



Addis Ababa University
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School of Multidisciplinary Engineering
Center for Materials Engineering

**Computational Modeling of ZnO/WS₂ van Der Waals
Heterostructures for solar cell applications**

**A Thesis Submitted to Center for Materials Engineering in Partial
Fulfillment of the Requirements for the degree of Master of
Science in Materials Engineering**

By

GIRMA MEKONNEN GOMORO

September, 2020
Addis Ababa, Ethiopia



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Declaration

I hereby declare that the work which is being presented in this thesis entitled “Computational Modeling of WSSe/ZnO Van Der Waals Heterostructures for solar cell application” is original work of my own, has not been presented for a degree of any other university and all the resource materials used for this thesis have been duly acknowledged.

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Abstract

Stacking of two-dimensional materials into layered Van der Waals heterostructures are recently considered as a promising candidate for applications on photovoltaic devices because they can combine advantages of individual's 2D materials. Janus transition metals dichalcogenides (WSSe) have emerged because of favorable electronic properties as an attractive absorbing material. We therefore systematically examine the geometric features, electronic properties, work function, and density of states, band alignment of monolayer ZnO and WSSe and their heterostructures in this work using density functional theory methods (DFT) with PBE calculations as implemented in the Quantum ESPRESSO and VASP codes. It was found that, the negative binding energies indicate all the four configurations of ZnO-WSSe heterostructures are stable and feasible. Moreover, three configurations B, C and D exhibit indirect band gaps of 1.6248 eV, 1.6319 eV and 1.3126 eV, respectively. But the other configuration A has direct band gap of 1.7106 eV. In addition, it is found that all four configurations show band alignment type-II. In type-II alignment, donor-acceptor interface band heterojunctions can easily promote electron and hole carrier transfer and separation at interface, which can significantly enhance the efficiency of photovoltaic solar cells. With direct band gap, configuration A is the preferred heterostructure for photovoltaic devices applications.

Keywords: 2D materials, Janus Transition metal dichalcogenides, ZnO, WSSe, density functional theory, photovoltaics.

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List of Abbreviations

SDGs	Sustainable Development Goals
EJ	Exajoules
PV	Photovoltaic
eV	Electron volt
TMDC	Transition Metal dichalcogenides
2D	Two dimensional
DFT	Density functional theory
ZnO	Zinc oxide
WSSe	Tungsten sulfide selenide
PBE	Perdew–Burke–Ernzerhof
CVD	Chemical vapor deposition
vdW	van der Waals
vdWHs	Van der Waals heterostructures
CBM	Conduction band minimum
VBM	Valence band maximum
LDA	Local density approximation
GGA	Generalized gradient approximations
Ecutwfc	Kinetic energy cut-off for wave functions
Ry	Rydberg
SCF	Self consistent field
Ecutrho	Cut off for Charge density
DOS	Density of states
PDOS	Projected density of states
HSE06	Heyd Scuseria-Ernzerhof

CHAPTER ONE: INTRODUCTION

1.1 Background of study

The Sustainable Development Goals (SDGs), adopted by the General Assembly of the United Nations (UNGA) in 2015, provide a powerful framework for international cooperation to reach a sustainable future for the planet. At the heart of "Agenda 2030," the 17 SDGs and their 169 targets define a path to end extreme poverty, fight inequality and injustice and protect the environment of the planets. Sustainable energy is at the heart of Agenda 2030 success. The global energy goal -SDG 7-encompasses three key objectives: ensuring affordable, reliable and universal access to modern energy services; substantially increasing the share of renewable energy in the global energy mix; and doubling the global energy efficiency improvement rate. The various SDG 7 targets contribute to the achievement of other SDG targets and this has recently been the focus of an increasing number of studies [1] .

There is an immediate need for a global energy transition to achieve the goals of reducing global average surface temperature rise below 2 ° Celsius. The implications of the Paris Agreement for the energy sector will be profound to an extent that existing energy scenarios do not yet fully capture. A transition away from fossil fuels to low-carbon solutions will play an important role, as energy-related carbon dioxide (CO₂) emissions constitute two-thirds of all greenhouse gases (GHG). Technological innovation, especially in the field of renewable energy, will allow this energy transition.

Figure .1 allows for a summary of implementation of renewables. A total of 222 EJ renewable energy sources are deployed in final energy terms. The power sector is 58 per cent. This includes electrification-related growth in renewable energy use (notably electric vehicles and heat pumps). This form of deployment of renewables may also be applied to end-use sectors. The main position of bioenergy (32 per cent including district heating) and wind (24 per cent) deserves special attention in terms of total renewables deployment.

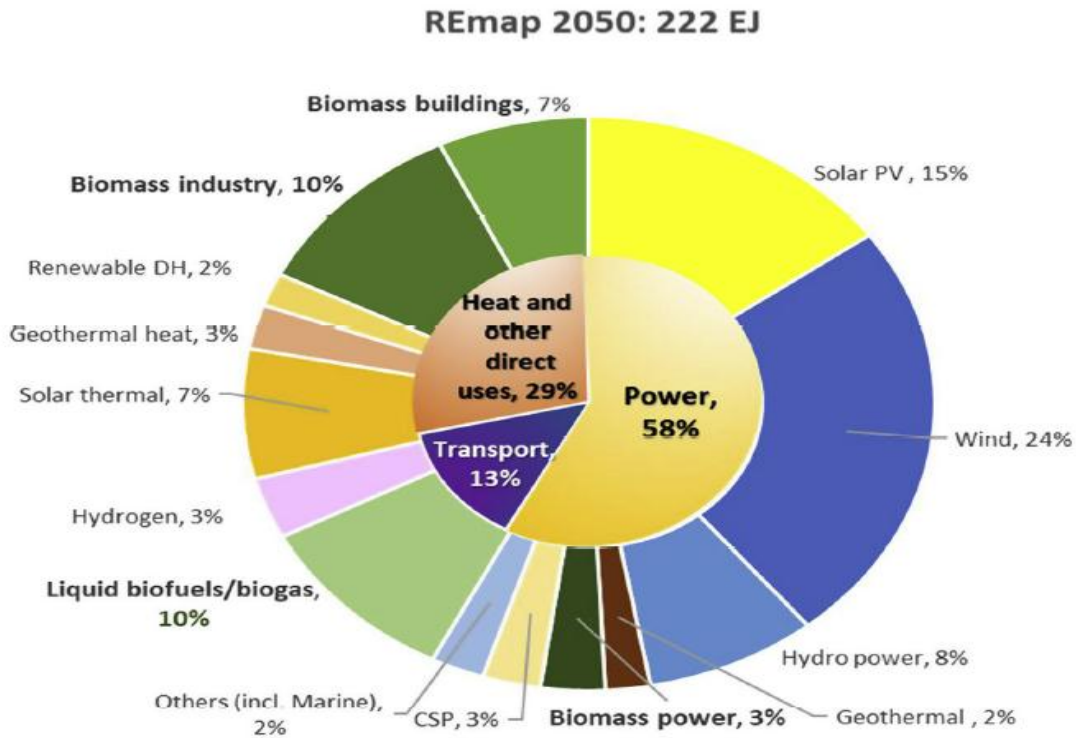


Figure 1. Breakdown of renewable energy use in total end-use terms. Renewable energy currently accounted for 19% of global final energy demand in 2015, increasing by 0.17% per annum since 2010. This growth rate needs to be increased seven-fold to achieve a two-thirds share of renewable energy in total global final energy demand by 2050, which according to the REmap study is required for the global energy transition. Based on the energy mix Remap, Table 1 reflects the growth of renewable energy technologies needed for the energy transition between 2017 and 2050.

Table 1: Breakdown of renewable energy growth in the Remap case, 2017-2050 [1].

Key technologies	renewable energy units	Recent growth	Future requirement	growth
		2017	2018-2050	
wind	GW/yr	53	154	
Solar PV	GW/yr	99	210	

Liquid biofuel and biogas	Billion liters/yr	5	24
Solar thermal	Million m ²	30	283
Hydro	GW/yr	25	17
Geothermal heat	PJ/yr	26	173
CSP	GW/yr	1	20
Geothermal(power)	GW/yr	0.6	7
Bioenergy(power)	GW/yr	5	12

Worldwide the electricity networks are evolving. Global demand for and reliance on energy is growing, and as environmental issues are becoming more urgent, so is the emphasis on greenhouse gas emissions reduction. This leads to a shift towards a decarbonized electricity system based on a large volume of variable renewables generation, provided mainly by wind and solar photovoltaic (PV) systems. Solar PV technology is one of the green technologies with the potential to form a future-oriented clean, efficient, scalable and affordable electric grid. Given this fact, governments all over the world are promoting the creation and deployment of solar photovoltaic technology. A large range of photovoltaic materials are available worldwide. Globally, the production of PV modules requires hundreds of companies with varying efficiencies and constraints. At the same time, the installation costs vary from one device to another and from one project to another.[2] Global economic, social and environmental problems and industrial issues are at the core of the growth of renewable energy sources. A vital challenge of this century is the conversion of solar energy, the main sustainable and ubiquitous source of energy, into efficiently usable forms. Photovoltaic (PV) research is currently focusing on third-generation devices based on advanced materials and/or novel designs and/or new chemical-physical effects, with the ultimate aim of achieving higher and higher efficiencies, at acceptable costs and with minimal polluting effects at various stages of production, use and disposal of devices. The material scientist's position is fundamental both in identifying optimal compounds for the absorption of solar radiation and in designing efficient devices [2].

A solar cell is an electronic system that transforms the sunlight directly into electricity.

First, this process involves a material in which the absorption of light lifts an electron to a higher energy level, and second, the transfer of that higher energy electron from the solar cell to an external circuit. Then the electron dissipates its energy into the outer circuit and returns to the solar cell. Materials science has gone a long way since Becquerel, in 1839, discovered the photovoltaic effect. The perspective of large-scale applications was first stated only with the discovery of the photosensitivity of selenium, the first technological semiconductor, and the manufacture of wafers with about 1 per cent conversion efficiency. The first silicon 'photocell to transform solar radiation into electrical power' was recorded at Bell Laboratories in 1954, with an efficiency of 6 percent and triggered the technology 's growth as this success turned photovoltaic technology into one of the best contenders for applications to power the nascent satellite industry. This first generation solar cell's working concepts are based on a p-n homojunction performed in a bulk semiconductor.

In the last 60 years, in a background of oil scarcity and rising global warming pressures, solar cells have emerged to deliver a credible alternative to fossil fuels, offering vast quantities of renewable energy at affordable prices. PV systems now account for 1.7% of gross electricity output in the Organization for Economic Co-operation and Development, while their contribution in 1990 was marginal (below 0.01%). Photovoltaics (PV) is the fastest-growing energy technology, according to the International Energy Agency, and should reach the global 300-GW installation in 2017. This rapid evolution shows the complementarity of basic science, committed to attaining the highest output and technological advances, converting experimental findings into commercial systems [3].

Two-dimensional (2D) layered materials, has opened new dimensions in electronics, optoelectronics, energy generation, and sensing applications. Two-dimensional materials can be fabricated with relatively inexpensive production methods, integrated into existing semiconductor technologies, and offer new physical and chemical properties. Electrically, they can behave as insulators, semiconductors, metals, or even superconductors [4].

In this paper, various heterostructures of the ZnO / WSSe van der Waals for photovoltaic solar cells application are presented using density functional theory (DFT) with PBE modeling as implemented in QUANTUM ESPRESSO and VASP codes.

1.2 Problem statement

We need highly efficient, low-cost and dependable energy sources. Solar cells which directly convert sunlight into electricity are promising candidates for commercialization on a large scale. As a promising mechanism for the design of highly efficient solar cells, heterojunctions consisting of two types of donor and acceptor semiconductors were proposed. However, a high-quality Heterojunctions solar cell requires both donor and semiconductor to have a direct band gap to absorb solar radiation, high carrier mobility to promote efficient transportation of electrons, and high stability in ambient conditions. The dependency on donor and acceptor semiconductors makes it necessary to look for suitable materials with ideal band gap, high carrier mobility and high stability.

Engineering the electronic properties of a material, specifically its band gap, is highly desirable for nano- and opto-electric applications and strain is one of the possible ways of doing so. 2D materials such as mono- and few-layer TMDCs can withstand much higher strain compared to bulk materials, which is why they are very useful for flexible electronic and optoelectronic devices as well as for strain-engineered materials as possible. Also very interesting is strain engineering as a possibility of raising the carrier mobility of 2D TMDCs.

In solar cells there has to be effective electron-hole separation and such heavy separation of the charge not only facilitates the dissociation of excitons into free electrons and holes, but also greatly decreases the recombination rates of the electron-hole, which may lead to the long lifetime of the minority carrier. Photo-generated charging carriers must be separated within a solar cell. Proper band alignment must be identified which is critical to the performance of solar cells.

Because of their wide range of applications in catalysis, electrochemical energy storage, photocatalysis, electronics, optoelectronics, spintronics, and photonic nanodevices, two-dimensional (2D) materials have largely emerged to date. Given their fascinating properties, TMDCs have received considerable interest among these. However, the monolayers of the TMDCs display some drawbacks, such as large effective masses, poor dielectric screening, and strong excitonic effect, leading to the rapid rate of photon-generated electron and hole

recombination. The short life span for the electron-hole pair results in extremely low quantum efficiency, thus drastically impeding the performance of the system. Many common strategies have been developed to break this limitation in 2D TMDCs, such as applying electric field, strain engineering, layer stacking and regulating their composition. Among these, stacking different 2D materials into layered vdW heterostructures is considered a realistic way to build applications of the next decade, ranging from nanoelectronics to optoelectronics and photonics, such as tunneling transistors, solar cells and bipolar transistors. Particularly in the layered vdW heterostructures, the formation of type-II band alignment is capable of modulating interlayer transition energy and responsible for charge separation, allowing intensive use of advanced optoelectronic devices in design.

1.3 Research objectives

1.3.1 General Objectives

The main objective of this study is to systematically examine electronic properties of WSSe/ZnO Van der Waals heterostructures for solar cell application using density functional theory with the help of Quantum ESPRESSO and VASP software.

1.3.2 Specific objectives

The specific objectives of this research are:

- To perform the band structure calculation for monolayer and heterostructures
- To investigate the band alignment type and identify if it is type (I,II or III)
- To investigate the photo-generated electron-hole pair recombination, calculate density of states, and also spin polarization and projected density of states , know planar average electrostatic potential ,calculate work functions
- To evaluate the stable and efficient heterostructure configurations for PV applications

1.4 Scope and limitations of research

The study is limited to solar cell applications based on ZnO and WSSe where only computational modeling is presented and for time being experimental work is not included. Soft wares like QUANTUM ESPRESSO, VASP, and Xcrysden are used .DFT based on PBE+D2 is considered due to shortage of time to finish the research work, even though it underestimates the band gap.HSE06 gives better results for electronic properties, but it were not used due to shortage of time and lack of access to supercomputer. In this work, only four configurations of heterostructures between ZnO and WSSe considered and analyzed.

1.5 Significance of the study

- The study can be used as preliminary base for future research works related to computational modeling of materials for solar cell applications based on heterostructure configurations.
- The results of the study can be used for solar cell manufacturing industries to design solar cell experimentally.
- The study will be great input for researchers working experimentally on materials for solar cell design.

1.6 Organization of the study

The thesis is organized and separated to five chapters. Chapter one is introduction part which discusses background of the study, problem statement, objectives of the study, its significance and the scope. Chapter two reviews related literature on the subject such as previous studies and findings. Chapter three discusses research methodology. Chapter four discusses the results of the study and includes, explains the results and discusses the findings of the study. Chapter five concludes the results of the study and recommends for action and directs future research directions.

CHAPTER TWO: LITERATURE REVIEW

"In 1959, in a single question, Richard Feynman first suggested the view of layered materials:" What could we do with layered structures with controlled layers? And "Novoselov et al. discovered graphene after years of unrelenting work [5] . Since its discovery in 2004, Graphene brings physicists and semiconductor engineers to a new world of 2D materials. After the great success of Graphene, the research on atomically thin two-dimensional (2D) materials with different physical properties has become compelling in recent years. Graphene has known to have outstanding electronic, thermal and mechanical properties, but it is not suitable for applications in various electronic and optoelectronic devices due to its zero bandgap. Therefore many researchers have shown significant attention to other 2D materials that have finite bandgap energies [6].

A host of 2D layered crystals are known, which include the TMDCs, transition metal oxides, and nitrides. Needless to say, such material systems push the limits of vertical scaling. In particular, the TMDCs exhibit a wide range of electronic, optical, mechanical, chemical, and thermal properties and have been known to us in their bulk form for decades [7].

