk and monolayer ZrS₂, ZrSe₂, HfS₂, HfSe₂ from van der Waals density-functional theory” *Phys. Status Solidi B*, 254(9), 1700033 (2017).
- [30] M. Abdulsalam, D. P. Joubert “Optical spectrum and excitons in bulk and monolayer MX₂ (M= Zr, Hf; X= S, Se)” *Phys. Status Solidi B*, 253(4), 705-711 (2016).
- [31] D. L. Greenaway, R. Nitsche “Preparation and optical properties of group IV–VI₂ chalcogenides having the CdI₂ structure” *J. Phys. Chem. Solids*, 26(9), 1445-1458 (1965).
- [32] P. A. Lee, G. Said, R. Davis, T. H. Lim “On the optical properties of some layer compounds” *J. Phys. Chem. Solids*, 30(12), 2719-2729 (1969).
- [33] L. Roubi, C. Carlone “Resonance Raman spectrum of HfS₂ and ZrS₂” *Phys. Rev. B*, 37(12), 6808 (1988).
- [34] H. I. Starnberg, H. E. Brauer, H. P. Hughes “Photoemission studies of the conduction band filling in Ti_{1.05}S₂ and Cs-intercalated TiS₂ and ZrSe₂” *J. Phys. Condens. Matter*, 8(9), 1229 (1996).
- [35] K. Terashima, I. Imai “Indirect absorption edge of ZrS₂ and HfS₂” *Solid State Commun.* 63(4), 315-318 (1987).

- [36] C. Gaiser, T. Zandt, A. Krapf, R. Serverin, C. Janowitz, R. Manzke “Band-gap engineering with $\text{HfS}_x\text{Se}_{2-x}$ ” *Phys. Rev. B*, 69(7), 075205 (2004).
- [37] M. Moustafa, T. Zandt, C. Janowitz, R. Manzke “Growth and band gap determination of the $\text{ZrS}_x\text{Se}_{2-x}$ single crystal series” *Phys. Rev. B*, 80(3), 035206 (2009).
- [38] A. K. Geim “Nobel Lecture: Random walk to graphene” *Rev. Mod. Phys.* 83(3), 851–862 (2011).
- [39] Novoselov, K. S. “Nobel lecture: Graphene: Materials in the flatland” *Rev. Mod. Phys.* 83(3), 837-849 (2011).
- [40] Jinbing Cheng, Chunlan Wang, Xuming Zou,* and Lei Liao “Recent Advances in Optoelectronic Devices Based on 2D Materials and Their Heterostructures” *Adv. Optical Mater.* 7(1), 1800441. (2018).
- [41] F. Xia, H. Wang, Y. Jia “Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics” *Nat. Commun.* 5, 4458 (2014).
- [42] M. Engel, M. Steiner, P. Avouris “Black phosphorus photodetector for multispectral, high-resolution imaging” *Nano Lett.* 14(11), 6414 (2014).
- [43] Z. Y. Zhu, Y. C. Cheng, U. Schwingenschlögl “Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors” *Phys. Rev. B*, 84(15), 153402 (2011).

- [44] A. Kormányos, G. Burkard, M. Gmitra, J. Fabian, V. Zólyomi, N. D. Drummond, V. Fal'ko “ k.p theory for two-dimensional transition metal dichalcogenide semiconductors” *2D Mater.* 2(2), 022001 (2015).
- [45] R. Tenne, L. Margulis, M Genut, G. Hodes “Polyhedral and cylindrical structures of tungsten disulfide”. *Nature*, 360, 444–446 (1992).
- [46] A. D. Yoffe “Layer compounds” *Annu. Rev. Mater. Sci.* 3(1), 147-170 (1973).
- [47] Y. Sun, H. Cheng, S. Gao, Q. Liu, Z. Sun, C. Xiao, C. Wu, S. Wei, and Y. Xie “Atomically Thick Bismuth Selenide Freestanding Single Layers Achieving Enhanced Thermoelectric Energy Harvesting” *J. Am. Chem. Soc.* 134, 20294-20297 (2012).
- [48] V. Goyal, D. Teweldebrhan, and A. A. Balandin “Mechanically-exfoliated stacks of thin films of Bi₂Te₃ topological insulators with enhanced thermoelectric performance” *Appl. Phys. Lett.* 97(13), 133117 (2010).
- [49] P. Ghaemi, R. S. K. Mong, and J. E. Moore “In-plane transport and enhanced thermoelectric performance in thin films of the topological insulators Bi₂Te₃ and Bi₂Se₃” *Phys. Rev. Lett.* 105(16), 166603 (2010).
- [50] F. Zahid and R. Lake “Thermoelectric properties of Bi₂Te₃ atomic quintuple thin films” *Appl. Phys. Lett.* 97(21), 212102 (2010).
- [51] J. Maassen and M. Lundstrom “A computational study of the thermoelectric performance of ultrathin Bi₂Te₃ films” *Appl. Phys. Lett.* 102(9), 093103 (2013).

- [52] D. Wickramaratne, F. Zahid, and R. K. Lake “Electronic and thermoelectric properties of few-layer transition metal dichalcogenides” *J. Chem. Phys.* 140, 124710 (2014).
- [53] K. X. Chen, X. M. Wang, D. C. Mo, S. S. Lyu, “Thermoelectric properties of transition metal dichalcogenides: from monolayers to nanotubes” *J. Phys. Chem. C*, 119(47), 26706-26711. (2015).
- [54] K. Hippalgaonkar, Y. Wang, Y. Ye, D. Y. Qiu, H. Zhu, Y. Wang, J. Moore, S. G. Louie, X. Zhang “High thermoelectric power factor in two-dimensional crystals of MoS₂” *Phys. Rev. B*, 95(11), 115407 (2017).
- [55] Z. Jin, Q. Liao, H. Fang, Z. Liu. W. Liu, Z. Ding, T. Luo, N. Yang “A revisit to high thermoelectric performance of single-layer MoS₂” *Sci. Rep.* 5 18342 (2015).
- [56] K. Ghosh U. Singiseti “Thermoelectric transport coefficients in mono-layer MoS₂ and WSe₂: role of substrate, interface phonons, plasmon, and dynamic screening” *J. Appl. Phys.* 118(13) 135711 (2015).
- [57] S. Kumar U. Schwingenschlögl “Thermoelectric response of bulk and monolayer MoSe₂ and WSe₂” *Chem. Mater.* 27 1278–1284 (2015).
- [58] W. Li, J. Carrete, N. Mingo “Thermal conductivity and phonon linewidths of monolayer MoS₂ from first principles” *Appl. Phys. Lett.* 103(25) 253103 (2013).
- [59] H. Y. Lv, W. J. Lu, D. F. Shao H. Y. Lu, Y. P. Sun “Strain-induced enhancement in the thermoelectric performance of a ZrS₂ monolayer” *J. Mater. Chem. C*, 4(20) 4538–4545 (2016).

- [60] W. Zhang, Z. Huang, W. Zhang, Y. Li “Two-dimensional semiconductors with possible high room temperature mobility” *Nano. Res.* 7(12) 1731–1737 (2014).
- [61] G. Yumnam, T. Pandey, A. K. Singh “High temperature thermoelectric properties of Zr and Hf based transition metal dichalcogenides: a first principles study” *J. Chem. Phys.* 143(23), 234704 (2015).
- [62] G. Li, G. Ding, G. Gao, “Thermoelectric properties of SnSe₂ monolayer” *J. Phys. Condens. Matter*, 29(1), 015001 (2016).
- [63] H. Y. Lv, W. J. Lu, X. Luo, H. Y. Lu, X. B. Zhu, Y. P. Sun “Enhancing the thermoelectric performance of a HfS₂ monolayer through valley engineering” *cond-mat.mes-hall* 1608.05464 2016.
- [64] G. Ding, G. Y. Gao, Z. Huang, W. Zhang, K. Yao Thermoelectric properties of monolayer MSe₂ (M= Zr, Hf): low lattice thermal conductivity and a promising figure of merit” *Nanotechnology*, 27(37), 375703 (2016).
- [65] D. Qin, X. J. Ge, G. Q. Ding, G. Y. Gao, J. T. Lü, “Strain-induced thermoelectric performance enhancement of monolayer ZrSe₂” *RSC Adv.* 7(75), 47243-47250. (2017).
- [66] H. L. Zhuang, R. G. Hennig “Computational Search for Single-Layer Transition-Metal Dichalcogenide Photocatalysts” *J. Phys. Chem. C* 117(40), 20440-20445. (2013).