The transition metal dichalcogenides consist of hexagonal layers of metal M atoms [from group 4B (e.g., Ti, Zr, Hf), group 5B (e.g., V, Nb, Ta) or group 6B (e.g., Mo, W), group 7B (e.g., Tc, Re), and group 10B (e.g., Pd, Pt)], which are sandwiched between two layers of chalcogen atoms X (S, Se or Te) with stoichiometry MX_2 ; As with transition metal dichalcogenides and many of the other layered material systems, the intralayer bonding is primarily due to the strong covalent in-plane bonding between the atoms, but the interlayer bonding is governed by the weaker van der Waals interaction. In fact, it is this weak van der Waals interaction that is responsible for the ease with which these materials can be mechanically cleaved through exfoliation into individual layers. Depending on the combination of the transition metal atom and the chalcogen atom, a wide variety of transition metal dichalcogenides are possible, as illustrated in Figure 4, each offering a unique set of properties.

excitonic effect, leading to the fast rate of the recombination of photogenerated electron and hole. The short lifetime for electron-hole pair leads to extremely low quantum efficiency, thus the device's performance is dramatically impeded. In order to break this limitation in 2D TMDCs, many common strategies have been developed, such as applying electric field, strain engineering, layer stackings and controlling their composition. Among these, stacking different 2D materials into layered vdW heterostructures are considered as a practical way for designing next-generation applications, ranging from nanoelectronics to optoelectronics and photonics, such as tunneling transistors, solar cells and bipolar transistors. Especially, the formation of type-II band alignment in the layered vdW heterostructures is capable to modulate interlayer transition energy and responsible for charge separation, hence intensively uses in designing advanced optoelectronic devices.

Recently, a Janus-type TMDC material (i.e., WSSe) has been synthesized experimentally by selective selenization of the top atomic layer in single-layer WS_2 using CVD. JTMDc monolayers have a standard chemical formula MXY (M =Mo, W; X/Y = S, Se, Te and $X \neq Y$). ZnO monolayer is gaining enormous interest from both theoretical and experimental scientific communities. The fascinating physical and chemical properties of ZnO monolayer, such as chemical bonding, large exciton binding energy make it fascinating material for transparent electronics, solar cells and gas sensor [9].

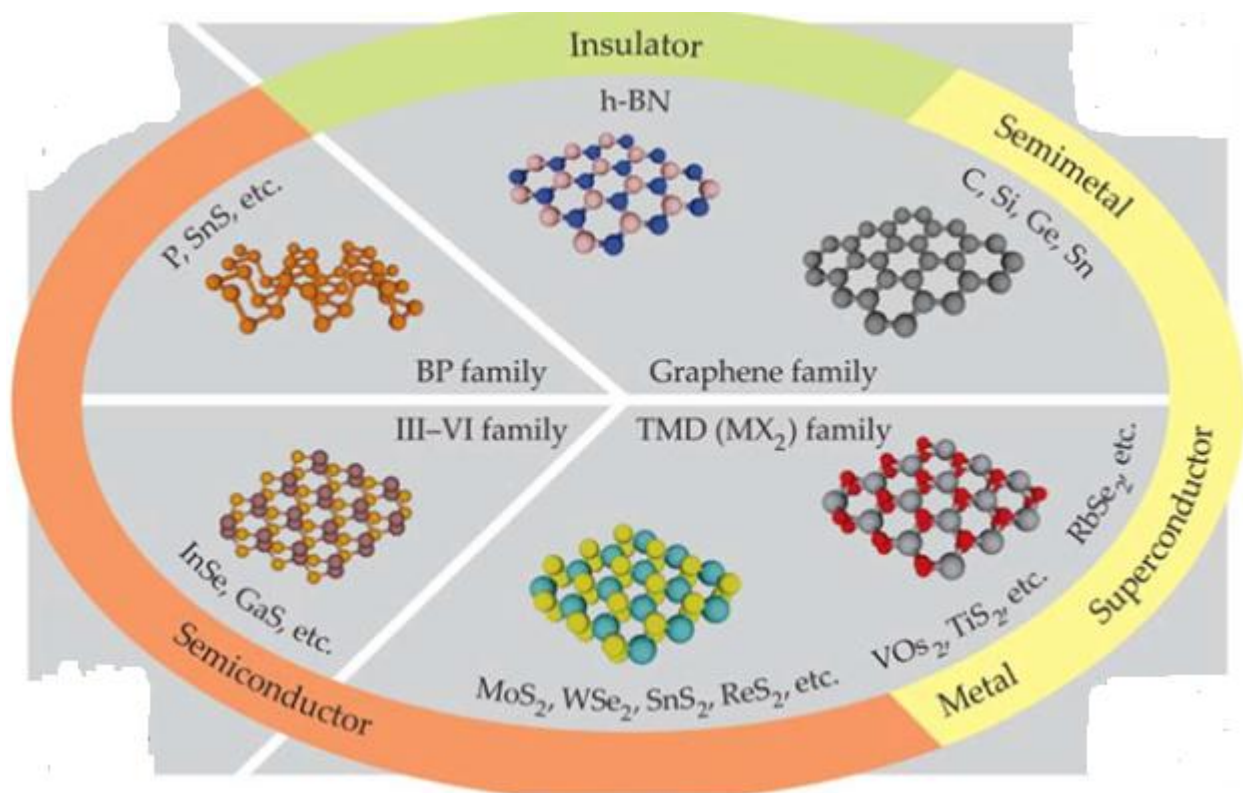


Figure 3. Two-Dimensional Materials (Graphene and its analogues, such as hexagonal boron nitride; black phosphorus (BP) and its analogues; the III–VI family of semiconductors; and TMDs [10].

Figure 4 shows the broad catalogue of 2D materials with varying bandgap utilized for various applications in different wavelength regimes. Specifically, research and development of 2D materials like transition-metal dichalcogenides (TMDCs) and black phosphorus have progressed rapidly due to their excellent mechanical properties, which have played extensive roles in designing flexible and stretchable next-generation electronic devices. These materials have attracted much attention not only due to their semiconducting nature, but also due to their ultralight weight, high Young's modulus, and high tensile strength. Also, the in-plane and out of plane mechanical properties of these materials are different from each other. Recently, they have been found to provide promising roles in photovoltaic devices.

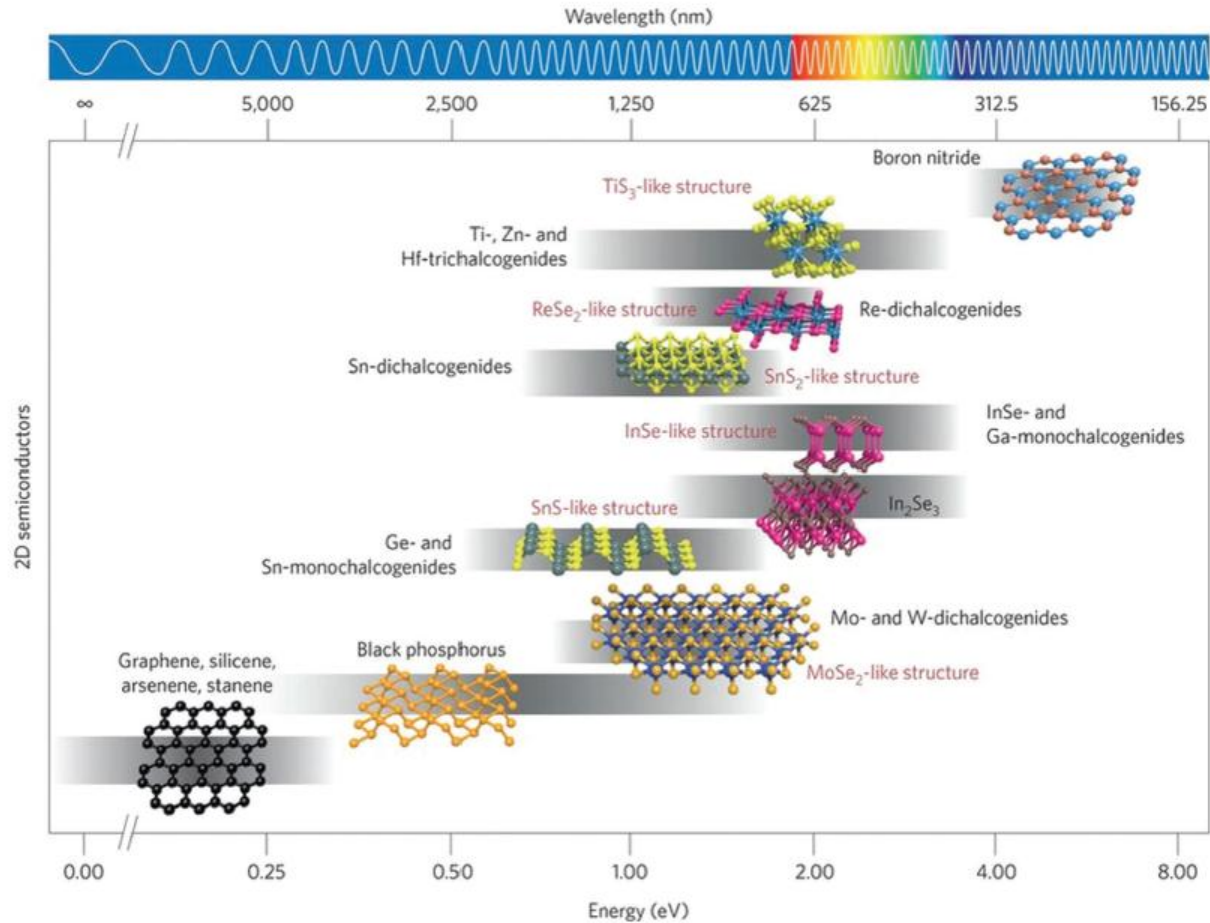


Figure 4. Comparison of the bandgap values for different 2D semiconductor materials families. The crystal structure is also displayed to highlight the similarities and differences between the different families. The gray horizontal bars indicate the range of bandgap values that can be spanned by changing the number of layers, straining, or alloying. This broad bandgap range spanned by all these 2D semiconductors can be exploited in a wide variety of photonics and optoelectronics applications, such as thermal imaging, fiber optics communication, photovoltaics, displays, and light-emitting diodes [11].

In the next generation of nano electronic and opto-electronic applications, layered transition metal dichalcogenides (TMDC) materials may be a candidate to replace traditional semiconductor materials. This is because different mechanical, optical, chemical, thermal, and electronic properties exhibit not only MX_2 monolayers possessing layered structural characteristics similar to graphene, but also TMD monolayers. These properties are similar and even better than graphene and are equivalent to graphene. The engineering of the electronic properties of monolayer and few-layer TMDs has been the hot topic for various theoretical and experimental studies, having identified the significance of TMDs in specific applications [12].

Their thickness-dependent (or layer number-dependent) bandgaps are a well-known nature of 2D layered materials. Such dependency implies discontinuities of the energy band at the interface of various layer-number films, creating a distinct natural heterojunction from traditional films. For various applications, including photovoltaics, research on this type of structure is likely to extend the domains of 2D materials [13]. Solar cells based on 2D materials are currently typically manufactured by stacking two semiconductors of p-type and n-type that can drive the separation of electron-hole pairs created by photographs. Many groups have shown that 2D heterojunctions, such as graphene / BN, graphene / MoS_2 , WSe_2 / MoSe_2 , and so on, can be used to create high-efficient solar cells [14].

Recently, two-dimensional (2D) materials-based van der Waals (vdW) heterostructures have attracted tremendous research attentions due to their novel properties and potential applications for the future nano-devices. By forming heterostructures, many promising features can be achieved, such as high carrier mobility, tunable band gap, broad spectrum, which are ideal for fabricating high-performance optoelectronic and electronic devices [15].

Two-dimensional (2D) semiconductors such as TMDCs and black phosphorous have drawn tremendous attention as an emerging optical material due to their unique and remarkable optical properties. In addition, the ability to create the atomically-controlled van der Waals (vdW) heterostructures enables realizing novel optoelectronic devices that are distinct from conventional bulk counterparts [6]. In van der Waals heterostructures, basic electronic and optical properties are convenient for regulating the generation, transport and recombination of

charge carriers, excitons, photons and are useful for the design of unique electronic and photo electronic devices. Assembling the heterostructures of van der Waals, which consist of atomically sharp interfaces and atomic layered structures, presents the ability for a new device to be designed at atomic level to invent the ultra-thin, low-power and versatile device [16].

Van der Waals heterostructures (vdWHs)-stacks of atomic thin two-dimensional (2D) layered materials [e.g., graphene or transition-metal dichalcogenides (TMDCs)]-have simulated intensive research interest as they allow a flexible integration of highly distinct 2D materials at the atomic scale, thus providing a versatile platform for diverse electronics and optoelectronics.

An essential feature of such heterostructures is the band alignment, which can be classified into three types, namely, straddling type-I, staggered type-II, and broken-gap type-III. Further, each type of band alignment corresponds to particular device applications. Type-I band alignment is beneficial for spatially confining electrons and holes so that efficient recombination can be achievable, and hence type-I band alignment is favorable for applications in optical devices. Different from type-I band alignment, the large band offset in type-II band alignment allows significant carrier separation, which is useful for unipolar electronic device applications and photocatalysis, whereas type-III band alignment can facilitate the engineering of the conduction-to valence-band transition energy, thus holding unique promise in tunnel field-effect transistors and wavelength photodetectors. Considering these valuable applications, intensive research has been devoted to vdWHs. However, most vdWHs reported to date harbor a type-I or type-II band alignment, and few vdWHs have been shown to be with a type-III band alignment, which severely limits the applications of 2D materials in tunnel field-effect transistors [17].

The ideal of forming the so-called van der Waals (vdW) heterostructure by vertically binding two different atomically thin two-dimensional (2D) materials together via the interlayer vdW interaction has not only resulted in the explosive expansion of the family of 2D materials but also opened up more possibilities in the applications of sustainable energy related areas. In particular, semiconducting type-II heterostructures have been widely investigated in the solar energy related areas like photovoltaic solar cells and visible light photocatalytic water splitting with their fascinating electronic structures and optical properties. In type-II heterostructures, the conduction band minimum (CBM) and valence band maximum (VBM) are located in different

layers. Hence, the photogenerated electrons and holes are spatially separated from each other to different layers, which may reduce the electron-hole recombination probability and is beneficial for the migration and separation of photo-generated electron-hole pairs for photo energy harvesting. The lifetime of the indirect excitons in type-II heterostructures was observed to be longer than that of the direct ones in individual layers from a recently experiment measurement [18].

Heterojunction solar cells are the most important optoelectronic devices of 2D van der Waals heterojunctions in both theory and experiment. From a theoretical perspective, much more types of 2D van der Waals heterojunctions than the experiment have been designed theoretically as high-efficient heterojunction solar cells, such as graphene/BN, graphene/MoS₂, MoS₂/MoSe₂, MoS₂/g-C₃N and phosphorene/MoS₂. Such theoretical simulations and designs can be used to not only figure out intrinsic physical mechanism of heterojunction solar cells fabricated in experiments but also predict new types of 2D van der Waals heterojunctions with high power conversion efficiency.

One important feature of 2D material used in heterojunction solar cells is their large photoreactive contact area for absorbing sunlight. Furthermore, 2D van der Waals heterojunctions with interlayer interaction and charge transfer at the heterojunction interface can further enhance sunlight capture. Such 2D van der Waals heterojunctions have unique atomic structures, showing high stability due to strong covalent bonds inside each 2D monolayer but relatively weak van der Waals interactions to keep them stack together with their intrinsic optoelectronic properties preserved. Notice that 2D materials also show tunable optoelectronic properties, such as ideal band gap, high carrier mobility and strong visible light absorption, as donor and acceptor semiconductors used in heterojunction solar cells.

There are at least three types of band alignment for heterojunction solar cells, as shown in Figure 5, including straddling gap (type I), staggered gap (type II) and broken gap (type III). In particular, the type-II donor-acceptor interface band heterojunctions can easily promote electron and hole carrier transfer and separation at the interface, which can significantly enhance the efficiency of photovoltaic solar cells [19].

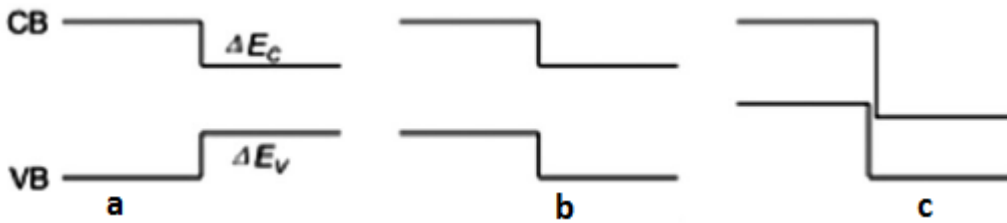


Figure 5 Three types of band alignment for semiconductor heterojunction solar cells, including a) straddling gap (type I), (b) staggered gap (type II) and (c) broken gap (type III). The VB and CB represent the valence and conduction band positions, respectively. ΔE_v and ΔE_c represent the valence and conduction band offsets, respectively.

For donor and acceptor semiconductors used in heterojunction solar cells, there are several crucial factors for absorbing sunlight, such as a small direct band gap of roughly 1.2–1.6 eV to absorb wide range sunlight and a high carrier mobility to facilitate efficient transport. Furthermore, the performance of heterojunction solar cells depends critically on the choice of donor and acceptor semiconductors with different VBM and CBM band positions.

The key energy losses during a solar cell's conversion of solar energy to electricity are transmission losses and thermalization losses, with different relative contributions as a function of the bandgap of semiconductors (see Figure 2 below). There are many techniques for reducing such losses, such as multijunction cells, solar hot carrier cells, solar intermediate band cells, or multiple exciton generation.