- [67] H. P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, A. V. Krasheninnikov “Two-dimensional transition metal dichalcogenides under electron irradiation: defect production and doping” *Phys. Rev. Lett.* 109(3), 035503 (2012).
- [68] X. Hong, J. Kim, S. F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang “Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures” *Nat. Nano technol.* 9(9), 682 (2014).
- [69] H. P. Komsa and A. V. Krasheninnikov “Electronic structures and optical properties of realistic transition metal dichalcogenide heterostructures from first principles” *Phys. Rev. B*, 88(8), 085318. (2013).
- [70] N. Lu, H. Guo, L. Wang, X. Wu, and X. C. Zeng “van der Waals trilayers and superlattices: modification of electronic structures of MoS₂ by intercalation” *Nanoscale*, 6(9), 4566-4571. (2014).
- [71] B. Amin, T. P. Kaloni, U. Schwingenschlögl, “Strain engineering of WS₂, WSe₂, and WTe₂” *RSC Adv.* 4(65), 34561-34565 (2014).
- [72] Y. Chen, J. Xi, D.O. Dumcenco, Z. Liu, K. Suenaga, D. Wang, Z. Shuai, Y.S. Huang, L. Xie “Tunable band gap photoluminescence from atomically thin transition-metal dichalcogenide alloys” *ACS Nano*, 7(5), 4610-4616 (2013).
- [73] A. Ramasubramaniam, D. Naveh, E. Towe “Tunable band gaps in bilayer transition-metal dichalcogenides” *Phys. Rev. B* 84(20), 205325 (2011).

- [74] S. Bertolazzi, J. Brivio, A. Kis “Stretching and breaking of ultrathin MoS₂. *ACS Nano*, 5(12), 9703-9709 (2011).
- [75] Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, Z. X. Shen “Uniaxial strain on graphene: Raman spectroscopy study and band-gap opening” *ACS Nano*, 2(11), 2301-2305 (2008).
- [76] V. M. Pereira, A. C. Neto, N. M. R. Peres “Tight-binding approach to uniaxial strain in graphene” *Phys. Rev. B*, 80(4), 045401 (2009).
- [77] P. Johari, V. B. Shenoy “Tuning the electronic properties of semiconducting transition metal dichalcogenides by applying mechanical strains” *ACS Nano*, 6(6), 5449-5456 (2012).
- [78] Q. Yue, J. Kang, Z. Shao, X. Zhang, S. Chang, G. Wang, S. Qin, J. Li, “Mechanical and electronic properties of monolayer MoS₂ under elastic strain” *Phys. Lett. A*, 376(12-13), 1166-1170 (2012).
- [79] H. Shi, H. Pan, Y. W. Zhang, B. I. Yakobson “Quasiparticle band structures and optical properties of strained monolayer MoS₂ and WS₂” *Phys. Rev. B*, 87(15), 155304 (2013).
- [80] W. Hu, J. Yang, “Two-dimensional van der Waals heterojunctions for functional materials and devices” *J. Mater. Chem. C*, 5(47), 12289–12297 (2017).
- [81] L. Dong, R. R. Namburu, T. P. O'Regan, M. Dubey, A. M. Dongare “Theoretical study on strain-induced variations in electronic properties of monolayer MoS₂” *J. Mater. Sci.* 49(19), 6762-6771 (2014).

- [82] M. Ghorbani-Asl, S. Borini, A. Kuc, T. Heine, “Strain-dependent modulation of conductivity in single-layer transition-metal dichalcogenides” *Phys. Rev. B*, 87(23), 235434 (2013).
- [83] N. Harada, S. Sato, N. Yokoyama “Computational study on electrical properties of transition metal dichalcogenide field-effect transistors with strained channel” *J. Appl. Phys.* 115(3), 034505 (2014).
- [84] S. Horzum, H. Sahin, S. Cahangirov, P. Cudazzo, A. Rubio, T. Serin, F. M. Peeters “Phonon softening and direct to indirect band gap crossover in strained single-layer MoSe₂” *Phys. Rev. B*, 87(12), 125415 (2013).
- [85] P. Lu, X. Wu, W. Guo, X. C. Zeng “Strain-dependent electronic and magnetic properties of MoS₂ monolayer, bilayer, nanoribbons and nanotubes” *Phys. Chem. Chem. Phys.* 14(37), 13035-13040 (2012).
- [86] E. Scalise, M. Houssa, G. Pourtois, V. V. Afanas, A. Stesmans “First-principles study of strained 2D MoS₂” *Physica E: Low-dimensional Systems and Nanostructures*, 56, 416-421 (2014).
- [87] L. Wang, A. Kutana, B. I. Yakobson “Many-body and spin-orbit effects on direct-indirect band gap transition of strained monolayer MoS₂ and WS₂”. *Ann. Phys. (Berl.)*, 526(9-10), L7-L12 (2014).
- [88] S. Bhattacharyya, T. Pandey, A. K. Singh “Effect of strain on electronic and thermoelectric properties of few layers to bulk MoS₂” *Nanotechnology*, 25(46), 465701 (2014).

- [89] L. Zhu, T. Zhang, Z. Sun, J. Li, G. Chen, S. A. Yang “Thermal conductivity of biaxial-strained MoS₂: sensitive strain dependence and size-dependent reduction rate” *Nanotechnology*, 26(46), 465707 (2015).
- [90] H. Rostami, R. Roldán, E. Cappelluti, R. Asgari, F. Guinea, “Theory of strain in single-layer transition metal dichalcogenides” *Phys. Rev. B*, 92(19), 195402 (2015).
- [91] T. Cheiwchanchamnangij, W. R. Lambrecht, Y. Song, H. Dery, “Strain effects on the spin-orbit-induced band structure splittings in monolayer MoS₂ and graphene” *Phys. Rev. B*, 88(15), 155404 (2013).
- [92] A. Kumar, P. K. Ahluwalia “Mechanical strain dependent electronic and dielectric properties of two-dimensional honeycomb structures of MoX₂ (X= S, Se, Te)” *Physica B*, 419, 66-75 (2013).
- [93] H. Zhu, Y. Wang, J. Xiao, M. Liu, S. Xiong, Z. J. Wong, Z. Ye, Y. Ye, X. Yin. X. Zhang “Observation of piezoelectricity in freestanding monolayer MoS₂” *Nat. Nanotechnol.* 10(2), 151–155 (2015).
- [94] S. Manzeli, A. Allain, A. Ghadimi, A. Kis, “Piezoresistivity and strain-induced band gap tuning in atomically thin MoS₂” *Nano Lett.* 15(8), 5330–5335 (2015).
- [95] D. Lloyd, X. Liu, J. W. Christopher, L. Cantley, A. Wadehra, B. L. Kim, B. B. Goldberg, A. K. Swan, J. S. Bunch, “Band gap engineering with ultralarge biaxial strains in suspended monolayer MoS₂” *Nano Lett.* 16(9), 5836–5841 (2016).
- [96] H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund Jr, S. T. Pantelides, K. I.

- Bolotin, “Bandgap engineering of strained monolayer and bilayer MoS₂” *Nano Lett.* 13(8), 3626–3630 (2013).
- [97] K. He, C. Poole, K. F. Mak, J. Shan, “Experimental demonstration of continuous electronic structure tuning via strain in atomically thin MoS₂” *Nano Lett.* 13(6), 2931–2936 (2013).
- [98] C. R. Zhu, G. Wang, B. L. Liu, X. Marie, X. F. Qiao, X. Zhang, X.X. Wu, H. Fan, P.H. Tan, T. Amand, B. Urbaszek, “Strain tuning of optical emission energy and polarization in monolayer and bilayer MoS₂” *Phys. Rev. B*, 88(12), 121301 (2013).
- [99] H. Li, A. W. Contryman, X. Qian, S. M. Ardakani, Y. Gong, X. Wang, J.M. Weisse, C.H. Lee, J. Zhao, P.M. Ajayan, J. Li ”Optoelectronic crystal of artificial atoms in strain-textured molybdenum disulphide” *Nat. Commun.* 6, 7381 (2015).
- [100] Y. Y. Hui, X. Liu, W. Jie, N. Y. Chan, J. Hao, Y. T. Hsu, L. J. Li, W. Guo, S. P. Lau “Exceptional tunability of band energy in a compressively strained trilayer MoS₂ sheet” *ACS Nano*, 7(8), 7126–7131 (2013).
- [101] G. Plechinger, A. Castellanos-Gomez, M. Buscema, H. S. van der Zant, G. A. Steele, A. Kuc, T. Heine, C. Schueller, T. Korn “Control of biaxial strain in single-layer molybdenite using local thermal expansion of the substrate” *2D Mater.* 2(1), 015006 (2015).
- [102] S. B. Desai, G. Seol, J. S. Kang, H. Fang, C. Battaglia, R. Kapadia, J.W. Ager, J. Guo, A. Javey “Strain-induced indirect to direct band gap transition in multilayer

- WSe₂” *Nano Lett.* 14(8), 4592–4597 (2014).
- [103] J. O. Island, A. Kuc, E. H. Diependaal, R. Bratschitsch, H. S. van der Zant, T. Heine, A. Castellanos-Gomez “Precise and reversible band gap tuning in single-layer MoSe₂ by uniaxial strain” *Nanoscale*, 8(5), 2589–2593 (2016).
- [104] Z. Liu, M. Amani, S. Najmaei, Q. Xu, X. Zou, W. Zhou, T. Yu, C. Qiu, A.G. Birdwell, F.J. Crowne, R. Vajtai “Strain and structure heterogeneity in MoS₂ atomic layers grown by chemical vapour deposition” *Nat. Commun.* 5, 5246 (2014).
- [105] C. Rice, R. J. Young, R. Zan, U. Bangert, D. Wolverson, T. Georgiou, R. Jalil, K. S. Novoselov “Raman-scattering measurements and first-principles calculations of strain-induced phonon shifts in monolayer MoS₂” *Phys. Rev. B*, 87(8), 081307 (2013).
- [106] K. A. N. Duerloo, M. T. Ong, E. J. Reed, “Intrinsic piezoelectricity in two-dimensional materials” *J. Phys. Chem. Lett.* 3(19), 2871–2876 (2012).
- [107] M. N. Blonsky, H. L. Zhuang, A. K. Singh, R. G. Hennig “Ab-initio prediction of piezoelectricity in two-dimensional materials” *ACS Nano*, 9(10), 9885–9891 (2015).
- [108] W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T.F. Heinz, J. Hone, “Piezoelectricity of single-atomic-layer MoS₂ for energy conversion and piezotronics”. *Nature*, 514(7523), 470–474 (2014).
- [109] A.D. Smith, F. Niklaus, A. Paussa, S. Vaziri, A.C. Fischer, M. Sterner, F.

- Forsberg, A. Delin, D. Esseni, P. Palestri, M. Ostling “Electromechanical piezoresistive sensing in suspended graphene membranes” *Nano Lett.* 13(7), 3237–3242 (2013).
- [110] M. Huang, T. A. Pascal, H. Kim, W. A. Goddard, J. R. Greer “Electronic-mechanical coupling in graphene from in situ nanoindentation experiments and multi scale atomistic simulations” *Nano Lett.* 11(3), 1241–1246 (2011).
- [111] Y. Kanda “Piezoresistance effect of silicon” *Sens. Actuators Phys.* 28(2), 83-91 (1991).
- [112] K. E. Petersen “Silicon as a mechanical material” *Proc. IEEE*, 70(5), 420–457 (1982).
- [113] P.M. Solomon, B.A. Bryce, M.A. Kuroda, R. Keech, S. Shetty, T.M. Shaw, M. Copel, L.W. Hung, A.G. Schrott, C. Armstrong, M.S. Gordon “Pathway to the piezoelectronic transduction logic device” *Nano Lett.* 15(4), 2391–2395 (2015).
- [114] D. Newns, B. Elmegreen, X. H. Liu, G. Martyna “A low-voltage high-speed electronic switch based on piezoelectric transduction” *J. Appl. Phys.* 111(8), 084509 (2012).
- [115] W. Wu, L. Wang, R. Yu, Y. Liu, S.H. Wei, J. Hone, Z.L. Wang “Piezophototronic effect in single-atomic-layer MoS₂ for strain-gated flexible optoelectronics” *Adv. Mater.* 28(38), 8463–8468 (2016).
- [116] K.S. Novoselov, A. Mishchenko, A. Carvalho, A. C. Neto, “2D materials and van der Waals heterostructures” *Science*, 353(6298), aac9439 (2016).

- [117] P. Ajayan, P. Kim, K. Banerjee, “Two-dimensional van der Waals materials” *Phys. Today*, 69, 9-38 (2016).
- [118] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, A.C. Ferrari “Production and processing of graphene and 2D crystals” *Mater. Today*, 15(12), 564–589(2012).
- [119] H. Li, X. Duan, X. Wu, X. Zhuang, H. Zhou, Q. Zhang, X. Zhu, W. Hu, P. Ren, P. Guo, L. Ma, X. Fan, X. Wang, J. Xu, A. Pan, X. Duan “Growth of alloy $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ nanosheets with fully tunable chemical compositions and optical properties” *J. Am. Chem. Soc.* 136 (10), 3756–3759 (2014).
- [120] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, H. Terrones, M. Terrones, B. K. Tay, J. Lou, S. T. Pantelides, Z. Liu, W. Zhou, and P. M. Ajayan “Vertical and in-plane heterostructures from WS_2/MoS_2 monolayers” *Nat. Mater.* 13(12), 1135 (2014).
- [121] B. Amin, N. Singh, and U. Schwingenschlogl “Heterostructures of transition metal dichalcogenides” *Phy. Rev. B*, 92(7), 075439 (2015).
- [122] A. Ramasubramaniam, D. Naveh, E. Towe “Tunable Band Gaps in Bilayer Graphene-BN Heterostructures” *Nano Lett.* 11(3), 1070-1075 (2011).
- [123] G. Fiori, A. Betti, S. Bruzzone, G. Iannaccone “Lateral Graphene-hBCN Heterostructures as a Platform for Fully Two-Dimensional Transistors” *ACS Nano*, 6(3), 2642-2648 (2012).

- [124] L. Kou, T. Frauenheim, C. Chen “Nanoscale Multilayer Transition-Metal Dichalcogenide Heterostructures: Band Gap Modulation by Interfacial Strain and Spontaneous Polarization” *J. Phys. Chem. Lett.* 4(10), 1730-1736(**2013**).
- [125] G. W. Shim, K. Yoo, S.-B. Seo, J. Shin, D. Y. Jung, I.-S. Kang, C. W. Ahn, B.J. Cho, S.-Y. Choi “Large-Area Single-Layer MoSe₂ and Its van der Waals Heterostructures” *ACS Nano*, 8(7), 6655-6662 (**2014**).
- [126] H. Zhang, Y.-N. Zhang, H. Liu, L.-M. Liu “Novel Heterostructures by Stacking Layered Molybdenum Disulfides and Nitrides for Solar Energy Conversion” *J. Mater. Chem. A*, 2(37), 15389-15395(**2014**).
- [127] H. Tributsch, J.C. Bennett “Electrochemistry and photochemistry of MoS₂ layer crystals. I”, *J. Electroanal. Chem.* 81(1), 97–111(**1977**).
- [128] A.K. Geim, I.V. Grigorieva, “Van der Waals heterostructures” *Nature*, 499(7459), 419–425 (**2013**).
- [129] H. Fang, C. Battaglia, C. Carraro, S. Nemsak, B. Ozdol, J.S. Kang, H.A. Bechtel, S.B. Desai, F. Kronast, A.A. Unal, G. Conti, C. Conlon, G.K. Palsson, M.C. Martin, A.M. Minor, C.S. Fadley, E. Yablonovitch, R. Maboudian, A. Javey “Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides” *Proc. Natl. Acad. Sci. U. S. A.* 111(17), 6198–6202(**2014**) .
- [130] C.H. Lee, G.-H. Lee, A.M. van der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T.F. Heinz, J. Guo, J. Hone, P. Kim “Atomically thin p-n junctions with van der Waals heterointerfaces”, *Nat. Nanotechnol.* 9(9), 676–681

(2014).