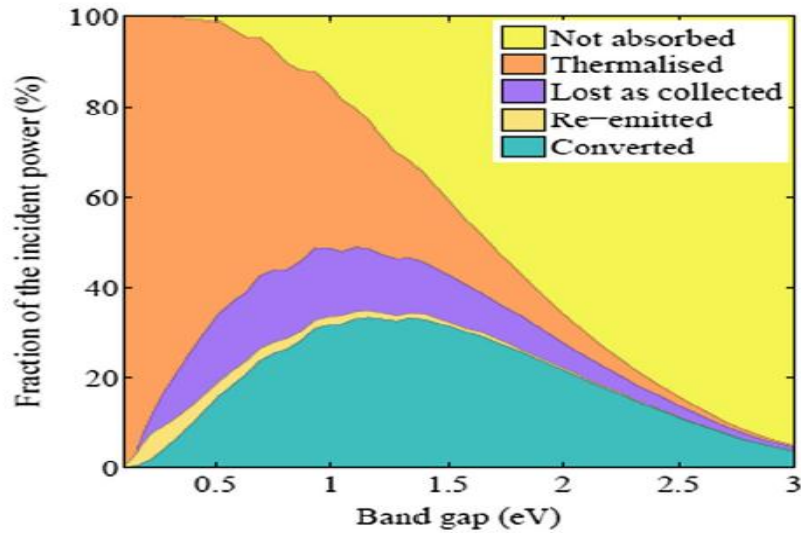


Figure 6. Fraction of incident power versus band gap

Even in ideal systems the incident power is only partially transformed. The plot demonstrates how devices transform sunlight (AM 1.5 standard spectrum) in the Shockley – Queisser limit and how the remainder is divided between various losses as a function of the device's fundamental absorption band gap: (i) the light cannot be absorbed (yellow), (ii) the excess energy of the absorbed photon is converted to heat (orange), (iii) the recombination of electron and holes results in the released photon (green), (iv) the movement of charges to the electrodes creates entropy (blue) [3].

Owing to their layered atomic structure and electronic and optical properties, two-dimensional (2D) semiconductors provide the optoelectronics with a unique opportunity. One of the main performance metrics which dictates device efficiency is light absorption in the active layers of a photovoltaic cell. For semiconductors like 2D materials, the absorption is controlled by the structure of the electronic band and the energy bandgap. There's an intrinsic trade-off between the absorption (and photocurrent) bandgap (and voltage). In Figure 7a, we summarize the bandgap energies and the coefficients of absorption for all major photovoltaic materials examined at commercial and research scales to date. As is obvious from Figure 7a and the above description, most materials considered for photovoltaic applications have energy bandgaps close to the optimum value of 1.34 eV [20].

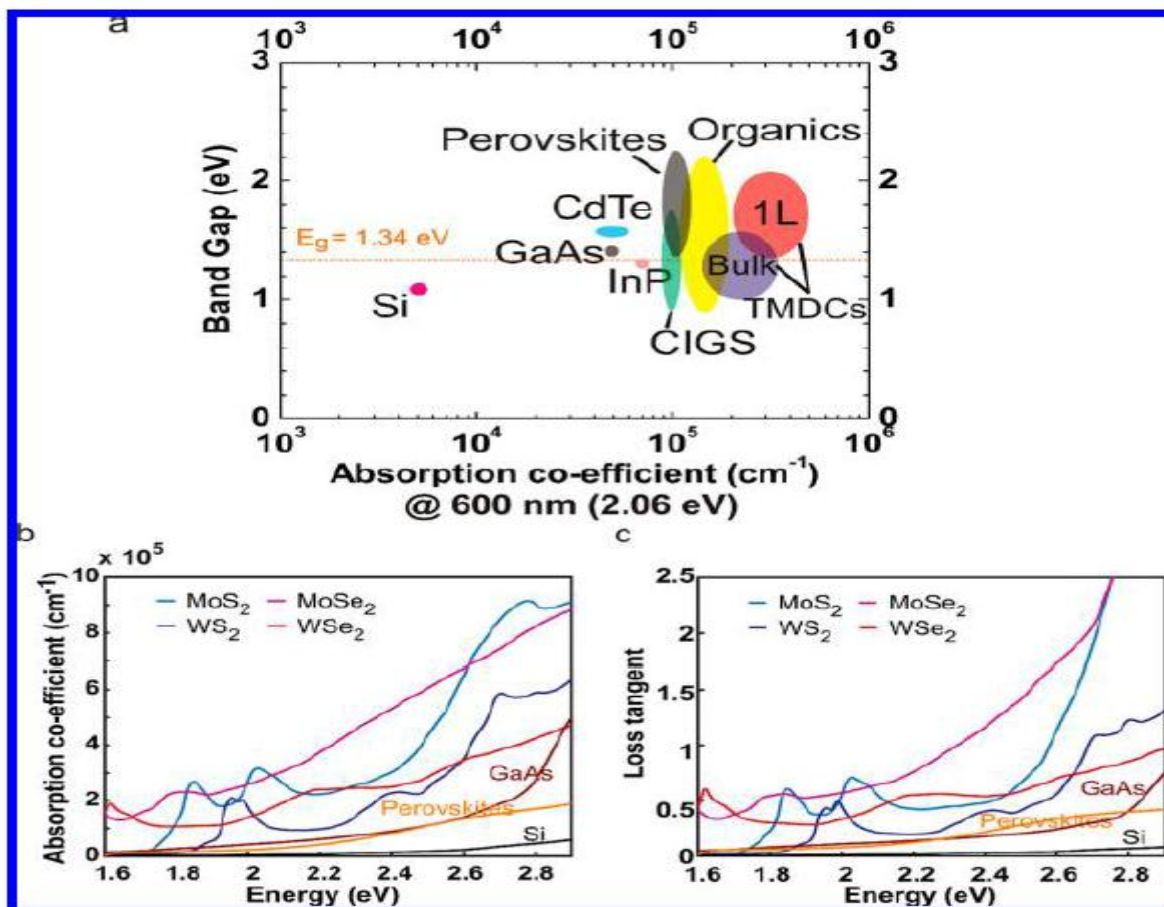


Figure 7. Semiconductor absorption of merit figures for photovoltaic applications: (a) Comparison of energy bandgaps (eV) and absorption coefficients (cm^{-1}) for a variety of semi-conductor materials used for commercial and photovoltaics study. The Mo and W TMDCs (both bulk and monolayers) have some of the highest coefficients of absorption among known materials. (b) Coefficient of spectral absorption for selected photovoltaic materials, including Si and GaAs, as well as newly emerging methyl ammonium lead iodide perovskites (MAPbI₃) alongside TMDC. (c) Tangent failure for the same materials set out in (b) [20].

Light trapping techniques are also utilized in modern photovoltaic systems to optimize incident light absorption and photocurrent generation in the active layer to improve cell performance, which also has the advantage of reducing thickness and therefore material usage and weight of systems. In both the ray optic (bulk) and nano-phonic (sub wavelength) regimes, the degree of

light trapping in a medium can be quantified by the ratio of imaginary and real sections of dielectric structure, that is, loss tangent. Figure 7 b, c shows spectral dependency of absorption coefficients and tangents of loss in Mo and W sulfides and selenides compared to Si, GaAs, and recent organic-inorganic perovskites. They exhibit substantially higher absorption per unit thickness compared to Si, GaAs, and even perovskites due to the high refractive indices of TMDCs. TMDCs are therefore best suited for highly absorbent photovoltaic ultrathin applications such as sensors, optical displays, transistors and super capacitors. Because of atomic thickness and in-plane covalent bonding; ultrathin 2D nanomaterials also exhibit excellent mechanical properties [21].

Owing to their nano- and atomic-level device applications, 2D materials have significance. After exfoliation (ultra-thin form), almost all the atoms on the surface of these materials are exposed; hence, the surface areas of 2D materials are noticeably increased, which dramatically increases their physical and chemical reactivity and affects the work of the 2D wave through the effects of quantum confinement. As a consequence, these ultra-thin 2D structures have special electrical, photonic, magnetic and catalytic properties that differ from their bulk counterparts, giving them remarkable advantages in the above-mentioned applications; but this cannot be uniformly applied in the manufacture of advanced devices. Materials can generally be split into a range of groups, from zero (0D) to three (3D) dimensions [22].

Significant advances in the synthesis and understanding of two-dimensional materials such as graphene, phosphorene, BN and MoS₂ have sparked a great deal of interest in exploiting their system heterostructures. Since graphene isolation in 2004, the 2D materials collection has grown considerably to include graphene, hexagonal boron nitride (hBN), 2D chalcogenides, 2D oxides, graphene derivatives, phosphorene, and so forth. In general, due to the pervasiveness and flexibility of vdW interaction as 'weak glue', any 2D material can be used as a layer in stack. Among these material candidates are widely utilized and studied graphene, hBN, and TMDCs, partly due to their availability (relatively high mechanical, thermal, and chemical stability), and distinct but complementary properties. Therefore incorporating the unique properties of these various 2D materials provides numerous possibilities to shape the future of nanoelectronics [23].

2D TMDCs show specific electrical and optical properties that emerge from the quantum confinement and surface effects that occur when bulk materials are scaled down to monolayers during the transition from an indirect bandgap to a direct bandgap. Powerful photoluminescence and broad exciton binding energy accompany this tunable bandgap in TMDCs, making them a promising candidate for a number of opto-electronic instruments, including solar cells, photo-detectors, light-emitting diodes and photo-transistors [24].

The monolayer semiconducting TMDCs such as MoS_2 and WSe_2 are novel material platforms for optoelectronic applications (such as telecommunication laser, blue laser, optical fiber, LED traffic light, photodiodes, solar cells), with direct band gaps in the visible electromagnetic spectrum, large exciton binding energies and intense photoluminescence. Optoelectronic devices based on a monolayer or a few layers of MoS_2 and WSe_2 were manufactured with strong photo responsiveness.

First studies on the optical properties of TMDCs were already performed back in the 1960s. It was understood these materials existed in a layered system. Layer of TMDC consists of a sheet of transition metal (M) atoms in between two sheets of chalcogen (X) atoms. Whereas the bonding inside a monolayer X-M-X is covalent, van der Waals forces are responsible for the bonding between individual layers. This unique property allowed the thin crystals to be prepared by cleaving using adhesive tape. The absorption spectra acquired were dominated by peaks that resulted from heavy excitonic absorption. This was due to the excitons being confined because of the materials' two-dimensional nature. It has been estimated that the exciton binding energy of a purely two-dimensional exciton is four times the three-dimensional value. Cleaved TMDC surfaces do not have dangling bond. Thus, heterostructures with a large lattice mismatch can be formed. [6] The common feature of 2D layered materials is that weak vdW interaction binds the covalently-bonded atomic layers together [6].

A new type of TMD material, namely Janus MoXY ($X / Y = \text{S, Se, Te}$) monolayers, has been successfully synthesized in experiments through the thermal selenization of a MoSe_2 monolayer or MoS_2 monolayer sulfurization. The Janus MoXY monolayers are formed by the complete replacement of one layer of X atoms with Y atoms, which tends to break the mirror symmetry

out of plane. Janus MXY monolayers display semi-conducting characters with band gap values between 1.37 eV and 1.96 eV [25].

Today, 2D material-based heterostructures are being studied to improve the characteristics of individual monolayers for various technological advantages, such as enhancing electrical, transport, optical and piezoelectric properties. To synthesize the lateral and vertical heterostructures, some techniques such as mechanical transfer, direct synthesis, and liquid-phase exfoliation mixing have developed. Mechanical transfer and other dry transfer methods are widely used among the many techniques to synthesize the vertical vdW hetero-structures for their advantages in getting around the problems of the lattice mismatch at the interface, which is a major issue that uses direct synthesis techniques to notify the lateral heterostructures [26]. There are two methods for heterostructure obtaining. In order to form lateral heterostructures, one is assembling the different layers in a plane and another is stacking different layered materials layer-by - layer (vertical heterostructure) vertically [27]. In recent years, two different groups of synthesis methods have been developed to produce most 2D materials in order to make 2D materials well used in practical technologies: top-down methods like mechanical exfoliation, chemical exfoliation and liquid phase exfoliation; and bottom-up methods are the other types of manufacturing methods, such as CVD [28].

For the regulation of system behavior, charge carrier injection and transport, electronic levels and energies of a solid, such as Fermi level, vacuum level , work function, ionization energy or electron affinity, are of vital importance. However, these amounts and quantities are sensitively dependent upon the solid's structure and surface morphology and chemical composition. A small amount of contaminants on the metal surface, or a change in the molecular orientation of the organic semiconductor surface, may alter the work function and the location of the vacuum level by a large fraction of the electron-volt and have a major effect on the electronic interface structure [29].

A critical problem for nanotechnology is that the materials, structures, and systems are in a size regime we have little understanding of about their fundamental behavior. The particles are too small for direct measurements, too large to be represented by current rigorous first principle

theoretical and computational methods, show too many variations in time and space to be viewed monolithically, and are too few to be represented by a statistical ensemble. Fundamental understanding and highly effective predictive methods are crucial to efficient nanostructured materials, electronics, and systems manufacturing. Nanomaterials are the field of material science dedicated to the study of nanometer-scale materials with at least one dimension. On this scale, the number of atoms or molecules forming the substance is related to qualitative changes in physicochemical properties and reactivity. Size-effect characteristics such as surface plasmon resonance in metal nanoparticles, quantum containment in semiconductor particles and super paramagnetism in magnetic nanomaterials can be observed, for example [30].

The most significant advances applicable to nanotechnology in the field of theory, modeling, and simulation have been associated with the introduction of more powerful computers and corresponding advances in software and algorithms, and to a lesser degree, with the broaching of new theories. These have allowed several different types of computational techniques to be combined to provide high-fidelity simulations of nanoscale artifacts based on the theory of first principles.

Although full modeling of nanoscale systems is difficult today, it is clear that theory, modeling, and simulation are the key enabling areas for the following:

- Shortening the time required to design new materials
- Nanoscale devices developed from the new materials
- Greater reliability and predictability of new devices operation
- The creation and optimization of emerging technologies on a nanoscale

Theory, modeling and simulation lead to immediate financial savings in terms of time spent, resources expended and end product quality. Theory, modeling and simulation is an empowering field in that it can provide new levels of understanding and numerical values when there are no experimental results. In addition, modeling and simulation are often necessary for proper interpretation of an experimental measurement due to the complexity of the measurement or the average under the experimental conditions.

Similar to the conventional TMDC monolayers, the single-layer Janus TMDCs have a sandwich structure with a trigonal prismatic coordination (i.e., H phase), as shown in Fig. 8. Nevertheless, Janus TMDC monolayers have a formula MXY where M is a transition metal element ($M = \text{Mo}, \text{W}$) and X and Y are different chalcogen elements ($X/Y = \text{S}, \text{Se}, \text{Te}$ and $\text{X}\square, \text{Y}$), and apparently they lack inversion and mirror symmetries [31].

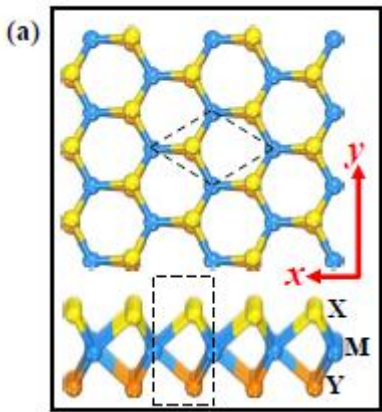


Figure 8. Top and side views of atomic structure of Janus monolayer transition metal dichalcogenides MX_2 ($M = \text{Mo}$ and W ; $X = \text{S}, \text{Se}, \text{Te}$). The dash frames indicate the range of unit cell.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Computational details

Electronic calculation using DFT with the software package QUANTUM ESPRESSO is implemented. The electronic exchange – correlation energy is handled using Perdew – Burke – Ernzerhof and generalized-gradient approximation. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) with the approach of Grimme (DFT-D2) is adopted to correct the weak Van der Waals like interaction between layers of heterostructures. A simulation begins from unit cell crystal. This information is stored in the so-called cif format in databases. Cif format is a common crystal structure specification format that is both human-readable and machine readable to effectively translate a set of atomistic simulation codes from a cif format into the native input format; we use software called the Cif2cell. In its own way, QUANTUM ESPRESSO reads crystal structure information. Translate the cif file to the QUANTUM ESPRESSO format, therefore. Finally, for further calculations, prepare the input file.

QUANTUM ESPRESSO is an open source implementation made available under the GNU General Public License of the DFT techniques and related codes. The central component of QE is the PWscf module, which carries out the self-consistent calculations that require most of the rest of QE to work. Calculations were carried out on a Linux 64-bit operating system. All ZnO and WSSe monolayer calculations were performed using QUANTUM ESPRESSO. Such calculations are K-mesh convergence, Lattice constant convergence, Ecutwfc convergence, Ecutrho convergence, band structure, state density, spin polarized state density. Calculations based on DFT in accordance with the projector augmented-wave (PAW) potential as implemented in the VASP for the execution of projected band structure, the average electrostatic plane potential and the four heterostructure configurations between ZnO monolayer and WSSe monolayer work functions are applied.

3.2 Density Functional Theory

3.2.1 Introduction

Currently, the most popular approach to measuring the electronic structure of matter is the density functional theory (DFT). Its applicability spans from nuclei and quantum and classical fluids to atoms, molecules and solids. The DFT provides the ground state properties of a system in its original formulation, and the density of electrons plays a key role. DFT is a very effective approach to calculating from first principles the (ground state) properties of many-electron systems [8].

Traditional methods of electronic structure try to find approximate solutions for the Schrödinger equation of N interacting electrons moving in an external, electrostatic potential (typically the Coulomb potential produced by the atomic nuclei). However, this approach has significant limitations: (i) the problem is highly nontrivial, even for very small numbers N and the resulting wave-functions are complicated artifacts, (ii) computational effort is which very rapidly with the N , and thus the analysis of larger systems is becoming prohibitive.

In DFT a particular approach is taken where the one-body density is used as a fundamental variable instead of the many-body wave-function. Since $n(r)$ density is a function of just three spatial co-ordinates (rather than wave-function $3N$ co-ordinates), the functional theory of density is computationally feasible even for broad systems.

The foundations of functional density theory are the theorems Hohenberg-Kohn and Kohn-Sham which will be examined in the section below. The so-called exchange-correlation-energy functional will be discussed at different levels of approximation to the central quantity of DFT.

3.2.2 Hohenberg-Kohn and Kohn-Sham Theorems

One is interested in systems of N interacting electrons defined by the Hamiltonian in ground-state DFT [32].

$$H = T + V + V_{ee} = -\sum_{i=1}^N \frac{\nabla_i^2}{2} + \sum_{i=1}^N v(r_i) + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \frac{1}{|r_i - r_j|} \quad (1)$$

With the kinetic, potential and electron-electron interaction energy operators T , V and V_{ee} , respectively

The fundamental statement of formal functional density theory is the celebrated Hohenberg-Kohn theorem, which can be summarized in the following three statements for non-degenerate ground states:

1. A system of interacting electrons' ground state electron density $n(r)$ uniquely defines the external potential $v(r)$ under which the electrons move and thus the Hamiltonian and all the system's physical properties.
2. The ground-state energy E_0 and the ground-state density $n_0(r)$ of a system characterized by the potential $v_0(r)$ can be obtained from a variational principle which involves only the density, i.e., the ground state energy can be written as a functional of the density, $E_{v_0}[n]$, which gives the ground-state energy E_0 if and only if the true ground-state density $n_0(r)$ is inserted. For all other densities $n(r)$, the inequality

$$E_0 = E_{v_0}[n_0] < E_{v_0}[n] \quad (2)$$

holds.

3. There exists a functional $F[n]$ such that the energy functional can be written as

$$E_{v_0}[n] = F[n] + \int d^3r v_0(r)n(r). \quad (3)$$

The functional $F[n]$ is universal in the sense that it is independent of the potential $v_0(r)$ of the particular system under consideration for a given particle-particle interaction (the Coulomb interaction in our case), i.e. it has the same functional form for all systems.

From the Hohenberg-Kohn variational principle, i.e., the second statement given above, the ground-state density $n(r)$ corresponding to the external potential $v(r)$ can be obtained as solution of the Euler equation

$$\frac{\delta E_v[n]}{\delta n(r)} = \frac{\delta F[n]}{\delta n(r)} + v(r) = 0, \quad (4)$$

The formal definition of the Hohenberg-Kohn functional $F[n]$ is well known,

$$F[n] = T[n] + V_{ee}[n] = \langle \psi[n] | T | \psi[n] \rangle + \langle \psi[n] | V_{ee} | \psi[n] \rangle, \quad (5)$$

where $[n]$ is that N-electron wave-function which yields the density n and minimizes the expectation value of $T + V_{ee}$. But $F[n]$'s explicit dependency on density remains unknown.

Approximations have been proposed, the oldest being the well-known Thomas-Fermi approximation (which traditionally precedes the theorem of Hohenberg-Kohn). Unfortunately in practical calculations the accuracy of known approximations to $F[n]$ is very limited. Consequently, Eq. (4) is seldom used in measuring electronic structures today.

Instead, the Hohenberg-Kohn theorem provides the basic theoretical basis for constructing an efficient single-particle scheme that allows the measurement of ground state density and energy of interacting electron systems. At the heart of modern density functional theory are the resulting equations, the so-called Kohn-Sham equations. They have the form of the single-particle Schrödinger equation

$$\left[-\frac{\nabla^2}{2} + v_s(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r), \quad (6)$$

The density can then be computed from the N single-particle orbitals occupied in the ground state Slater determinant

$$n(r) = \sum_i^{occ} |\varphi_i(r)|^2 \quad (7)$$

The core idea of the Kohn-Sham system is to create the $v_s(r)$ single-particle potential in such a way that the density of the non-interacting auxiliary system is equal to the density of the system of interest that interacts. One partition of the Hohenberg-Kohn functions in the following way for this reason.

$$F[n] = T_s[n] + U[n] + E_{xc}[n], \quad (8)$$

Where

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|} \quad (9)$$

is the classical electrostatic energy of the charge distribution $n(r)$, and $E_{xc}[n]$ is the so-called exchange-correlation energy which is formally defined by

$$E_{xc}[n] = T[n] + V_{ee}[n] - U[n] - T_s[n] \quad (10)$$

From the above definitions one can derive the form of the effective potential entering Eq. (6)

$$v_s[n](r) = v(r) + \int d^3r' \frac{n(r')}{|r-r'|} + v_{xc}[n](r) \quad (11)$$

where the exchange-correlation potential v_{xc} is defined by

$$v_{xc}[n](r) = \frac{\delta E_{xc}[n]}{\delta[n]} \quad (12)$$

Since $v_{xc}[n](r)$ depends on the density, Eqs. (6), (7) and (11) have to be solved self consistently. This is known as the Kohn-Sham scheme of density functional theory and the algorithm is shown in figure 9 below.

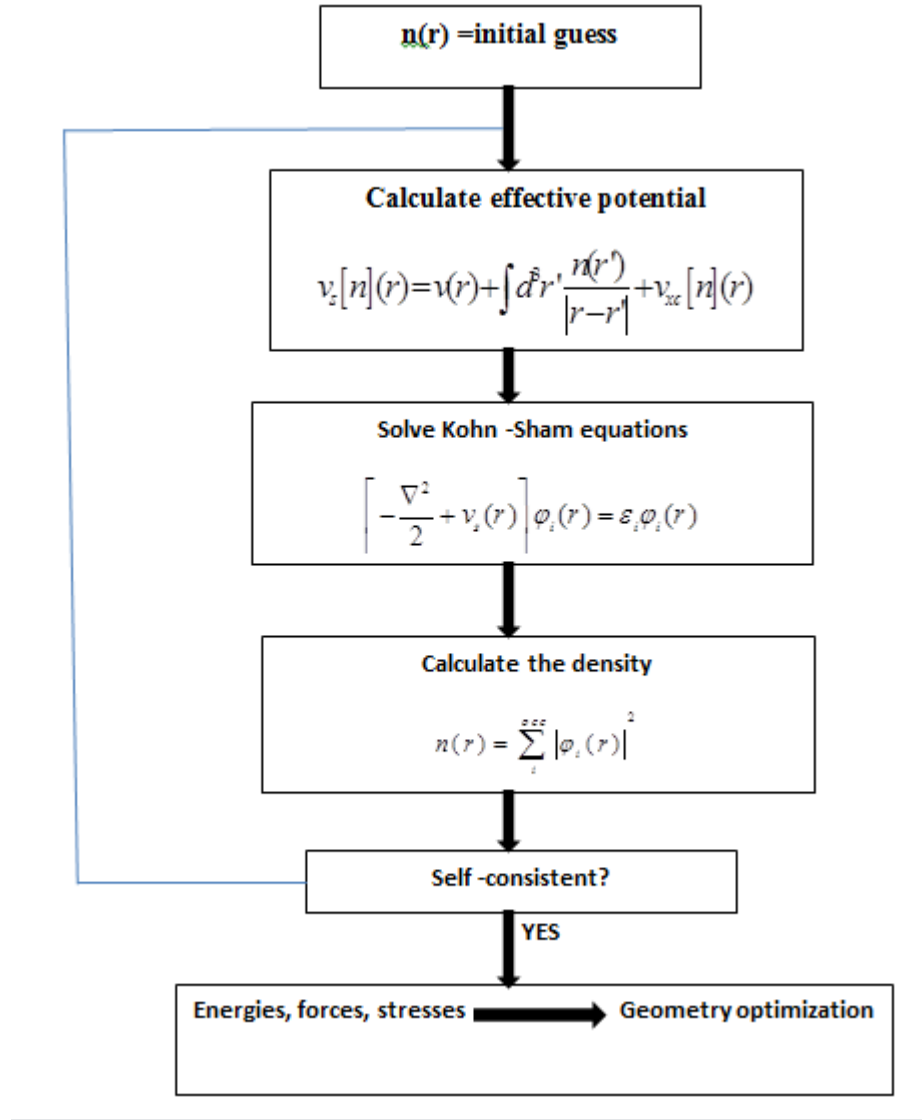


Figure 9. Flowchart of self-consistent Kohn-Sham calculation

3.2.3 Approximations for the Exchange-Correlation Energy

Clearly, for practical calculations, the formal description (equation 10) of exchange-correlation energy is not helpful and an approximation of this quantity needs to be used. Some of those approximations are discussed below.

While DFT itself does not give any hint on how to construct approximate exchange correlation functionals, it holds both the promise and the challenge that the true E_{xc} is a universal functional

of the density, i.e., it has the same functional form for all systems. On one hand this is a promise because an approximate functional, once constructed, may be applied to any system of interest. On the other hand this is a challenge because a good approximation should perform equally well for very different physical situations.

Both the promise and the challenge are reflected by the fact that the simplest of all functionals, the so-called local density approximation (LDA) has remained the approximation of choice for quite many years after the formulation of the Kohn-Sham theorem. In LDA, the exchange correlation energy is given by

$$E_{xc}^{LDA}[n] = \int d^3r n(r) e_{xc}^{unif}(n(r)) \quad (13)$$

where $e_{xc}^{unif}(n)$ is the exchange-correlation energy per particle of an electron gas with spatially uniform density n . It can be obtained from the calculations of the quantum Monte Carlo, and there are simple parameterizations. The LDA is supposed to be a good approximation for slowly changing densities spatially through its very architecture. Although this requirement for real electronic systems is hardly ever met, for a wide variety of systems, LDA has proven to be remarkably accurate.

With the advent of the so-called generalized gradient approximations (GGAs), a major breakthrough was made in the search for improved functionals. In GGA the energy of exchange-correlation for spin-unpolarized systems is written as

$$E_{xc}^{GGA}[n] = \int d^3r f(n(r), \nabla n(r))$$

While the input e_{xc}^{unif} in LDA is unique, the function f in GGA is not and many different forms have been suggested. Typically, one tries to integrate a number of known properties of the exact functional into the restricted functional form of the approximation when constructing a GGA. The impact of GGAs has been very dramatic, particularly in quantum chemistry where DFT is now competitive in precision with more conventional methods while being less costly in computational terms.

Following the lines of GGA development, meta-GGA functionals has been proposed. Meta-GGA functionals are dependent on the kinetic energy density of the Kohn-Sham orbitals in addition to the density and its first gradient.

$$\tau(r) = \frac{1}{2} \sum_i^{occ} |\nabla \varphi_i(r)|^2, \quad (15)$$

The meta-GGA functional then takes the form

$$E_{xc}^{MGA} [n] = \int d^3r g(n(r), \nabla n(r), \tau(r)) \quad (16)$$

In order to integrate more of the exact properties into the approximation, the additional versatility in the functional form obtained by the implementation of the new variable can be used. In this way, the accuracy of GGA for certain physical properties can be enhanced without worsening the results for others.

Unlike LDA or GGA, which are explicit functionals of the density, meta-GGAs often rely explicitly on the Kohn-Sham orbitals. It is important to note, however, that we are still in the domain of DFT because, via the Kohn-Sham equation (6), the orbitals are functionals of the Kohn-Sham potential and thus, by virtue of the Hohenberg-Kohn theorem, also functionals of the density.

Orbital functionals, or implicit density functionals, constitute a wide field of active research. Probably the most familiar orbital functional is the exact exchange energy functional (EXX)

$$E_{xc}^{EXX} [n] = -\frac{1}{2} \sum_{\sigma} \int d^3r \int d^3r' \sum_{i,j}^{occ} \frac{\varphi_{i\sigma}(r) \varphi_{i\sigma}^*(r') \varphi_{j\sigma}(r') \varphi_{j\sigma}^*(r)}{|r - r'|} \quad (17)$$

At this point, some remarks about similarities and differences to Hartree-Fock theory are in order. If one uses the exact exchange functional (17) and neglects correlation, the resulting total energy functional is exactly the Hartree-Fock functional. However, this feature is assessed with Kohn-Sham rather than Hartree-Fock orbitals in exact-exchange DFT. In addition, Hartree-Fock orbitals are obtained from a constraint-free minimization (except for orthonormality) that leads to the non-local potential of Hartree-Fock. On the other hand, the exact exchange of Kohn-Sham orbitals is obtained by minimizing the same functional under the additional constraint that the

orbitals of single particles derive from a local potential. The total Hartree-Fock energy is therefore always lower in exact-exchange DFT than the total energy, but the difference has turned out to be very small. However, in both methods, single particle a property such as orbitals and orbital self-values can be somewhat different. Kohn-Sham 's exact exchange energy spectra, for instance, are typically far closer to experiment than Hartree-Fock spectra, suggesting that exact-exchange DFT might be a better starting point than Hartree-Fock to provide correlation.

To go beyond exact-exchange DFT one could be tempted to use the exact functional exchange in combination with a conventional correlation approximation such as LDA or GGA. Since both LDA and GGA gain from an error cancelation between their exchange and correlation elements, an approach that uses LDA or GGA is bound to fail for only one of these energy components. Approximate, orbitally dependent correlation energy functionals are the obvious alternative. G'orling-Levy perturbation theory is regarded as one systematic way to construct such functionals. Structurally, this is similar to what is known as Møller- Plesset perturbation theory in quantum chemistry. However, it is only practical for low orders. A more promising route uses the fluctuation-dissipation theorem which establishes a connection to linear response theory in time-dependent DFT.

A final class of approximations to the exchange-correlation energy is the so-called hybrid functionals which mix a fraction of exact exchange with GGA exchange,

$$E_x^{HYB}[n] = aE_x^{EXX}[n] + (1-a)E_x^{GGA}[n], \quad (18)$$

where a is the (empirical) mixing parameter. This exchange functional is then combined with some GGA for correlation. Hybrid functionals are tremendously popular and successful in quantum chemistry but much less so in solid-state physics.

This latter reality illustrates a problem related to the construction of enhanced functionals: usable approximations are already very precise and difficult to improve. Furthermore, and this makes it a very difficult question, not only for one specific property or one specific class of systems, but for as many properties and systems as possible, one would like to have improved performance. The true energy of exchange-correlation is after all a universal density functional.

3.3 The plane wave pseudopotential method

3.3.1 Plane wave basis sets

According to Bloch theorem, in a periodic solid (potential) each wave function (ψ) can be written as a product of a lattice-periodic part $u(k, r)$ and a plane wave e^{ikr}

$$\psi(k, r) = e^{ikr} \cdot u(k, r) \quad (19)$$

The lattice-periodic part can be expanded in plane waves whose wave vectors G are reciprocal lattice vectors:

$$u(k, r) = \sum_G c_k, G e^{iGr} \quad (20)$$

Kohn-sham states,

$$\psi_j(k, r) = \sum_G c_j, (k + G) e^{i(k+G)r} \quad (21)$$

Where C_j is plane wave coefficient

There is a problem, which is, near the nucleus, there are strong oscillations in the wave functions. A definition of these oscillations is needed for this large number of plane waves. These oscillations, which are less necessary for bonding, are due to core states. But all-electron plane wave calculations can't be done for systems of practical interest. The implementation of pseudopotentials will reduce oscillations in the core zone.

3.3.2 Pseudopotentials

The potential inside some core radius r_c is replaced by a pseudopotential describing the nucleus and core radius. Outside r_c the wave functions for all-electron (ψ_{AE}) and wave functions for pseudopotentials (ψ_{pseudo}) are the same and much smaller realistic basis sets can be used.

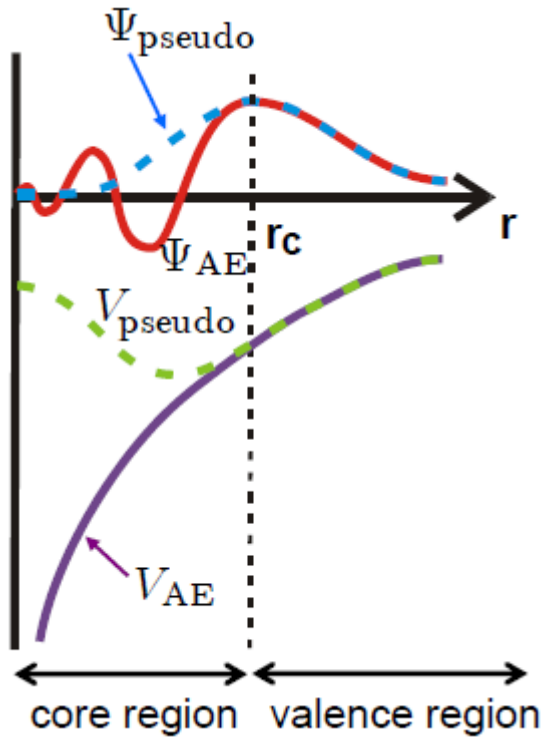


Figure 10. Approximations of Pseudopotentials

A plane wave cutoff, which is the highest kinetic energy of all basis functions and specifies the number of basis functions, specifies the size of the basis group. The basis set for convergence can be managed systematically by growing the cutoff on the plane wave

$$E_{cut} = \frac{\hbar^2}{2m} |G_{max}|^2 \quad (22)$$

3.4 Computational Codes

3.4.1 QUANTUM ESPRESSO

QUANTUM ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling, based on density-functional theory, plane waves, and

pseudopotentials (norm-conserving, ultrasoft, and projector-augmented wave). The acronym ESPRESSO stands for opEn Source Package for Research in Electronic Structure, Simulation, and Optimization. It is freely available to researchers around the world under the terms of the GNU General Public License. QUANTUM ESPRESSO builds upon newly-restructured electronic-structure codes that have been developed and tested by some of the original authors of novel electronic-structure algorithms and applied in the last twenty years by some of the leading materials modeling groups worldwide. Innovation and efficiency are still its main focus, with special attention paid to massively parallel architectures, and a great effort being devoted to user friendliness. QUANTUM ESPRESSO is evolving towards a distribution of independent and interoperable codes in the spirit of an open-source project, where researchers active in the field of electronic-structure calculations are encouraged to participate in the project by contributing their own codes or by implementing their own ideas into existing codes [33].