- [131] L. Britnell, R.M. Ribeiro, A. Eckmann, R. Jalil, B.D. Belle, A. Mishchenko, Y.-J. Kim, R.V. Gorbachev, T. Georgiou, S.V. Morozov, A.N. Grigorenko, A.K. Geim, C. Casiraghi, A.H.C. Neto, K.S. Novoselov “Strong light-matter interactions in heterostructures of atomically thin films” *Science* 340(6138), 1311–1314 (2013).
- [132] F. Withers, O. Del Pozo-Zamudio, A. Mishchenko, A.P. Rooney, A. Gholinia, K. Watanabe, T. Taniguchi, S.J. Haigh, A.K. Geim, A.I. Tartakovskii, K.S. Novoselov “Light-emitting diodes by band-structure engineering in van der Waals heterostructures” *Nat. Mater.* 14(3), 301–306 (2015).
- [133] P. Rivera, J.R. Schaibley, A.M. Jones, J.S. Ross, S. Wu, G. Aivazian, P. Klement, K. Seyler, G. Clark, N.J. Ghimire, J. Yan, D.G. Mandrus, W. Yao, X. Xu “Observation of long-lived interlayer excitons in monolayer MoSe₂-WSe₂ heterostructures” *Nat. Commun.* 6, 6242 (2015).
- [134] M. Bernardi, M. Palummo, J.C. Grossman “Extraordinary sunlight absorption and one nanometer thick photovoltaics using two-dimensional monolayer materials” *Nano Lett.* 13(8), 3664–3670 (2013).
- [135] X.Q. Zhang, C.-H. Lin, Y.-W. Tseng, K.-H. Huang, Y.-H. Lee “Synthesis of lateral heterostructures of semiconducting atomic layers” *Nano Lett.* 15(1), 410–415 (2015).
- [136] C. Huang, S. Wu, A.M. Sanchez, J.J.P. Peters, R. Beanland, J.S. Ross, P.

- Rivera, W. Yao, D.H. Cobden, X. Xu, “Lateral heterojunctions within monolayer MoSe₂-WSe₂ semiconductors” *Nat. Mater.* 13(12), 1096–1101 (2014).
- [137] Y. Son, M.Y. Li, C.-C. Cheng, K.H. Wei, P. Liu, Q.H. Wang, L.J. Li, M.S. Strano “Observation of switchable photoresponse of a monolayer WSe₂-MoS₂ lateral heterostructure via photocurrent spectral atomic force microscopic imaging” *Nano Lett.* 16(6), 3571–3577 (2016).
- [138] H. Kumar, , D. Er, L. Dong, J. Li, V. B. Shenoy “Elastic deformations in 2D van der Waals hetero structures and their impact on optoelectronic properties: predictions from a multiscale computational approach” *Sci. Rep.* 5, 10872 (2015).
- [139] M. Sharma, A. Kumar, P. K Ahluwalia, R. Pandey “Strain and electric field induced electronic properties of two-dimensional hybrid bilayers of transition-metal dichalcogenides” *J. Appl. Phys.* 116(6), 063711 (2014).
- [140] S. Yu, V Zhu, K. Eshun, C. Shi, , M. Zeng, , Q. Li “Strain-engineering the anisotropic electrical conductance in ReS₂ monolayer” *Appl. Phys. Lett.* 108(19), 191901 (2016).
- [141] J. D. Werking, C. R. Bolognesi, L. D.Chang, C. Nguyen, E. L. Hu, H. Kroemer “High-Transconductance InAs/AlSb Heterojunction Field-Effect Transistors with Delta-Doped AlSb Upper Barriers” *IEEE Electr. Device Lett.* 13(3), 164–166 (1992).
- [142] A. Levi, T. Chiu, “Room-Temperature Operation of Hot-Electron Transistors” *Appl. Phys. Lett.* 51(13), 984–986 (1987).

- [143] F. Capasso, S. Sen, A. C. Gossard, A. L. Hutchinson, J. H. English “Quantum-Well Resonant Tunneling Bipolar Transistor Operating at Room Temperature” *IEEE Electr. Device Lett.* 7, 573–576 (**1986**).
- [144] S. O. Koswatta, S. J. Koester, W. Haensch “On the Possibility of Obtaining MOSFET-Like Performance and Sub-60-mV/dec Swing in 1-D Broken-Gap Tunnel Transistors” *IEEE Trans. Electron Devices*, 57(12), 3222–3230 (**2010**).
- [145] Y. Zhang, W. Ma, Y. Cao, J. Huang, Y. Wei, K. Cui, J. Shao “Long Wavelength Infrared InAs/GaSb Superlattice Photodetectors with InSb-Like and Mixed Interfaces” *IEEE J. Quantum Electron.* 47(12), 1475–1479 (**2011**).
- [146] J. Meyer, C. Hoffman, F. Bartoli, L. Ram-Mohan “Type-II Quantum-Well Lasers for the Mid-Wavelength Infrared” *Appl. Phys. Lett.* 67(6), 757–759 (**1995**).
- [147] J. Y. Ji, H. X. Ji, L.L. Zhang, X. Zhao, X. Bai, X. B. Fan, F. B. Zhang, R. S. Ruoff, “Graphene-Encapsulated Si on Ultrathin- Graphite Foam as Anode for High Capacity Lithium-Ion Batteries” *Adv. Mater.* 25(33), 4673–4677 (**2013**).
- [148] Y. Yu, S. Hu, L. Su, L. Huang, Y. Liu, Z. Jin, A. A. Purezky, D. B. Geohegan, K. W. Kim, Y. Zhang, and L. Cao “Equally efficient interlayer exciton relaxation and improved absorption in epitaxial and nonepitaxial MoS₂/WS₂ heterostructures” *Nano Lett.* 15(1), 486 (**2015**).
- [149] H. Terrones, F. López-Urías, M. Terrones “Novel hetero-layered materials with tunable direct band gaps by sandwiching different metal disulfides and diselenides”. *Sci. Rep.* 3, 1549 (**2013**).

- [150] K. Kořmider, J. Fernandez-Rossier “Electronic properties of the MoS₂-WS₂ heterojunction” *Phys. Rev. B*, 87(7), 075451 (2013).
- [151] T. Jiang, H. Liu, D. Huang, S. Zhang, Y. Li, X. Gong, Y. R. Shen, W. T. Liu, S. Wu “Valley and band structure engineering of folded MoS₂ bilayers” *Nat. Nanotechnol.* 9(10), 825 (2014).
- [152] M. Xu, T. Liang, M. Shi, H. Chen “Graphene-like two-dimensional materials” *Chem. Rev.* 113(5), 3766-3798 (2013).
- [153] F. Ceballos, M. Z. Bellus, H. Y. Chiu, H. Zhao, “Ultrafast charge separation and indirect exciton formation in a MoS₂–MoSe₂ van der Waals heterostructure” *ACS Nano*, 8(12), 12717-12724 (2014).
- [154] B. Peng, P. K., Ang, K. P. Loh “Two-dimensional dichalcogenides for light-harvesting applications”. *NANO TODAY*, 10(2), 128-137 (2015).
- [155] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L.M. Herz, A. Petrozza, H.J. Snaith, “Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber” *Science*, 342, 341—344 (2013).
- [156] E.J. Sie, J.W. McIver, Y.-H. Lee, L. Fu, J. Kong, N. Gedik, “Valley-selective optical Stark effect in monolayer WS₂” *Nat. Mater.* 14(3), 290-294, (2014).
- [157] M. Y. Su, S. G. Carter, M. S. Sherwin, A. Huntington, L. A. Coldren “Voltage-controlled wavelength conversion by terahertz electro-optic modulation in double quantum wells” *Appl. Phys. Lett.* 81(9), 1564-1566 (2002).

- [158] Z. Yuan, B.E. Kardynal, R.M. Stevenson, A.J. Shields, C.J. Lobo, K. Cooper, N.S. Beattie, D.A. Ritchie, M. Pepper “Electrically driven single-photon source” *Science*, 295(5552), 102-105 (**2002**).
- [159] G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, L. Colombo “Electronics based on two-dimensional materials” *Nat. Nanotechnol.* 9(10), 768-779 (**2014**).
- [160] D. Akinwande, N. Petrone, J. Hone “Two-dimensional flexible nanoelectronics”. *Nat. Commun.* 5, 5678 (2014).
- [161] Thermoelectrics Handbook: Macro to nano, ed. D. M. Rowe, Taylor & Francis Group, New York, 2006.
- [162] F. Ghahari, H. Y. Xie, T. Taniguchi, K. Watanabe, M. S. Foster, P. Kim “Enhanced thermoelectric power in graphene: Violation of the Mott relation by inelastic scattering” *Phys. Rev. Lett.* 116(13), 136802 (**2016**).
- [163] A. A. Balandin, “Thermal properties of graphene and nanostructured carbon materials” *Nat. Mater.* 10(8), 569 (**2011**).
- [164] B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyc, R. A. Segalman “Organic thermoelectric materials for energy harvesting and temperature control” *Nat. Rev. Mater.* 1(10), 16050 (**2016**).
- [165] Wang, D., Shi, W., Chen, J., Xi, J., & Shuai, Z. (2012). Modeling thermoelectric transport in organic materials. *Phys. Chem. Chem. Phys.* 14(48), 16505-16520 (**2012**).