QUANTUM ESPRESSO implements a variety of methods and algorithms aimed at a chemically realistic modeling of materials from the nanoscale upwards and the codes are constructed around the use of periodic boundary conditions, which allows for a straightforward treatment of infinite crystalline systems, and an efficient convergence to the thermodynamic limit for aperiodic but extended systems, such as liquids or amorphous materials.

Many different exchange–correlation functionals are available in the framework of the local-density (LDA) or generalized-gradient approximation (GGA), plus advanced functionals like Hubbard U corrections and a few meta-GGA and hybrid functionals.

The basic computations/simulations that can be performed include:

- a) Ground state calculations
- b) Structural optimization, molecular dynamics, potential energy surfaces
- c) Electrochemistry and special boundary conditions
- d) Response properties (density functional perturbation theory)
- e) Spectroscopic properties
- f) Quantum transport

3.4.2 VASP

The Vienna Ab initio Simulation Package (VASP) is a computer program for atomic scale materials modeling, e.g. electronic structure calculations and quantum-mechanical molecular dynamics, from first principles. VASP is a complex package for performing ab-initio quantum-mechanical molecular dynamics (MD) simulations and electronic structure calculations using pseudopotentials or the projector-augmented wave method and a plane wave basis set. The approach implemented in VASP is based on the (finite-temperature) local-density approximation with the free energy as variational quantity and an exact evaluation of the instantaneous electronic ground state at each MD time step.

Using the projector-augmented wave method to explain the electron-core interaction, VASP is a plane-wave all-electron code. The code uses rapid iterative techniques for DFT Hamiltonian diagonalization and allows total energy measurements and structural optimizations to be performed for systems with thousands of atoms and simulations of molecular dynamics ab initio [34].

3.4.3 Material Studio

Material studio is a complete modeling and simulation software designed to allow researchers in materials science and chemistry to predict and understand the relationships of a material's atomic and molecular structure with its properties and behavior.

3.4.4 Xcrysden

XCrySDen is a crystalline- and molecular-structure visualization program. The name of the program stands for Crystalline Structures and Densities and X because it runs under the X-Window environment. It facilitates a display of isosurfaces and contours, which can be superimposed on crystalline structures and interactively rotated and manipulated. It also possesses some tools for analysis of properties in reciprocal space such as interactive selection of k-paths in the Brillouin zone for the band-structure plots, and visualization of Fermi surfaces. XCrySDen also provides a graphical user interface for a visualization system for Quantum ESPRESSO. XCrySDen is a visualization program for molecular and crystalline-structure, but its main purpose is as a program for property analysis. It can run on most UNIX platforms, without any special requirements for hardware or software. Special efforts have been made to allow the

proper display of 3D isosurfaces and 2D contours that can be superimposed on the crystalline structure and rotated and manipulated interactively [35].

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Convergence tests of monolayers ZnO and WSSe

For geometric optimization, we have to run the ‘relax’ calculation in the prepared input file. The structure of the monolayers ZnO and WSSe is hexagonal structure with $ibrav=4$. To start calculations, first perform convergence test, which guarantees to obtain numerically sound results. The choice of exchange-correlation functional is mandatory. In these calculations PBE exchange-correlation functional is used throughout the study.

Pseudo potential files of the ZnO monolayer and WSSe monolayer were obtained from cifcell database. From those pseudo potential files, the suggested minimum cutoff for wave functions and minimum cutoff for charge density was obtained. K-mesh choice for geometric optimization is done starting from $1 \times 1 \times 1$ grid up to $15 \times 15 \times 1$ grid. Different convergence tests for K-mesh, kinetic energy cutoff for wave functions, cutoff for charge density was performed and sound results are obtained i.e. criteria at which convergence reached at minimum total energy.

4.2 Convergence Tests

4.2.1 Convergence tests for ZnO monolayer

4.2.1.1 K- points convergence

For performing convergence test for K-points, SCF calculations were done using K-point from $1 \times 1 \times 1$ up to $15 \times 15 \times 1$. Finally total energy is plotted against K-points as shown in figure 11

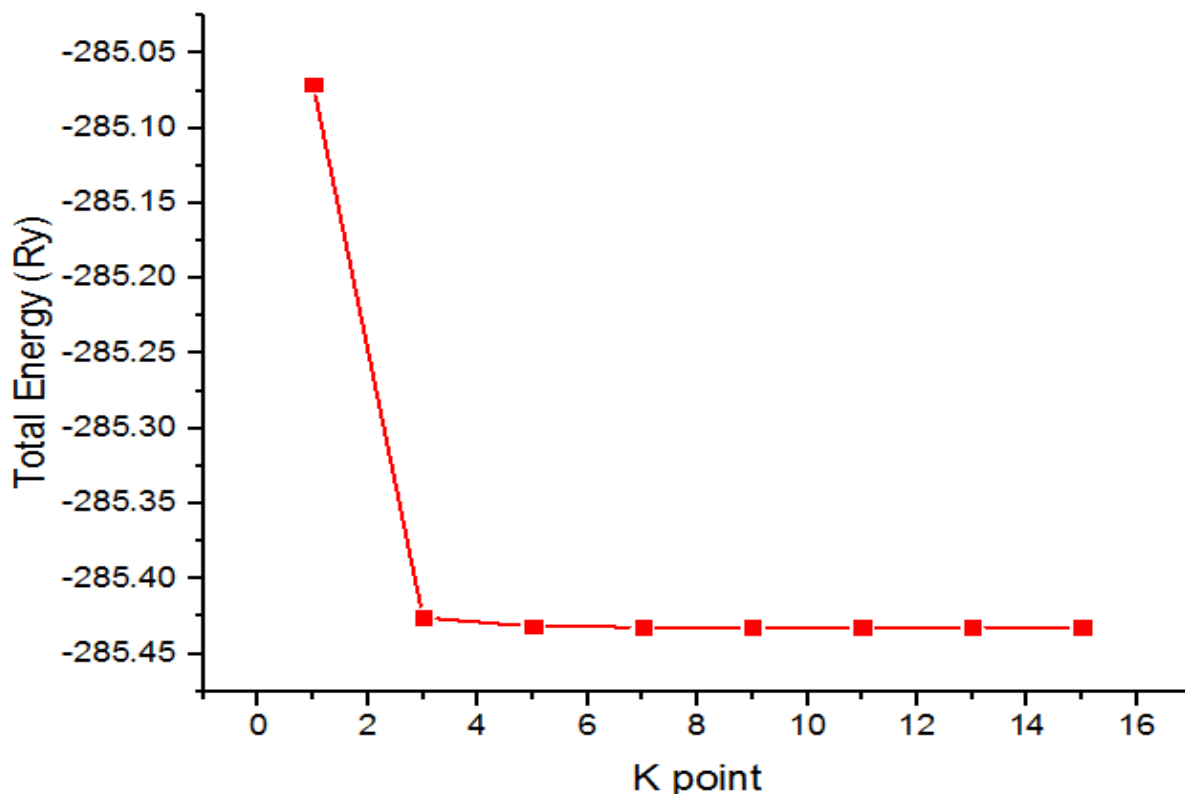


Figure 11. Total energy versus K point for ZnO monolayer

The desired convergence precision threshold has been reached for a k-point size of 9 X 9 X 1 and it will be used for further calculations to get accurate results.

4.2.1.2 Kinetic energy cut-off (E_{cutwfc}) convergence

The kinetic energy cut off convergence is checked by changing the cut off energy. To take both E_{cutwfc} and E_{cutoff} in SCF calculations, $E_{\text{cutoff}}=7E_{\text{cutwfc}}$ is used since suggested value of $E_{\text{cutwfc}}=47$ Ry and $E_{\text{cutoff}}=323$ Ry. Finally Total energy against kinetic energy cut-off is plotted in figure 12.

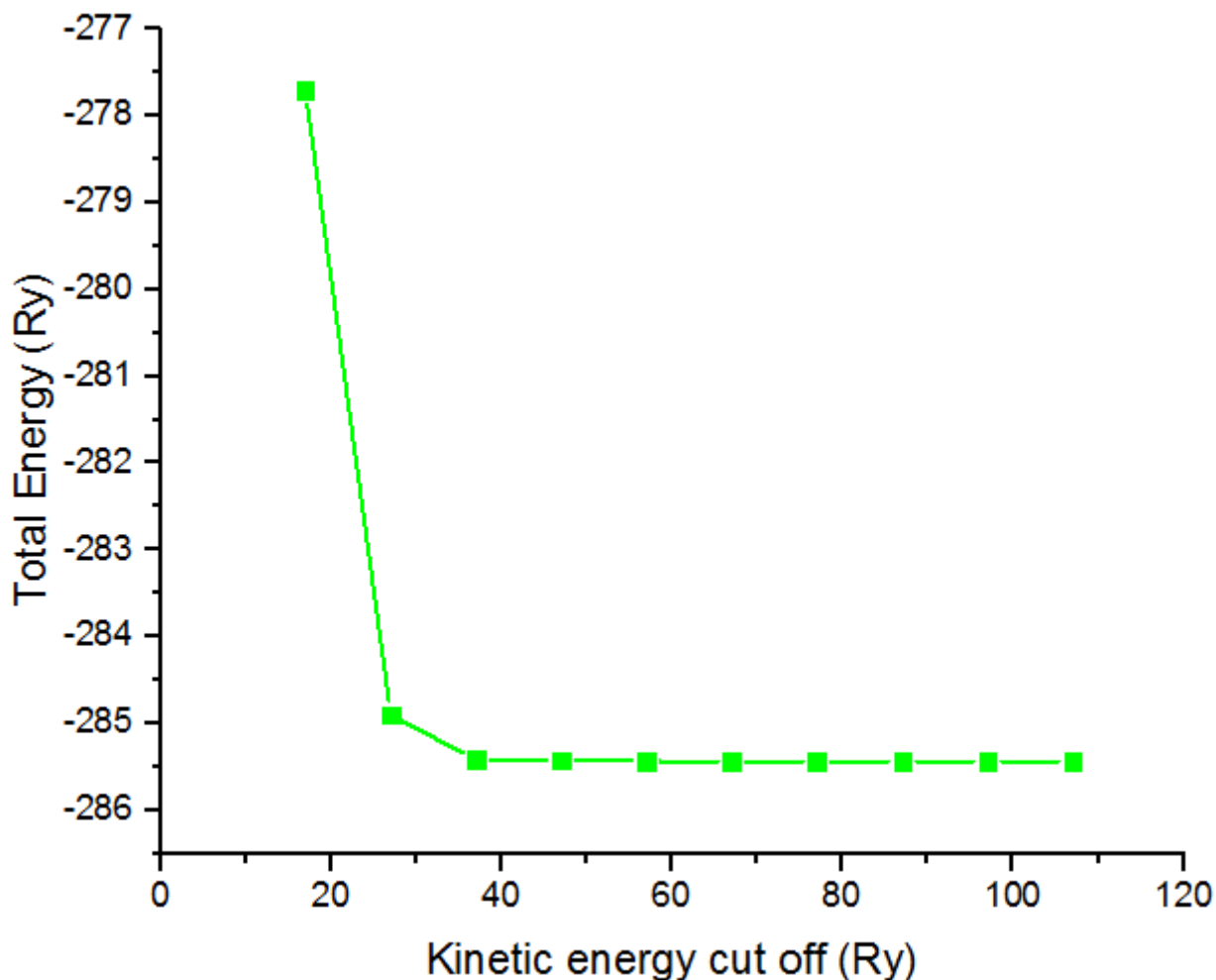


Figure 12. Total energy versus Kinetic energy cut-off

The convergence for kinetic energy cut off is reached around 87 Ry. For further calculations it is appropriate to use cut off energy of 90 Ry.

4.2.1.3 Charge density (Ecutrho) Convergence

For charge density convergence different factor from 2 up to 10 is used. After that the kinetic energy cut off converged value of 90 Ry is taken and multiplying by each factor different charge density is obtained i.e. $E_{\text{cutrho}} = \text{factor} \times 90 \text{ Ry}$. Finally, total energy is plotted against charge density (E_{cutrho}) as shown in figure 13.

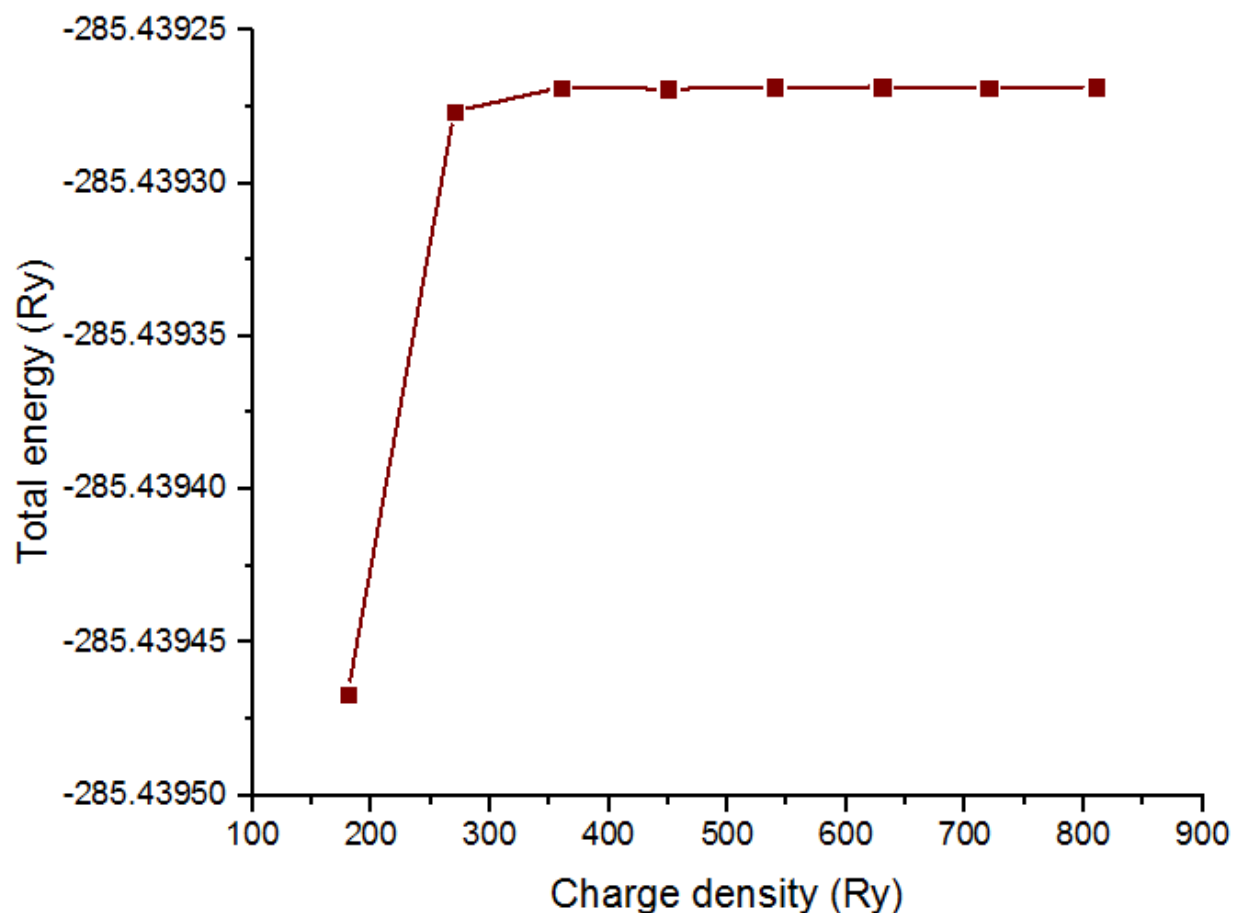


Figure 13.Total energy versus Charge density

The desired convergence of charge density of 450 Ry is obtained and applied for rest of the calculations.

4.2.1.4 Lattice parameter convergence

The converged values of K-Point (9X9X1), Kinetic energy cut off (90Ry) and charge density (450Ry) is used to perform convergence test for lattice parameter. Lattice constant ranging from 3.238 angstrom to 3.338 angstrom with difference of 0.01 is taken and total energy plotted against that lattice constant and shown in figure 14.

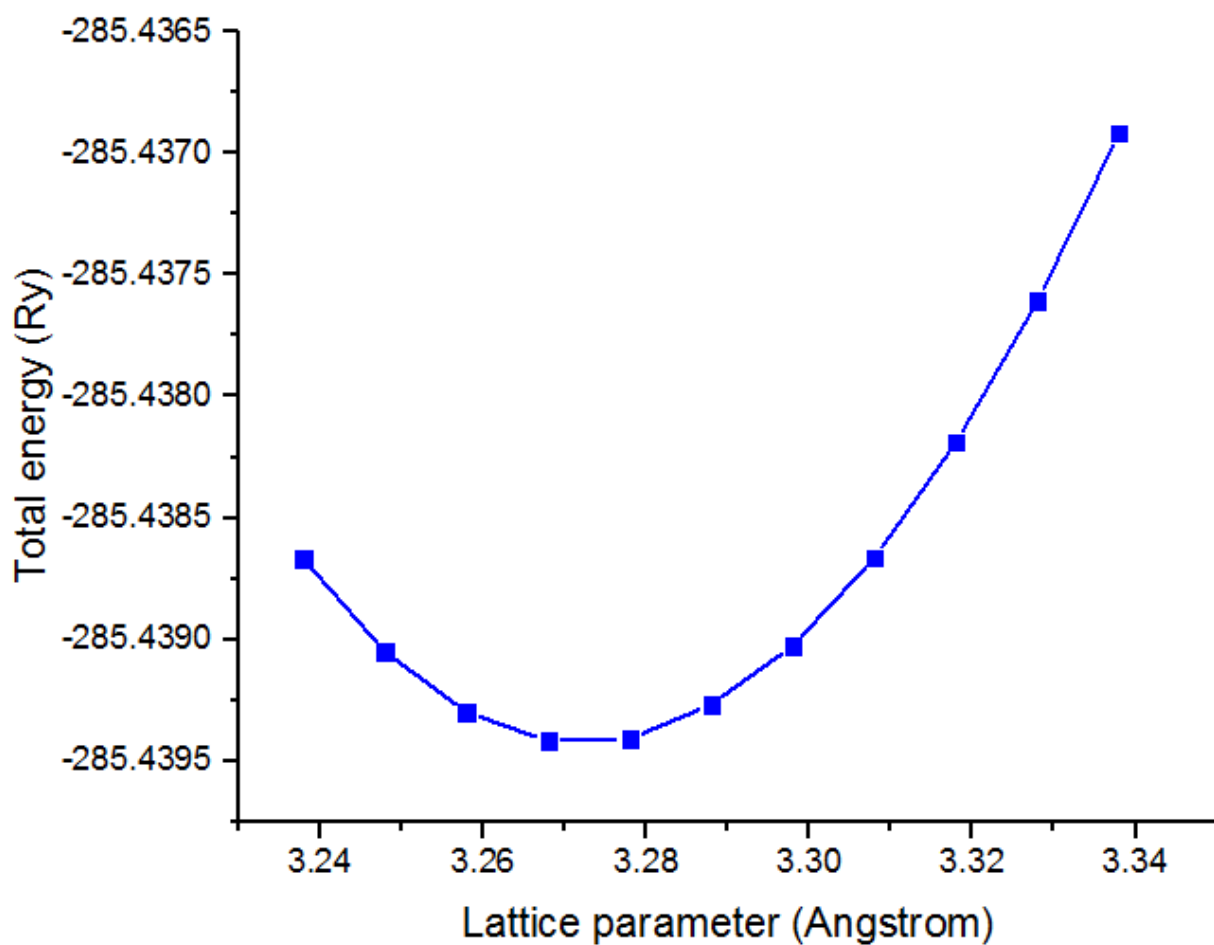


Figure 14. Total Energy versus lattice parameter

As shown on figure 14, lattice constant convergence reached at 3.268 angstrom which is the value for which we get minimum total energy and this value is used for further calculations.

4.2.2 Convergence tests for WSe monolayer

4.2.2.1 Lattice parameter convergence for WSe monolayer

Using the maximum value from pseudopotential file for $E_{\text{cutrho}}=475$ Ry, K point of 9X9X1 and value of E_{cutwfc} of 60 Ry, lattice parameter is done and plot is shown in figure 15.

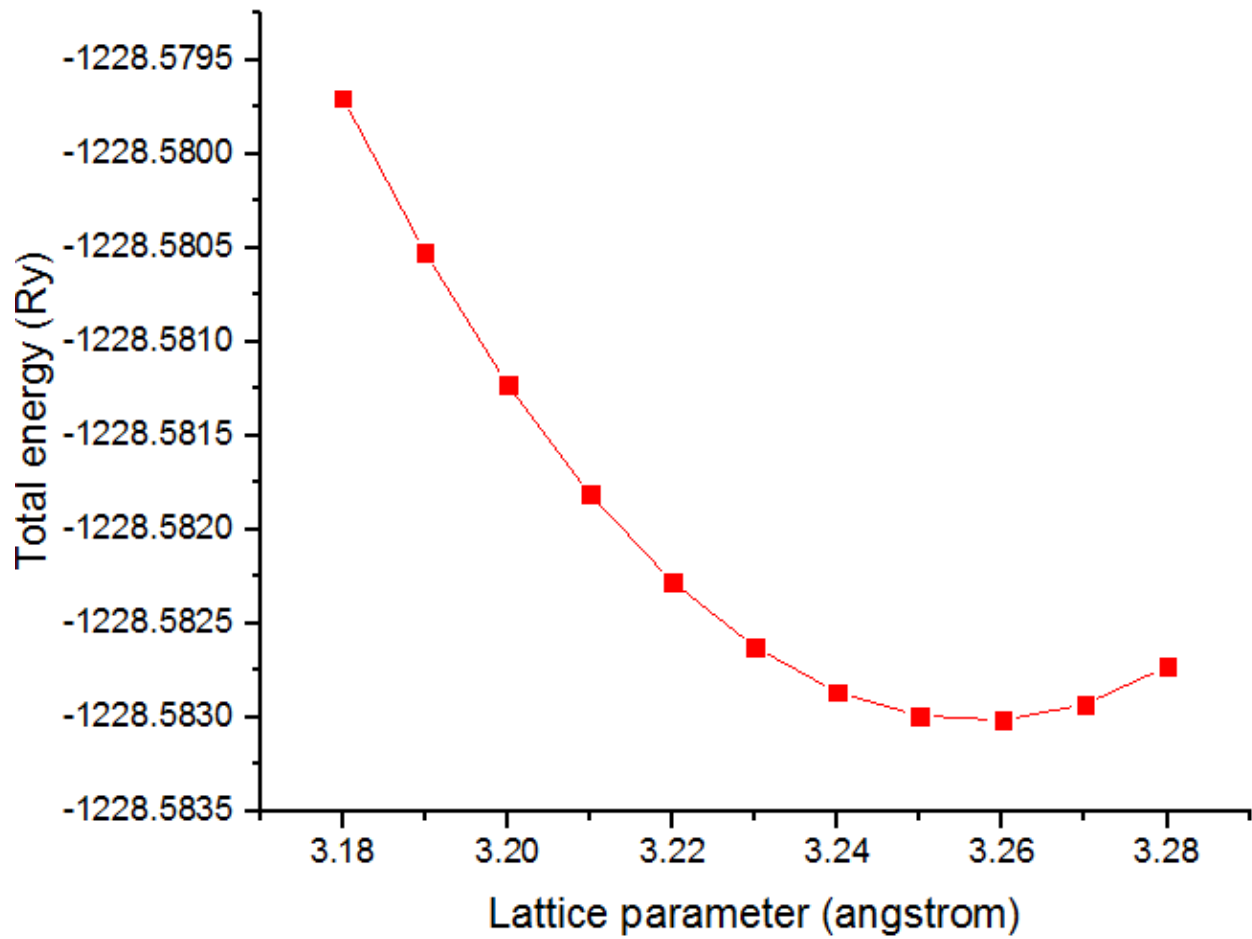


Figure 15. Total energy versus lattice parameter for WSe monolayer

The desired convergence is reached at lattice parameter of $a=3.26$ and used for further calculations.

4.3 Band structure Calculations

The band structure is a good way to visualize the wave vector-dependence of the energy states, the band-gap, and the possible electronic transitions.

The optimized geometric structure for ZnO and WSSe monolayer is shown in figure

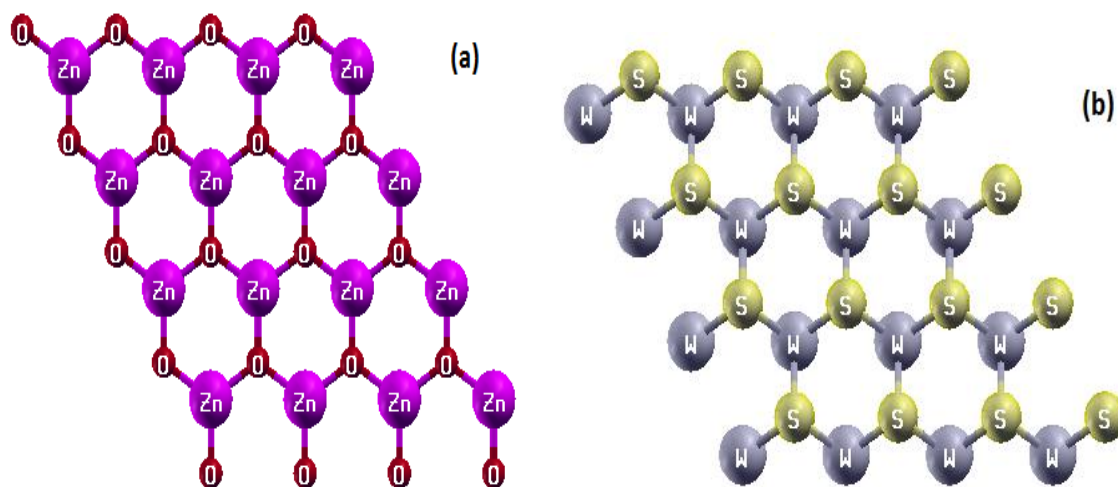


Figure 16 (a) optimized geometric structure of ZnO (b) optimized geometric structure of WSSe monolayers.

4.3.1. Band structure plot for ZnO monolayer

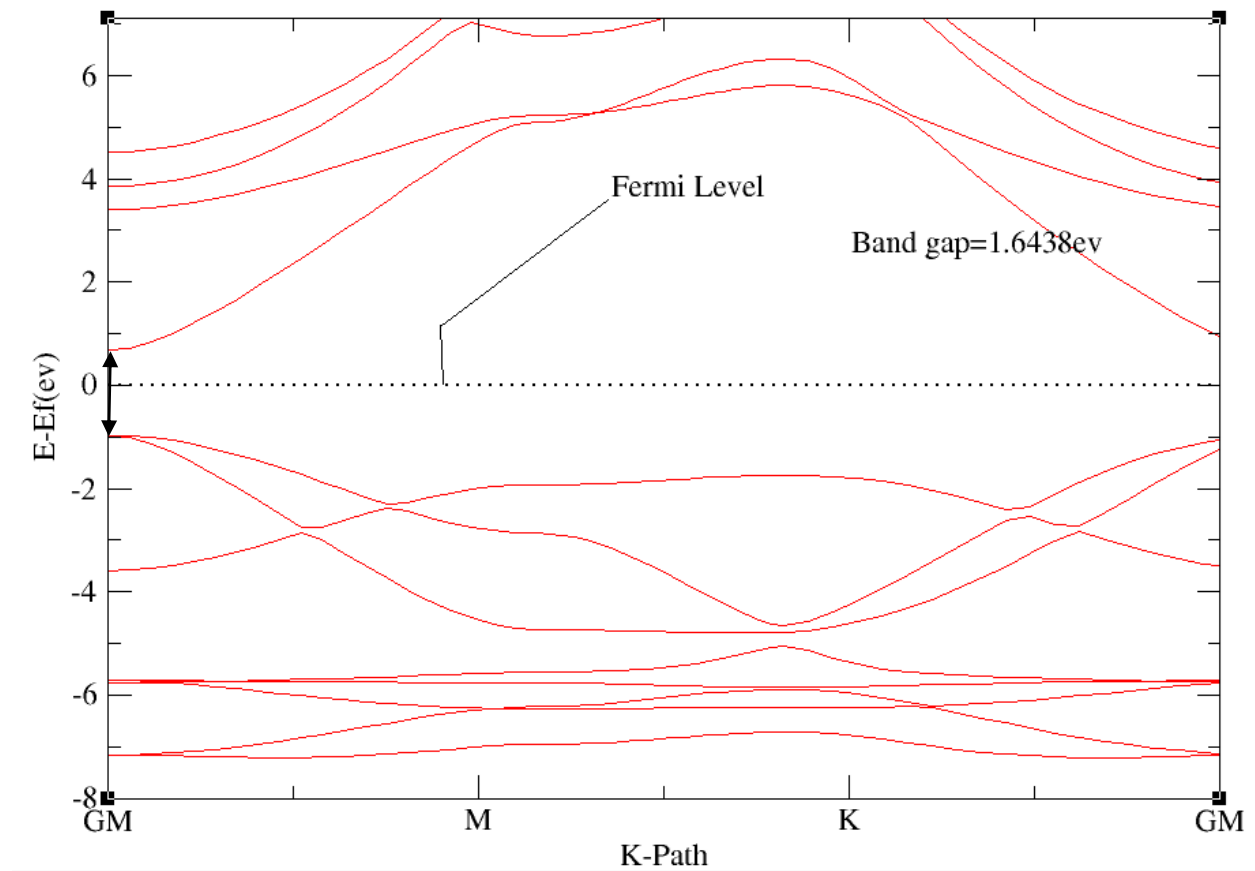


Figure 17. Band structure plot for ZnO monolayer. (Fermi energy is indicated at 0eV).PBE calculation employed.

As shown in figure 17, maximum of valence band at gamma (GM) coincides with minimum of conduction band at gamma (GM) in left part of the plot shown by arrow. Therefore, ZnO monolayer is a direct band gap semiconductor with band gap of 1.6438eV. In a direct gap semiconductor, the minimum of the conduction band and the maximum of the valence band occur at the same momentum. The values are consistent with previous reports [36] [37].

4.3.2. Band structure Plot for WSe₂ monolayer

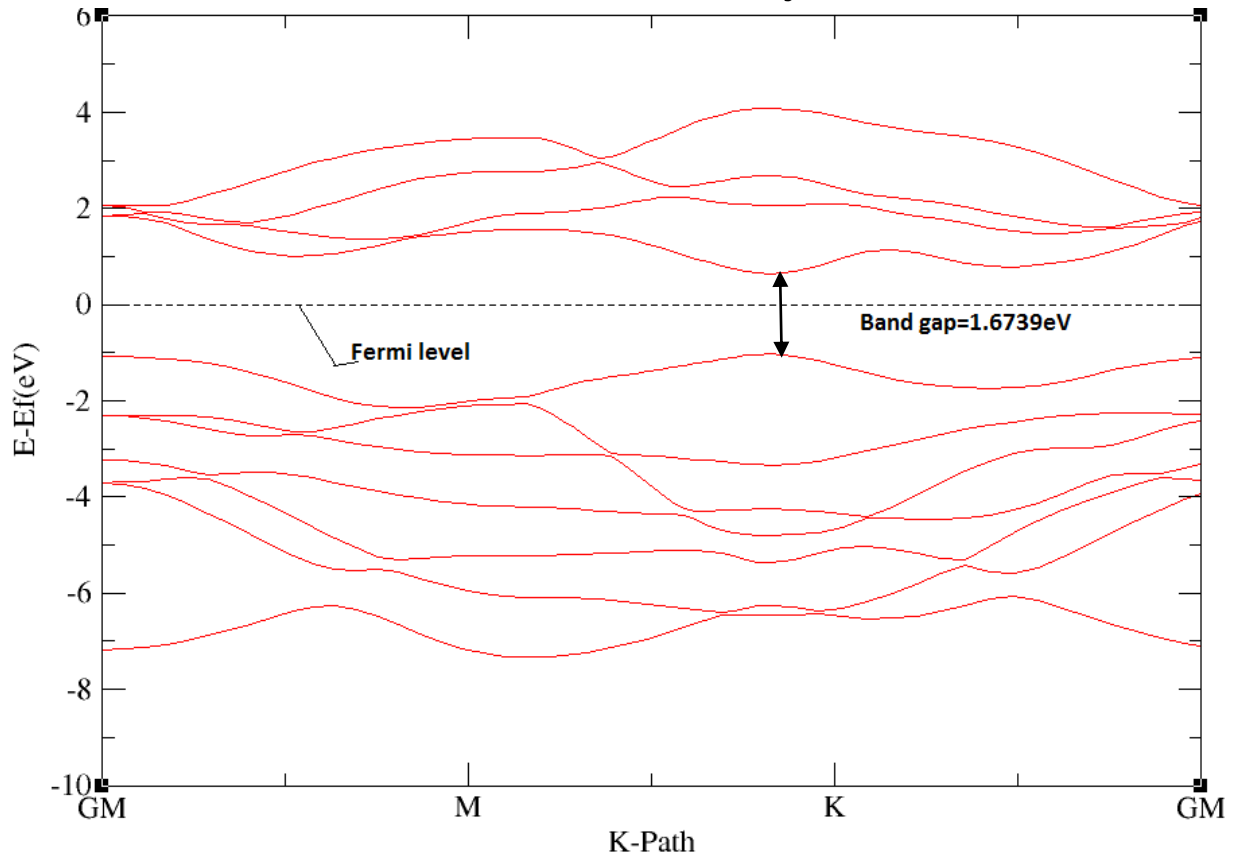


Figure 18 Band structure plot for WSe₂ monolayer. (Fermi level is indicated at 0 eV).PBE calculation employed.