- [166] Shuai, Z., Geng, H., Xu, W., Liao, Y., & André, J. M. (2014). From charge transport parameters to charge mobility in organic semiconductors through multiscale simulation. *Chem. Soc. Rev.* 43(8), 2662-2679 (2014).
- [167] V. Sorkin, H. Pan, H. Shi, S. Y. Quek, Y. W. Zhang, “Nanoscale transition metal dichalcogenides: structures, properties, and applications”. *CRIT REV SOLID STATE* 39(5), 319-367 (2014).
- [168] S. Balendhran, S. Walia, H. Nili, J.Z. Ou, S. Zhuiykov, R.B. Kaner, S. Sriram, M. Bhaskaran, K. Kalantar-zadeh, “Two-dimensional molybdenum trioxide and dichalcogenides” *Adv. Funct. Mater.* 23(32),3952-3970 (2013).
- [169] D. L. Trimm, Z. I. Önsan “Onboard fuel conversion for hydrogen-fuel-cell-driven vehicles” *CATAL REV.*, 43(1-2), 31-84.(2001)
- [170] A. Kudo, Y. Miseki, “Heterogeneous photocatalyst materials for water splitting” *Chem. Soc. Rev.* 38(1), 253-278 (2009).
- [171] N. S. Lewis, D. G. Nocera “Powering the planet: Chemical challenges in solar energy utilization” *Proc. Natl. Acad. Sci. U. S. A.* 103(43), 15729-15735 (2006).
- [172] J. Sato, N. Saito, Y. Yamada, K. Maeda, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, Y. Inoue, “RuO₂-loaded β -Ge₃N₄ as a non-oxide photocatalyst for overall water splitting” *J. Am. Chem. Soc.* 127(12), 4150-4151 (2005).
- [173] Y. Li, Y. L. Li, C. M. Araujo, W. Luo, R. Ahuja, “Single-layer MoS₂ as an efficient photocatalyst” *Catal. Sci. Technol.* 3(9), 2214-2220 (2013).

- [174] T. Li, Ideal strength and phonon instability in single-layer MoS₂. *Phys. Rev. B*, 85(23), 235407 (2012).
- [175] E. Scalise, M. Houssa, G. Pourtois, V. Afanas'ev, A. Stesmans "Strain-induced semiconductor to metal transition in the two-dimensional honeycomb structure of MoS₂". *Nano Res.* 5(1), 43-48 (2012).
- [176] Y. Shi, J. K. Huang, L. Jin, Y. T. Hsu, S. F. Yu, L. J. Li, H. Y. Yang "Selective decoration of Au nanoparticles on monolayer MoS₂ single crystals" *Sci. Rep.* 3, 1839 (2013).
- [177] M. S. Choi, D. Qu, D. Lee, X. Liu, K. Watanabe, T. Taniguchi, W. J. Yoo, "Lateral MoS₂ p-n junction formed by chemical doping for use in high-performance optoelectronics" *ACS Nano*, 8(9), 9332-9340 (2014).
- [178] K. Dolui, I. Rungger, C. D. Pemmaraju, S. Sanvito "Possible doping strategies for MoS₂ monolayers: An ab-initio study" *Phys. Rev. B*, 88(7), 075420 (2013).
- [179] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D.C. Alves, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda, M. Chhowalla "Enhanced catalytic activity in strained chemically exfoliated WS₂ nanosheets for hydrogen evolution" *Nat. Mater.* 12(9), 850 (2013).
- [180] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda, M. Chhowalla "Conducting MoS₂ nanosheets as catalysts for hydrogen evolution reaction" *Nano Lett.* 13(12), 6222-6227 (2013).

- [181] A. Fujishima, Y. Noguchi, K. Honda, B. H. Loo “Photoelectrochemical Studies of MoS₂ Electrode by Rotating Ring-disk Electrode Technique” *Bull. Chem. Soc. Jpn.* 55(1), 17-22 (**1982**).
- [182] L. F. Schneemeyer, M. S. Wrighton, “Flat-band potential of n-type semiconducting molybdenum disulfide by cyclic voltammetry of two-electron reductants: interface energetics and the sustained photooxidation of chloride” *J. Am. Chem. Soc.* 101(22), 6496-6500 (**1979**).
- [183] S. W. Tong, Y. Wang, Y. Zheng, M. F. Ng, K. P. Loh, “Graphene intermediate layer in tandem organic photovoltaic cells” *Adv. Funct. Mater.* 21(23), 4430-4435 (**2011**).
- [184] A. Polman, H. A. Atwater “Photonic design principles for ultrahigh-efficiency photovoltaics” *Nat. Mater.* 11(3), 174 (**2012**).
- [185] B. W. Baugher, H. O. Churchill, Y. Yang, P. Jarillo-Herrero, “Optoelectronic devices based on electrically tunable p-n diodes in a monolayer dichalcogenide” *Nat. Nanotechnol.* 9(4), 262 (**2014**).
- [186] H. Fang, S. Chuang, T. C. Chang, K. Takei, T. Takahashi, A. Javey “High-performance single layered WSe₂ p-FETs with chemically doped contacts” *Nano Lett.* 12(7), 3788-3792 (**2012**).
- [187] M. M. Furchi, A. Pospischil, F. Libisch, J. Burgdörfer, T. Mueller “Photovoltaic effect in an electrically tunable van der Waals heterojunction” *Nano Lett.* 14(8), 4785-4791 (**2014**).

- [188] M.L. Tsai, S.H. Su, J.K. Chang, D.S. Tsai, C.H. Chen, C.I. Wu, L.J. Li, L.J. Chen, J.H. He, “Monolayer MoS₂ heterojunction solar cells” *ACS Nano*, 8(8), 8317-8322 (2014).
- [189] Z. L. Wang, G. Zhu, Y. Yang, S. Wang, C. Pan, “Progress in nanogenerators for portable electronics” *Mater. Today*, 15(12), 532-543 (2012).
- [190] M. K. Gupta, J. H. Lee, K. Y. Lee, S. W. Kim “Two-dimensional vanadium-doped ZnO nanosheet-based flexible direct current nanogenerators” *ACS Nano*, 7(10), 8932-8939 (2013).
- [191] K. H. Kim, B. Kumar, K. Y. Lee, H. K. Park, J. H. Lee, H. H. Lee, H. Jun, D. Lee, S. W. Kim “Piezoelectric two-dimensional nanosheets/anionic layer heterojunction for efficient direct current power generation” *Sci. Rep.* 3, 2017 (2013).
- [192] H. Zhu, Y. Wang, J. Xiao, M. Liu, S. Xiong, Z. J. Wong, Z. Ye, Y. Ye, X. Yin, X. Zhang “Observation of piezoelectricity in free-standing monolayer MoS₂” *Nat. Nanotechnol.* 10(2), 151 (2015).
- [193] J. Qi, Y. W. Lan, A. Z. Stieg, J. H. Chen, Y. L. Zhong, L. J. Li, C. D. Chen, Y. Zhang, K. L. Wang “Piezoelectric effect in chemical vapour deposition-grown atomic-monolayer triangular molybdenum disulfide piezotronics” *Nat. Commun.* 6, 7430 (2015).

- [194] I. Cacelli, “The Hartree-Fock Method” *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, 1st ed.; Reedijk, J., Ed, 1-14 2015.
- [195] P. Hohenberg, W. Kohn “Inhomogeneous electron gas” *Phys. Rev.* 136, 864-887 (1964).
- [196] W. Kohn, L. Sham “Self-consistent equations including exchange and correlation effects” *Phys. Rev.* 140, 1133 (1965).
- [197] Mel Levy “Universal variational functionals of electron densities, first order density matrices, and natural spin-orbitals and solution of the v-representability problem” *Proc.Natl. Acad.Sci. U.S.A*, 76(12), 6062–6065 (1979).
- [198] O. Gunnarsson, B. I. Lundqvist “Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism” *Phys. Rev. B*, 13, 4274–4298, (1976).
- [199] E. K. U. Gross, L. N. Oliveira, W. Kohn “Density-functional theory for ensembles of fractionally occupied states. I. basic formalism” *Phys. Rev. A*, 37(8), 2809–2820 (1988).
- [200] A K Theophilou “The energy density functional formalism for excited states” *J. Phys. C: Solid State Phys.* 12(24), 5419 (1979).
- [201] G. Vignale, Walter Kohn “Current-dependent exchange-correlation potential for dynamical linear response theory” *Phys. Rev. Lett.* 77(10), 2037–2040 (1996).

- [202] G. Vignale, M. Rasolt “Density-functional theory in strong magnetic fields” *Phys. Rev. Lett.* 59(20), 2360–2363 (**1987**).
- [203] A K Rajagopal “Inhomogeneous relativistic electron gas” *J. Phys. C: Solid State Phys.* 11(24), L943 (**1978**).
- [204] A. K. Rajagopal, J. Callaway “Inhomogeneous electron gas” *Phys. Rev. B*, 7, 1912–1919 (**1973**).
- [205] M.A.L. Marques, N.T. Maitra, F.M.D.S. Nogueira, E.K.U. Gross, A. Rubio “Fundamentals of Time-Dependent Density Functional Theory” volume 837, Springer Science & Business Media, **2012**.
- [206] U. von Barth, L. Hedin “A local exchange-correlation potential for the spin polarized case. I” *J. Phys. C: Solid State Phys.* 5(13), 1629 (**1972**).
- [207] S. H. Vosko, L. Wilk, M. Nusair “Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis” *Can. J. Phys.* 58(8), 1200–1211 (**1980**).
- [208] J.P. Perdew, A. Zunger “Self-interaction correction to density-functional approximations for many-electron systems” *Phys. Rev. B*, 23, 5048 (**1981**).
- [209] J. P. Perdew, K. Burke, M. Ernzerhof “Generalized gradient approximation made simple” *Phys. Rev. Lett.* 77(18), 3865 (**1996**).
- [210] P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, J. Sun “Workhorse semilocal density functional for condensed matter physics and quantum chemistry” *Phys. Rev. Lett.* 103(2), 026403 (**2009**).

- [211] A. D. Becke "Density-functional exchange-energy approximation with correct asymptotic behavior" *Phys. Rev. A*, 38(6), 3098 (**1988**).
- [212] C. Lee, W. Yang, R. G. Parr "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density" *Phys. Rev. B*, 37(2), 785 (**1988**).
- [213] J. P. Perdew "Density-functional approximation for the correlation energy of the inhomogeneous electron gas" *Phys. Rev. B*, 33(12), 8822 (**1986**).
- [214] J. P. Perdew "Erratum: Density-functional approximation for the correlation energy of the inhomogeneous electron gas" *Phys. Rev. B*, 34(10), 7406 (**1986**).
- [215] J. P. Perdew "Electronic Structure of Solids" 91, Akademie Verlag, Berlin **1991**.
- [216] E. Engle, S. H. Vosko "Exact exchange-only potentials and the virial relation as microscopic criteria for generalized gradient approximations" *Phys. Rev. B*, 47(20), 13164 (**1993**).
- [217] Z. Wu, R. E. Cohen "More accurate generalized gradient approximation for solids" *Phys. Rev. B*, 73(23), 235116 (**2006**).
- [218] A. D. Becke "Phys. Re V. A 1988, 38, 3098.(b) Becke." *J. Chem. Phys.* 98(1372), 5648 (**1993**).
- [219] C. A. White, B. G. Johnson, P. M. Gill, M. Head-Gordon "The continuous fast multipole method" *Chem. Phys. Lett.* 230(1-2), 8-16 (**1994**).

- [220] J. C. Burant, G. E. Scuseria, M. J. Frisch “A linear scaling method for Hartree-Fock exchange calculations of large molecules” *J. Chem. Phys.* 105(19), 8969 (1996).
- [221] G. E. Scuseria “Linear scaling density functional calculations with Gaussian orbitals” *J. Phys. Chem.* 103(25), 4782 (1999).
- [222] K. N. Kudin, G. E. Scuseria “Linear-scaling density-functional theory with Gaussian orbitals and periodic boundary conditions: Efficient evaluation of energy and forces via the fast multipole method” *Phys. Rev. B*, 61(24), 16440 (2000).
- [223] V. Rokhlin, L. Greengard “A fast algorithm for particle simulations” *J. Comput. Phys.* 73, 325-348 (1987).
- [224] R. Kutteh, E. Apra', J. Nichols “A generalized fast multipole approach for Hartree-Fock and density functional computations” *Chem. Phys. Lett.* 238(1-3), 173 (1995).
- [225] M. C. Strain, G. E. Scuseria, M. J. Frisch “Achieving linear scaling for the electronic quantum Coulomb problem” *Science*, 271(5245), 51-53 (1996).
- [226] K. N. Kudin, G. E. Scuseria “A fast multipole algorithm for the efficient treatment of the Coulomb problem in electronic structure calculations of periodic systems with Gaussian orbitals” *Chem. Phys. Lett.* 289(5-6), 611-616 (1998).
- [227] K. N. Kudin, G. E. Scuseria “Analytic stress tensor with the periodic fast multipole method” *Phys. Rev. B*, 61(8), 5141 (2000).

- [228] E. Schwegler, M. Challacombe “Linear scaling computation of the Hartree-Fock exchange matrix” *J. Chem. Phys.* 105(7), 2726-2734 (**1996**).
- [229] C. Ochsenfeld, C. A. White, M. Head-Gordon “Linear and sublinear scaling formation of Hartree-Fock-type exchange matrices” *J. Chem. Phys.* 109(5), 1663-1669 (**1998**).
- [230] J. Heyd, G. E. Scuseria, M. Ernzerhof, “Hybrid functionals based on a screened Coulomb potential” *J. Chem. Phys.* 118(18), 8207-8215 (**2003**).
- [231] R. Kubo, M. Yokota, S. Nakajima “Statistical-mechanical theory of irreversible processes. II. Response to thermal disturbance” *J. Phys. Soc. Jpn.*, 12, 570-786 (**1957**).
- [232] J. M. Ziman “Electrons and phonons: The theory of transport phenomena in solids” Oxford University Press, USA, **2001**
- [233] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, “QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials” *J. Phys. Condens. Matter*, 21(39), 395502 (**2009**).
- [234] G. Kresse, J. furthmüller “Software vasp, vienna, 1999” *Phys. Rev. B*, 54(11), 169 (**1996**).
- [235] S. A. Khan, B. Amin, L. Y. Gan, I. Ahmad “Strain engineering of electronic structures and photocatalytic responses of MXenes functionalized by oxygen” *Phys. Chem. Chem. Phys.* 19(22), 14738-14744 (**2017**).

- [236] G. Rehman, S.A. Khan, B. Amin, I. Ahmad, L.Y. Gan, M. Maqbool “Intriguing electronic structures and optical properties of two-dimensional van der Waals heterostructures of Zr_2CT_2 (T= O, F) with $MoSe_2$ and WSe_2 ” *J. Mater. Chem. C*, 6(11), 2830-2839 (2018).
- [237] B. Amin, T. P. Kaloni, G. Schreckenbach, M. S. Freund “Materials properties of out-of-plane heterostructures of MoS_2 - WSe_2 and WS_2 - $MoSe_2$ ” *Appl. Phys. Lett.* 108(6), 063105 (2016).
- [238] X. Wang, F. Xia “Van der Waals heterostructures: Stacked 2D materials shed light” *Nat. Mater.* 14(3), 264 (2015).
- [239] Y. Liu, N. O. Weiss, X. Duan, H.C. Cheng, Y. Huang, X. Duan “Van der Waals heterostructures and devices” *Nat. Rev. Mater.* 1(9), 16042 (2016).
- [240] R. Bose, G. Manna, S. Jana, N. Pradhan, “ Ag_2S - $AgInS_2$: p-n junction heteronanostructures with quasi type-II band alignment” *ChemComm*, 50(23), 3074-3077 (2014).
- [241] Y. Zhao, Y. Zhang, Z. Yang, Y. Yan, K. Sun “Synthesis of MoS_2 and MoO_2 for their applications in H_2 generation and lithium ion batteries: a review” *Sci. Technol. Adv. Mater.* 14(4), .043501 (2013).
- [242] D. J. Late, Y. K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare, V. P. Dravid, C. N. R. Rao “Sensing behavior of atomically thin-layered MoS_2 transistors” *ACS Nano*, 7(6), 4879-4891 (2013).