As shown in figure 18; maximum of valence band near K coincides with minimum conduction band near K. Therefore, the WSe₂ monolayer is a direct band gap semiconductor with band gap of 1.6739 eV. The values are consistent with previous reports [31, 38].

4.4 Density of States

The band structure is a good way to visualize the wave vector-dependence of the energy states, the band-gap, and the possible electronic transitions. The actual transition probability depends on how many states are available in both the initial and final energies. The band structure is not a reliable guide here, since it only tells about the bands along high symmetry directions.

What we need is the full density of states across the whole Brillouin zone, not just the special directions. We have to sample the Brillouin zone evenly, just as we do for the calculation of the ground state.

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy.

4.4.1. Density of states plot for ZnO monolayer

For ZnO monolayer, the plot of density of states is given in figure 19.

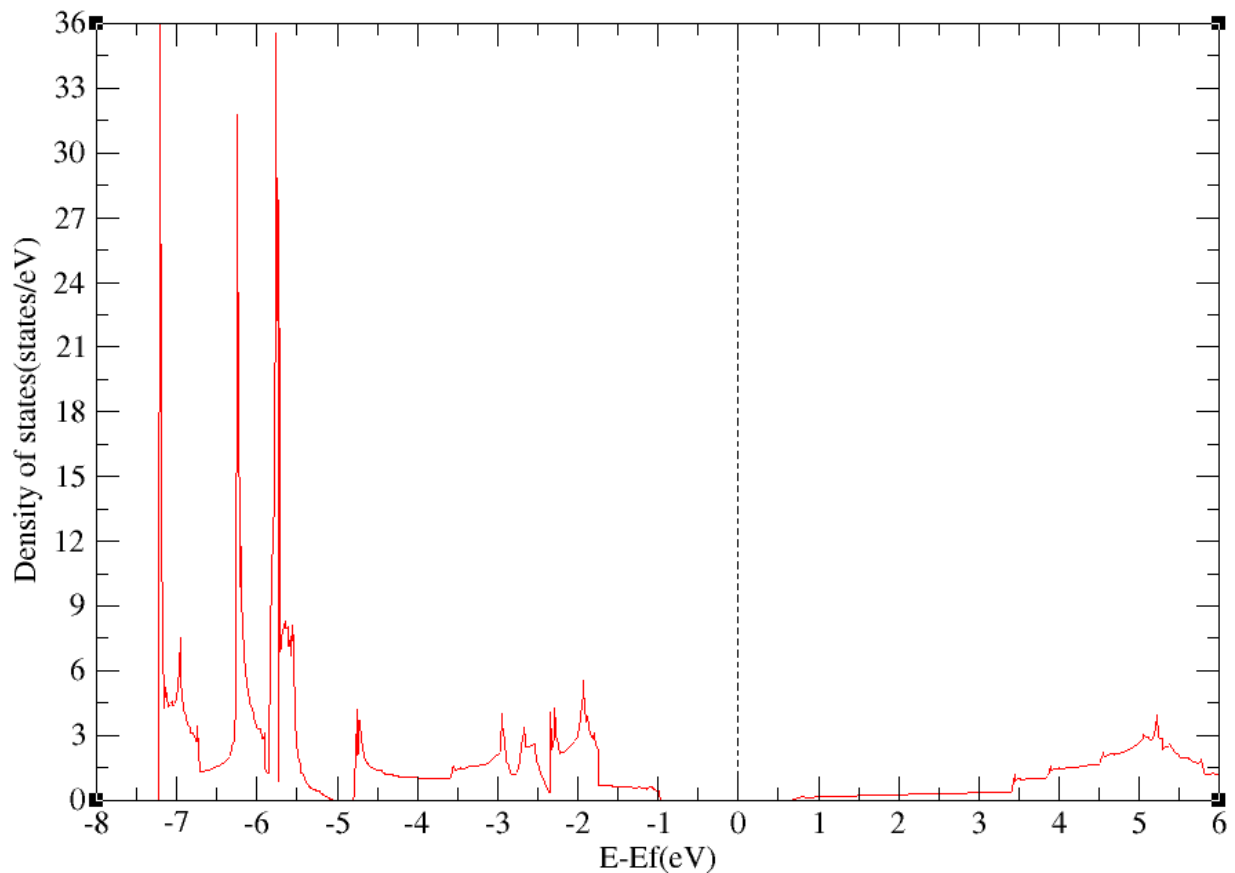


Figure 19 Density of states for ZnO monolayer. (Fermi level is indicated at 0 eV). PBE calculation employed.

The filled state is below Fermi level and empty state is above Fermi level. The vertical line around -7.5 eV marks the highest occupied level. The density of states becomes zero from -1 eV to 0.6 eV and highest density of states found at -7.5 eV. From curve higher density of states are also found at -6 eV and -6.4 eV.

4.4.2 Density of states for WSe₂ monolayer

The density of states for WSe₂ monolayer is plotted in figure 20.

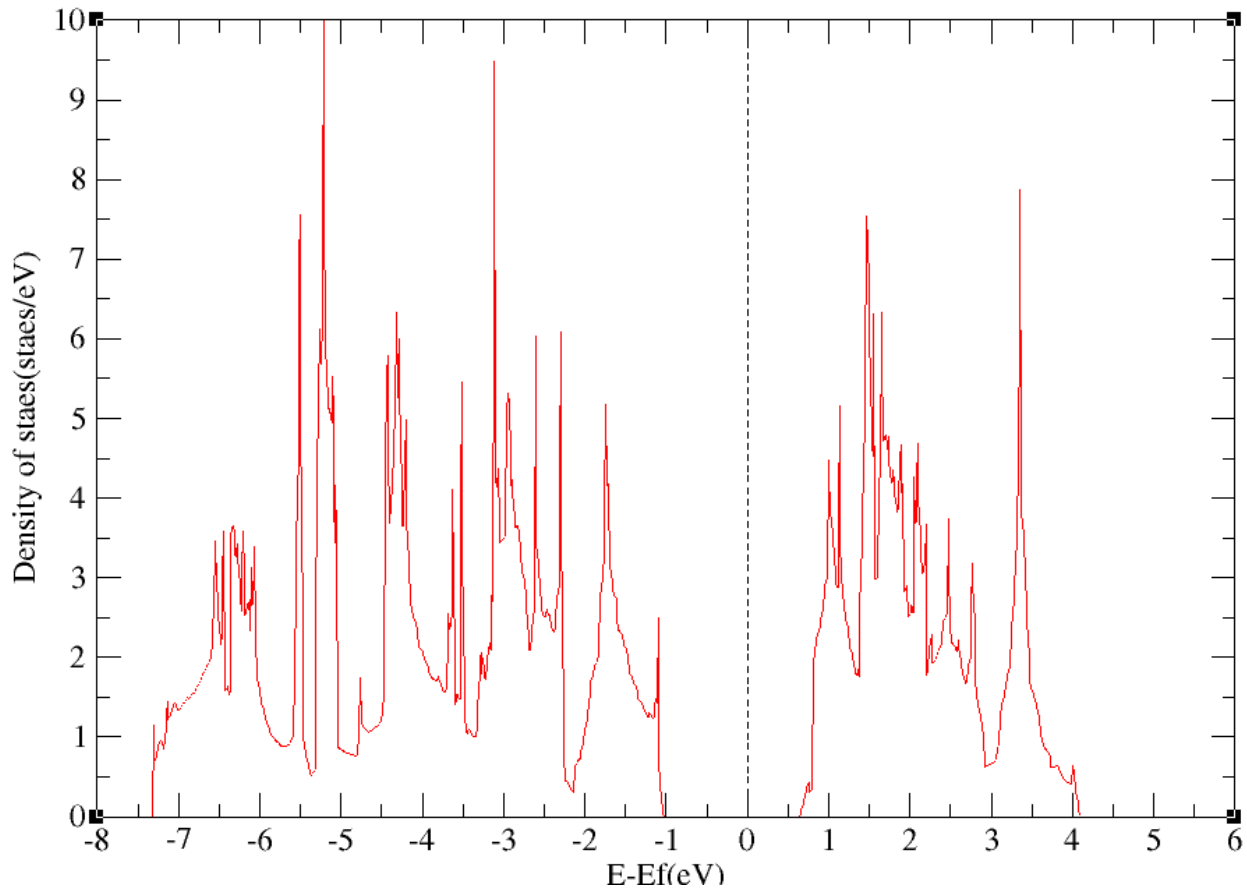


Figure 20. Density of states for WSe₂ monolayer. (Fermi level is indicated at 0 eV).PBE calculation employed.

The vertical line at -5.4 eV indicates highest occupied level. The density of states becomes zero from 1 eV to 0.6 eV. Highest density of state found at -5.4 eV. From curve higher density of states are also found at -3.3 eV, 1.5 eV and 3.5 eV.

4.5 Projected density of states

The projected density of states (PDOS) is the relative contribution of a particular atom/orbital to the total DOS.

4.5.1. Projected density of states of ZnO monolayer

The projected density of ZnO monolayer is plotted and shown in figure 21.

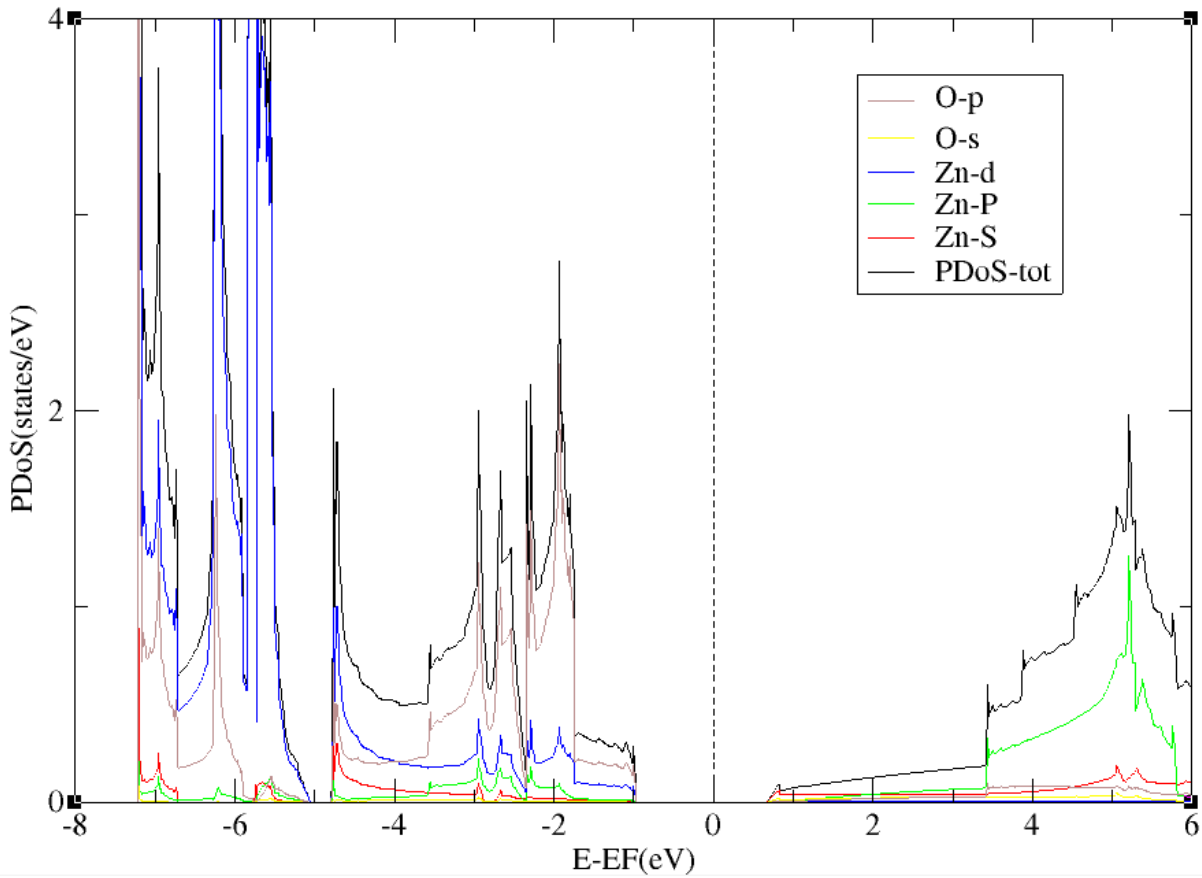


Figure 21. Projected density states for ZnO monolayer. (Fermi level is at 0eV).PBE calculation employed.

The total and PDOS of ZnO monolayer originate from O-p, O-s, Zn-p, Zn-d and Zn-s states and Zn-d and Zn-p are dominant states. The valence band, located from -8eV to 0eV, is mainly made up of Zn-d, O-p, Zn-p, and Zn-s and states Zn-d is dominant state. The conduction band, located from 0eV to 6eV is mainly made up of Zn-p, Zn-s, O-p and Zn-p is a dominant state.

4.5.2. Projected density of states of WSe monolayer

The projected density of states for WSe monolayer given in figure 22 below

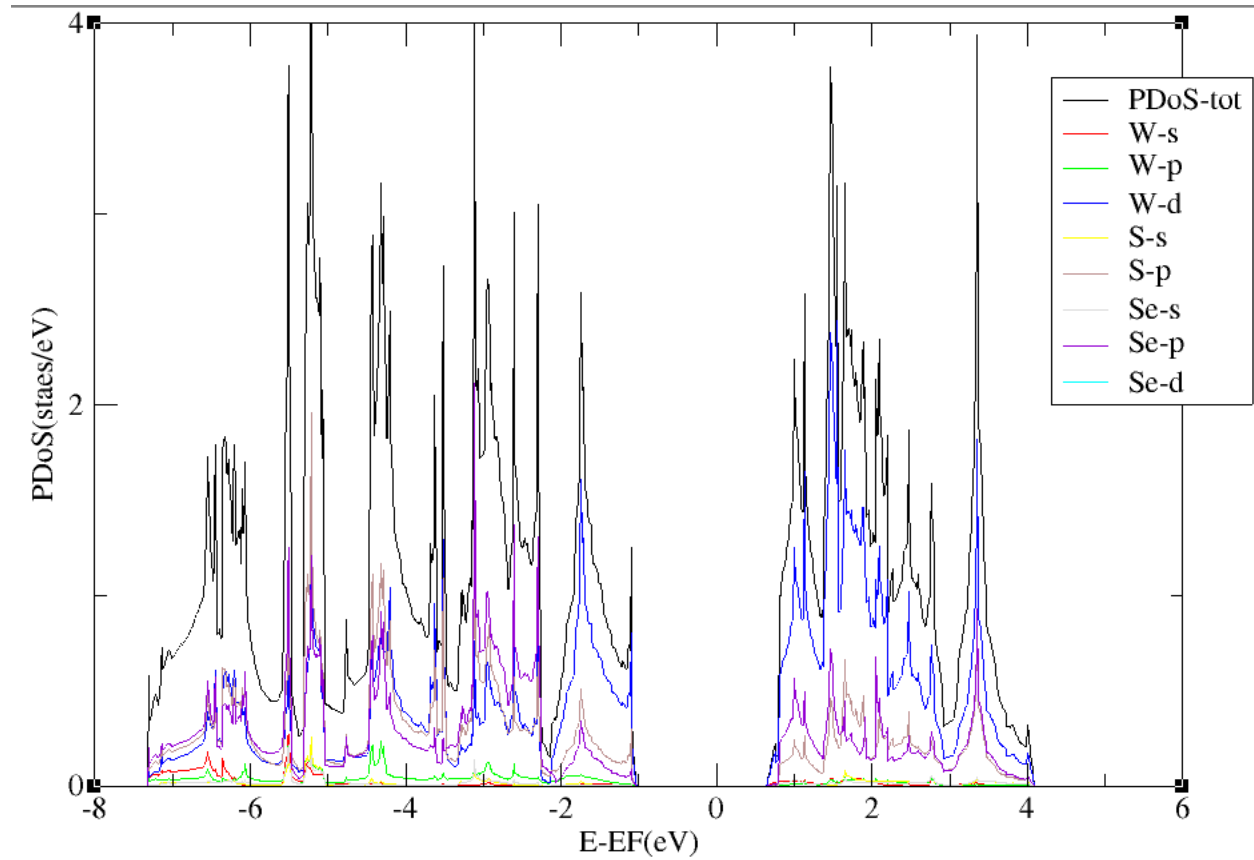


Figure 22. Projected density of states for WSe monolayer. (Fermi level is at 0eV).PBE calculation employed.

The total and PDOS of WSe monolayer originate from W-s, W-p, W-d, S-s, S-p, Se-s, Se-p, Se-d and Se-p and W-d are dominant states. The valence band is mainly from -8eV to 0eV and Se-p is dominant state. The conduction band is from 0eV to 6eV and W-d is dominant state.

4.6 Spin polarized density of states

Spin polarization is the degree to which the spin, i.e., the intrinsic angular momentum of elementary particles, is aligned with a given direction. To see the magnetic properties, the density of state for spin up and density of state for spin down is plotted for both ZnO monolayer and WSe monolayer.