- [243] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai “MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction” *J. Am. Chem. Soc.* 133(19), 7296-7299 (**2011**).
- [244] Chhowalla, M., Shin, H.S., Eda, G., Li, L.J., Loh, K.P. and Zhang, H., 2013. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* 5(4), .263 (**2013**).
- [245] B. Radisavljevic, M. B. Whitwick, A. Kis, “Integrated circuits and logic operations based on single-layer MoS₂”. *ACS Nano*, 5(12), 9934-9938 (**2011**).
- [246] K. Xu, Z. Wang, X. Du, , M. Safdar, C Jiang, J. He, “Atomic-layer triangular WSe₂ sheets: synthesis and layer-dependent photoluminescence property” *Nanotechnology*, 24(46), 465705 (**2013**).
- [247] S. Bertolazzi, D. Krasnozhan, A. Kis “Nonvolatile memory cells based on MoS₂/graphene heterostructures” *ACS Nano*, 7(4), .3246-3252 (**2013**).
- [248] S. D. Guo, “Biaxial strain tuned thermoelectric properties in monolayer PtSe₂” *J. Mater. Chem. C*, 4(39),.9366-9374 (**2016**).
- [249] W. J. Yu, Y. Liu, H. Zhou, A. Yin, Z. Li, Y Huang, X., Duan “Highly efficient gate-tunable photocurrent generation in vertical heterostructures of layered materials” *Nat. Nanotechnol.* 8(12), 952 (**2013**).
- [250] J. Shang, S. Zhang, X. Cheng, Z. Wei, J. Li “Electric field induced electronic properties modification of ZrS₂/HfS₂ van der Waals heterostructure” *RSC Adv.* 7(24), 14625-14630 (**2017**).

- [251] J. Li, Z. Shan, E. Ma “Elastic strain engineering for unprecedented materials properties” *MRS Bull.*, 39(2), 108-114 (**2014**).
- [252] S. Shimizu, M. S. Bahramy, T. Iizuka, S. Ono, K. Miwa, Y. Tokura, Y. Iwasa “Enhanced thermopower in ZnO two-dimensional electron gas” *Proc. Natl. Acad. Sci. U.S.A.* 113(23), 6438-6443 (**2016**).
- [253] Cai, Y., Lan, J., Zhang, G. and Zhang, Y.W., 2014. Lattice vibrational modes and phonon thermal conductivity of monolayer MoS₂. *Phys. Rev. B*, 89(3), p.035438.
- [254] H. Guo, T. Yang, P. Tao, Y. Wang, Z. Zhang “High pressure effect on structure, electronic structure, and thermoelectric properties of MoS₂” *J. Appl. Phys.* 113(1), 013709 (**2013**).
- [255] Y. Li, J. Kang, J. Li “Indirect-to-direct band gap transition of the ZrS₂ monolayer by strain: first-principles calculations” *RSC Adv.* 4(15), 7396-7401 (**2014**).
- [256] M. Zhang, Y. Zhu, X. Wang, Q. Feng, S. Qiao, W. Wen, Y. Chen, M. Cui, J. Zhang, C. Cai, L. Xie “Controlled synthesis of ZrS₂ monolayer and few layers on hexagonal boron nitride” *J. Am. Chem. Soc.* 137(22), 7051-7054 (**2015**).
- [257] C. Gong, H. Zhang, W. Wang, L. Colombo, R. M. Wallace, K. Cho “Band alignment of two-dimensional transition metal dichalcogenides: Application in tunnel field effect transistors” *Appl. Phys. Lett.* 103(5), 053513 (**2013**).
- [258] X. Gu, R. Yang, Phonon transport in single-layer transition metal dichalcogenides: A first-principles study” *Appl. Phys. Lett.* 105(13), 131903 (**2014**).

- [259] X. Zhang, Z. Meng, D. Rao, Y. Wang, Q. Shi, Y. Liu, H. Wu, K. Deng, H. Liu, R. Lu, “Efficient band structure tuning, charge separation, and visible-light response in ZrS₂-based van der Waals heterostructures” *Energy Environ. Sci.* 9(3), 841-849(2016).
- [260] C. H. Lui, Z. Ye, C. Ji, K. C. Chiu, C. T. Chou, T. I. Andersen, C. Means-Shively, H. Anderson, J.M. Wu, T. Kidd, Y. H. Lee “Observation of interlayer phonon modes in van der Waals heterostructures” *Phys. Rev. B*, 91(16), 165403 (2015).
- [261] H. U. Din, M. Idrees, G. Rehman, C. V. Nguyen, L. Y. Gan, I. Ahmad, M. Maqbool, B. Amin “Electronic structure, optical and photocatalytic performance of SiC-MX₂ (M= Mo, W and X= S, Se) van der Waals heterostructures” *Phys. Chem. Chem. Phys.* 20(37), 24168-24175 (2018).
- [262] B. K. Ridley “**Large-Bandgap Semiconductors**” *Tr. J. Phy.* 23 (1999) 577 (2018).
- [263] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, “Atomically thin MoS₂: a new direct-gap semiconductor” *Phys. Rev. Lett.* 105(13), 136805 (2010).
- [264] A. Kuc, N. Zibouche, T. Heine “Influence of quantum confinement on the electronic structure of the transition metal sulfide TS₂” *Phys. Rev. B*, 83(24), 245213 (2011).
- [265] C. Ataca, S. Ciraci “Functionalization of single-layer MoS₂ honeycomb structures” *J. Phys. Chem. C*, 115(27), 13303-13311 (2011).

- [266] W. Wei, Y. Dai, B. Huang “In-plane interfacing effects of two-dimensional transition-metal dichalcogenide heterostructures” *Phys. Chem. Chem. Phys.* 18(23), 15632-15638 (2016).
- [267] N. Wu, X. Zhao, X. Ma, Q. Xin, X. Liu, T. Wang, S. Wei “Strain effect on the electronic properties of 1T-HfS₂ monolayer” *Physica E: Low-dimensional Systems and Nanostructures*, 93, 1-5 (2017).
- [268] M. G. Rabbani, S. R. Patil, M. P. Anantram “Moderate bending strain induced semiconductor to metal transition in Si nanowires” *Semicond. Sci. Technol.* 31(12), 125019 (2016).
- [269] J. Kang, S. Tongay, J. Zhou, J. Li, J. Wu, “Band offsets and heterostructures of two-dimensional semiconductors” *Appl. Phys. Lett.* 102(1), 012111 (2013).
- [270] Y. Guo, J. Robertson “Band engineering in transition metal dichalcogenides: Stacked versus lateral heterostructures” *Appl. Phys. Lett.* 108(23), 233104 (2016).
- [271] G. K. Madsen, D.J. Singh “BoltzTraP. A code for calculating band-structure dependent quantities” *Comput. Phys. Commun.* 175(1), 67-71 (2006).
- [272] M. Onoue, F. Ishii, T. Oguchi, “Electronic and thermoelectric properties of the intermetallic compounds MNiSn (M= Ti, Zr, and Hf)” *J. Phys. Soc. Jpn.*, 77(5), 054706-054706 (2008).
- [273] L. Hao, T. K. Lee, “Thermopower of gapped bilayer graphene” *Phys. Rev. B*, 81(16), 165445 (2010).

- [274] Y. Pei, A. D. LaLonde, H. Wang, G. J. Snyder, “Low effective mass leading to high thermoelectric performance” *Energy Environ. Sci.* 5(7), 7963-7969 (**2012**).
- [275] N. Jena, A. De Sarkar “Compressive strain induced enhancement in thermoelectric-power-factor in monolayer MoS₂ nanosheet” *J. Phys. Condens. Matter*, 29(22), 225501 (**2017**).
- [276] T. Inoue, A. Fujishima, S. Konishi, K. Honda “Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders” *Nature*, 277(5698), 637 (**1979**).
- [277] K. Rajeshwar, N. R. De Tacconi “Solution combustion synthesis of oxide semiconductors for solar energy conversion and environmental remediation” *Chem. Soc. Rev.* 38(7), 1984-1998 (**2009**).
- [278] J. Yang, D. Wang, H. Han, C. Li, “Roles of cocatalysts in photocatalysis and photoelectrocatalysis” *Acc. Chem. Res.* 46(8), 1900-1909 (**2013**).
- [279] Y. Bi, S. Ouyang, N. Umezawa, J. Cao, J. Ye “Facet effect of single-crystalline Ag₃PO₄ sub-microcrystals on photocatalytic properties” *J. Am. Chem. Soc.* 133(17), 6490-6492 (**2011**).
- [280] D. Voiry, A. Mohite, M. Chhowalla “Phase engineering of transition metal dichalcogenides” *Chem. Soc. Rev.* 44(9), 2702-2712 (**2015**).
- [281] J. Ji, H. Ji, L. L. Zhang, X. Zhao, X. Bai, X. Fan, F. Zhang, R. S. Ruoff “Graphene-encapsulated Si on ultrathin-graphite foam as anode for high capacity lithium-ion batteries” *Adv. Mater.* 25(33),4673-4677 (**2013**).

- [282] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis “Solar water splitting cells” *Chem. Rev.* 110(11), 6446–6473 (**2010**).
- [283] S. Ghatak, A. N. Pal, A. Ghosh “Nature of electronic states in atomically thin MoS₂ field-effect transistors” *ACS Nano*, 5(10), 7707-7712 (**2011**).
- [284] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis “Single-layer MoS₂ transistors” *Nat. Nanotechnol.* 6(3), 147-150 (**2011**).
- [285] N. Singh, G. Jabbour, U. Schwingenschlögl “Optical and photocatalytic properties of two-dimensional MoS₂” *Eur. Phys. J. B*, 85(11), 392 (**2012**).
- [286] X. Li, J. Wang, D. Xu, Z. Sun, Q. Zhao, W. Peng, Y. Li, G. Zhang, F. Zhang, X. Fan “NbSe₂ nanosheet supported PbBiO₂Br as a high performance photocatalyst for the visible light-driven asymmetric alkylation of aldehyde” *ACS Sustainable Chemistry & Engineering*, 3(5), 1017-1022 (**2015**).
- [287] D. Chen, G. Ji, B. Ding, Y. Ma, B. Qu, W. Chen, J. Y., Lee “In situ nitrogenated graphene few-layer WS₂ composites for fast and reversible Li⁺ storage” *Nanoscale*, 5(17), 7890-7896 (**2013**).
- [288] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang “Single-layer MoS₂ phototransistors” *ACS Nano*, 6(1), 74-80 (**2011**).
- [289] L. Cao, S. Yang, W. Gao, Z. Liu, Y. Gong, L. Ma, G. Shi, S. Lei, Y. Zhang, S. Zhang, R. Vajtai “Direct laser-patterned micro-supercapacitors from paintable MoS₂ films” *Small*, 9(17), 2905-2910 (**2013**).

- [290] J. Zhang, Z. Zhu, X. Feng “Construction of Two-Dimensional MoS₂/CdS p-n Nanohybrids for Highly Efficient Photocatalytic Hydrogen Evolution” *Chem.: Eur. J.* 20(34), 10632-10635 (2014).
- [291] Y. Zhu, Q. Ling, Y. Liu, H. Wang, Y. Zhu “Photocatalytic H₂ evolution on MoS₂-TiO₂ catalysts synthesized via mechanochemistry” *Phys. Chem. Chem. Phys.* 17(2), 933-940 (2015).
- [292] S. P. Vattikuti, C. Byon, C. V. Reddy, R. V. S. S. N. Ravikumar “Improved photocatalytic activity of MoS₂ nanosheets decorated with SnO₂ nanoparticles” *RSC Adv.* 5(105), 86675-86684 (2015).
- [293] D. Merki, S. Fierro, H. Vrubel, X. Hu “Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water” *Chem. Sci.* 2(7), 1262-1267 (2011).
- [294] J. P. Perdew “Density functional theory and the band gap problem” *Int. J. Quantum Chem.* 30(3), 451-451 (1986).
- [295] J. J. Liu, X. L. Fu, S. F. Chen, Y. F. Zhu “Electronic structure and optical properties of Ag₃PO₄ photocatalyst calculated by hybrid density functional method” *Appl. Phys. Lett.* 99(19), 191903 (2011).
- [296] H. L. Zhuang, R. G. Hennig “Theoretical perspective of photocatalytic properties of single-layer SnS₂” *Phys. Rev. B*, 88(11), 115314 (2013).

- [297] V. Chakrapani, J. C. Angus, A. B. Anderson, S. D. Wolter, B. R. Stoner, G. U. Sumanasekera “Charge transfer equilibria between diamond and an aqueous oxygen electrochemical redox couple” *Science*, 318(5855), 1424-1430 (**2007**).
- [298] K. S. Novoselov, A. C. Neto “Two-dimensional crystals-based heterostructures: materials with tailored properties” *Phys. Scr.* 2012(T146), 014006 (**2012**).
- [299] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov “Electric field effect in atomically thin carbon films” *Science*, 306(5696), 666-669 (**2004**).
- [300] A. K. Geim, K. S. Novoselov “The rise of graphene” *Nat. Mater.* 6, 183-191 (**2007**).
- [301] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, S. Ciraci, “Two-and one-dimensional honeycomb structures of silicon and germanium” *Phys. Rev. Lett.* 102(23), 236804 (**2009**).
- [302] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, G. Le Lay, “Silicene: compelling experimental evidence for graphene like two-dimensional silicon” *Phys. Rev. Lett.* 108(15), 155501 (**2012**).
- [303] V. O. Özçelik, E. Durgun, S. Ciraci “New phases of germanene” *J. Phys. Chem. Lett.* 5(15), 2694-2699 (**2014**).
- [304] V. O. Özçelik, S. Cahangirov, S. Ciraci “Stable single-layer honeycomb blike structure of silica” *Phys. Rev. Lett.* 112(24), 246803 (**2014**) .

- [305] B. Yang, S. Shaikhutdinov, H. J. Freund “Ultrathin silicatene/silicon-carbide hybrid film on a metal substrate” *Surf. Sci.* 632, 9-13 (**2015**).
- [306] P. Joensen, R. F. Frindt, S. R. Morrison “Single-layer MoS₂” *Mater. Res. Bull.* 21(4), 457-461 (**1986**).
- [307] S. Tongay, J. Zhou, C. Ataca, K. Lo, T. S. Matthews, J. Li, J. C. Grossman, J. Wu Thermally driven crossover from indirect toward direct band gap in 2D semiconductors: MoSe₂ versus MoS₂” *Nano Lett.* 12(11), 5576-5580 (**2012**).
- [308] S. Nakamura, M. Senoh, N. Iwasa, S. I. Nagahama “High-brightness InGaN blue, green and yellow light-emitting diodes with quantum well structures” *Jpn. J. Appl. Phys.* 34(7A), L797 (**1995**).
- [309] A. F. J. Levi, T. H. Chiu “Room-temperature operation of hot-electron transistors” *Appl. Phys. Lett.* 51(13), 984-986 (**1987**).
- [310] J. R. Meyer, C. A. Hoffman, F. J. Bartoli, L. R. Ram-Mohan “Type-II quantum-well lasers for the mid-wavelength infrared” *Appl. Phys. Lett.* 67(6), 757-759 (**1995**).
- [311] E. V. Calman, C. J. Dorow, M. M. Fogler, L. V. Butov, S. Hu, A. Mishchenko, A. K. Geim “Control of excitons in multi-layer van der Waals heterostructures” *Appl. Phys. Lett.* 108(10), p.101901 (**2016**).
- [312] D. Ruzmetov, K. Zhang, G. Stan, B. Kalanyan, G. R. Bhimanapati, S. M. Eichfeld, R. A. Burke, P. B. Shah, T. P. O’Regan, F. J. Crowne, A. G. Birdwell

“Vertical 2D/3D semiconductor heterostructures based on epitaxial molybdenum disulfide and gallium nitride” *ACS Nano*, 10(3), 3580-3588 (**2016**).

- [313] J. Yuan, S. Najmaei, Z. Zhang, J. Zhang, S. Lei, P. M. Ajayan, B.I. Yakobson, J. Lou “Photoluminescence quenching and charge transfer in artificial heterostacks of monolayer transition metal dichalcogenides and few-layer black phosphorus” *ACS Nano*, 9(1), 555-563 (**2015**).