4.6.1 Spin Polarized Density of state for ZnO monolayer

The spin polarized density of states for ZnO monolayer is plotted and shown in figure 23

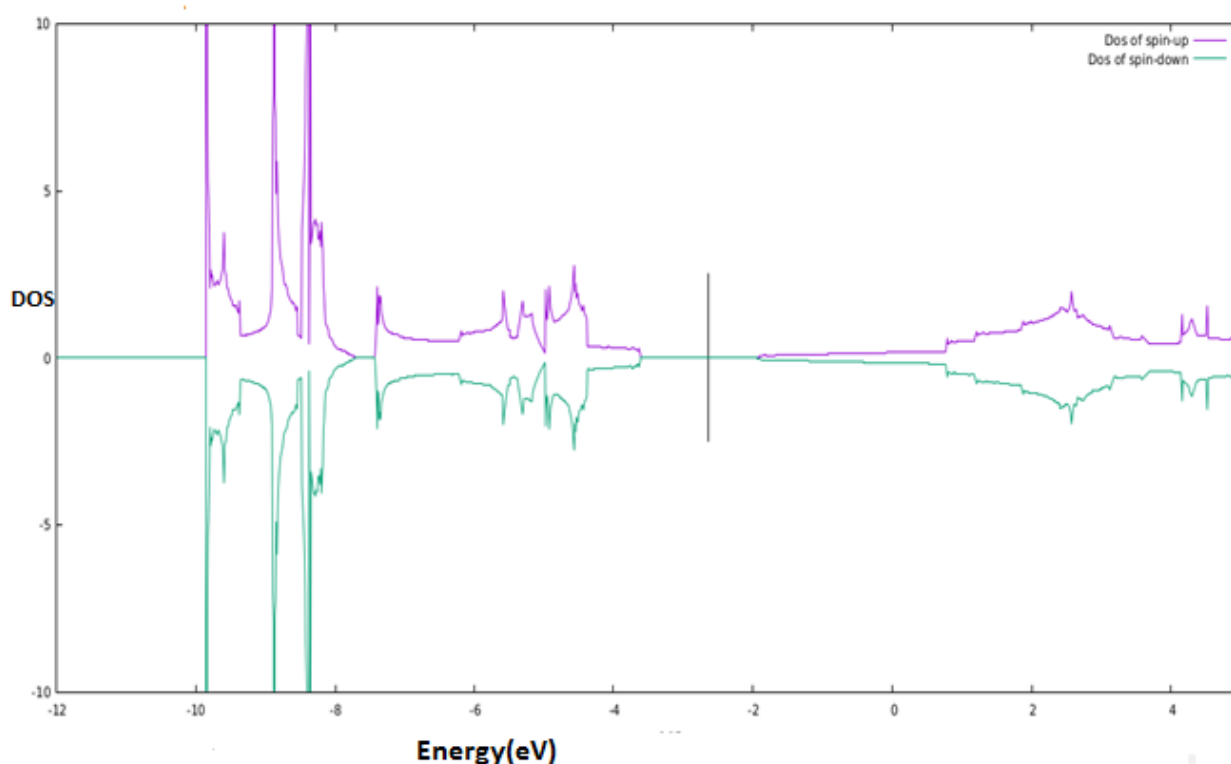


Figure 23 Spin polarized density of states for ZnO monolayer. PBE calculation employed.

The output scf calculation of spin polarized ZnO monolayer shows total magnetization=0.00 Bohr mag/cell which indicates it is Anti ferromagnetic. The other evidence is the spin up and spin down DOS is symmetrical. In Anti ferromagnetic, some spins go up and some down cancelling each other out. Thus magnetization should be zero.

4.6.2 Spin polarized density of state for WSe monolayer

The spin polarized density of states for WSe monolayer is plotted and shown in figure 24

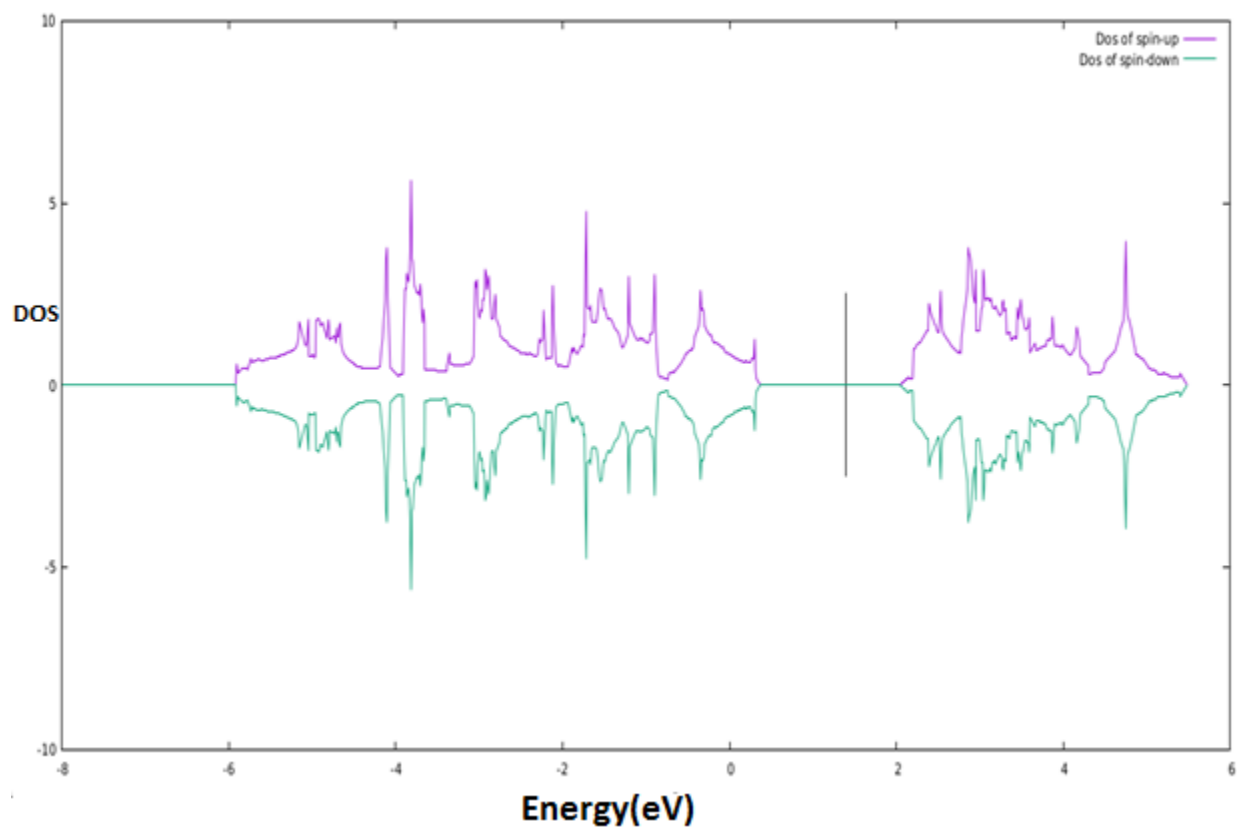


Figure 24 Spin polarized density of states for WSSe monolayer. PBE calculation employed. The output scf calculation of spin polarized WSSe monolayer shows total magnetization=0.00 Bohr mag/cell which indicates it is Anti ferromagnetic. The other evidence is the spin up and spin down DOS is symmetrical. In Anti ferromagnetic, some spins go up and some down cancelling each other out. Thus magnetization should be zero.

4.7 Binding energy and lattice mismatch calculations for heterostructures configurations

4.7.1 Lattice Mismatch

Table 2 Lattice mismatch for different heterostructures.

Configuration name	Lattice constant (for ZnO)	Lattice constant (for WSSe from hetero structure)	Lattice Mismatch
A	3.268	3.25530	0.388%
B	3.268	3.25693	0.338%
C	3.268	3.25747	0.322%
D	3.268	3.26051	0.229%

For monolayers A and B:

$$\text{Lattice mismatch} = \frac{Lat(A) - Lat(B)}{Lat(A)} \times 100\%$$

For heterostructures to be formed and stable, the lattice mismatch should be smaller. As seen from the table 2, all configurations have lattice mismatch of less than 0.5%, which is very small. Smaller lattice mismatch means the two materials can be stacked into heterostructure easily without requiring strain. This is important in experimental studies to synthesis the material without requiring large strain.

4.7.2 Binding Energy

To compare the relative stability of different configurations of the heterostructures, the interface binding energies (E_{binding}) were calculated using Binding energy= $E(\text{AB}) - E(\text{A}) - E(\text{B})$, where E denotes total energy obtained from “relax” Calculations and result is indicated in Table 3.

Table 3 Binding energy for different configurations

Configuration name	E(ZnO)	E(WSSe)	E(hetero structure)	E _{binding}
A	-285.0708Ry	-1227.9393Ry	-1514.0348Ry	-1.0247Ry
B	-285.0708Ry	-1227.9393Ry	-1514.0407Ry	-1.0306Ry
C	-285.0708Ry	-1227.9393Ry	-1514.0410Ry	-1.0309Ry
D	-285.0708Ry	-1227.9393Ry	-1514.0377Ry	-1.0276Ry

A negative value of binding energy suggests that a given heterostructure interface is stable. [30]

The lower absolute value of binding energy indicates stronger interactions between the ZnO and WSSe monolayers forming the heterostructures. The stacking with large binding energy is referred to be the most favorable one.

The four configurations A, B, C and D have negative binding energy and this shows that the heterostructures can formed and used for further calculations.

4.8 Electronic band structure for Heterostructures

There are four different configurations (A, B, C and D) that are considered and analyzed in this study. By Using VASP software, the plain band structure and projected band structures for all heterostructures are plotted and shown in figure 25 to 28.

4.8.1 Band structure for configuration A

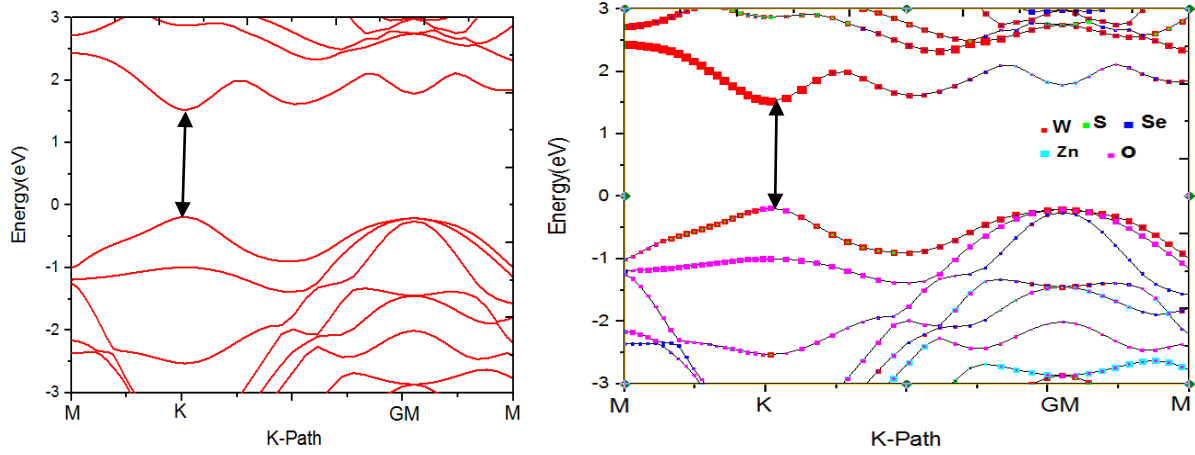


Figure 25 a) Plain band structure for configuration A b) projected band structure for configuration A

As seen from the figures 25 (a) and (b), CBM comes from contribution of W from WSe monolayer and VBM comes from contribution of O from ZnO monolayer, both at K point. The heterostructure is Type II band alignment since the CBM and VBM of the heterostructure are located in two different materials (the monolayers). The band gap of the heterostructures under configuration A is direct band gap with band gap of 1.7106 eV.

4.8.2 Band structure for Configuration B

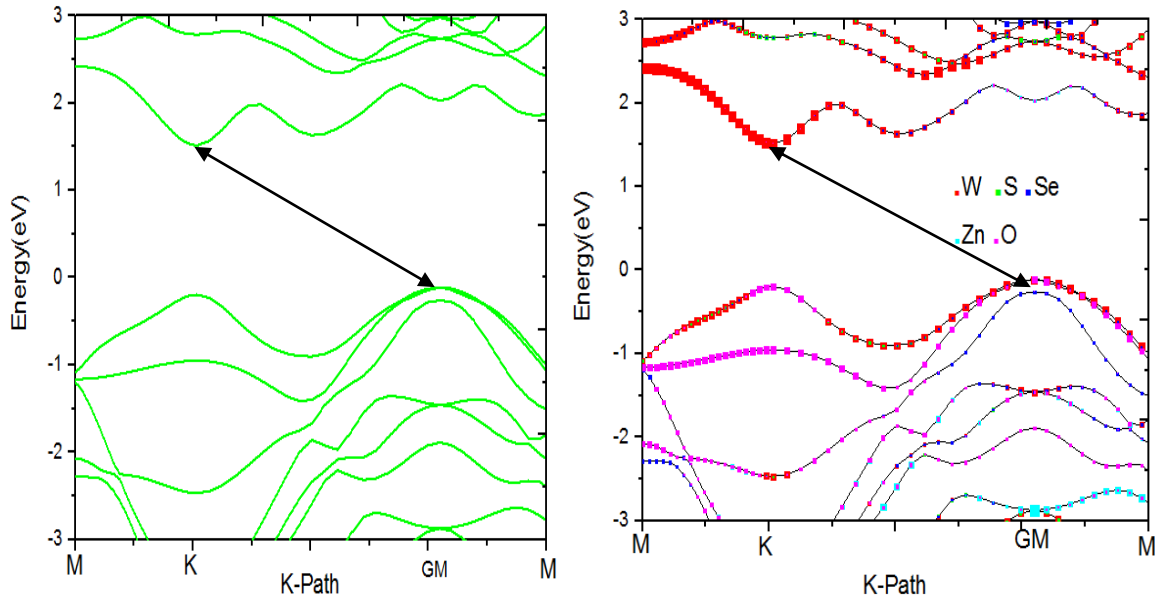


Figure 26 a) Plain band structure for configuration B b) projected band structure for configuration B

For Indirect gap semiconductor, the bottom of the conduction band and the top of valence band occur at different momentum. They tend to recombine in a way that gives off heat rather than light. Heterostructure configuration B is indirect band with Band Gap of 1.6248 eV. As seen from figure 26 (a) and (b), CBM comes from contribution of W from WSe monolayer at K point and VBM comes from contribution of O from ZnO monolayer around GM point. The heterostructure is Type II band alignment since the CBM and VBM of the heterostructure are located in two different materials (the monolayers).

4.8.3 Band structure for Configuration C

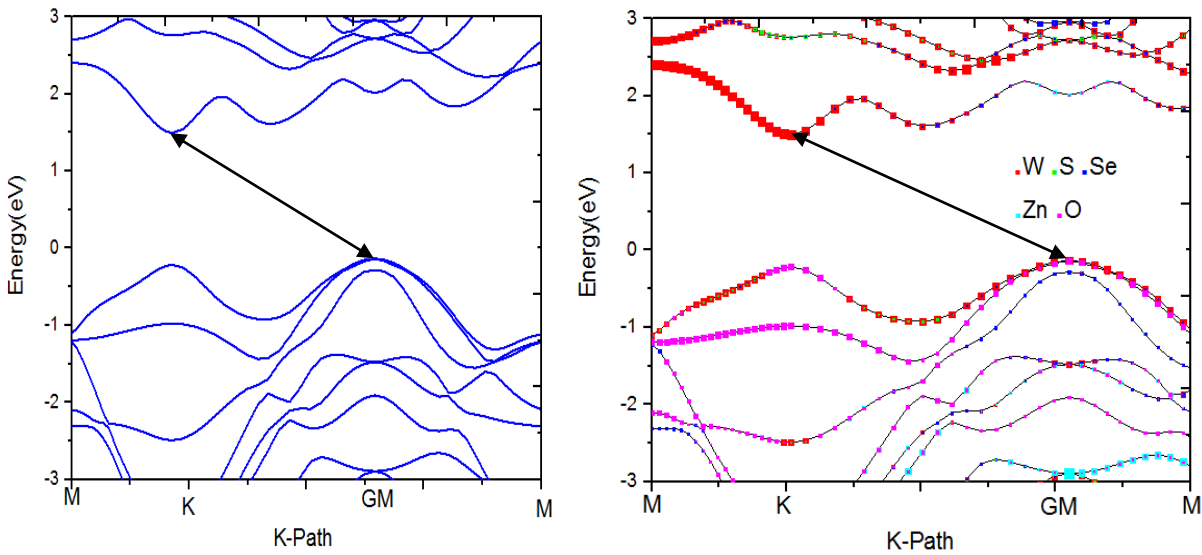


Figure 27 a) Plain band structure for configuration C b) Projected band structure for configuration C

Heterostructure under configuration C has indirect band with Band Gap of 1.6319 eV.

As seen from figure 27 (a) and (b), CBM comes from contribution of W from WSe monolayer at K point and VBM comes from contribution of O from ZnO monolayer around GM point. The heterostructure is Type II band alignment since the CBM and VBM of the heterostructure are located in two different materials (the monolayers).

4.8.4 Band structure for Configuration D

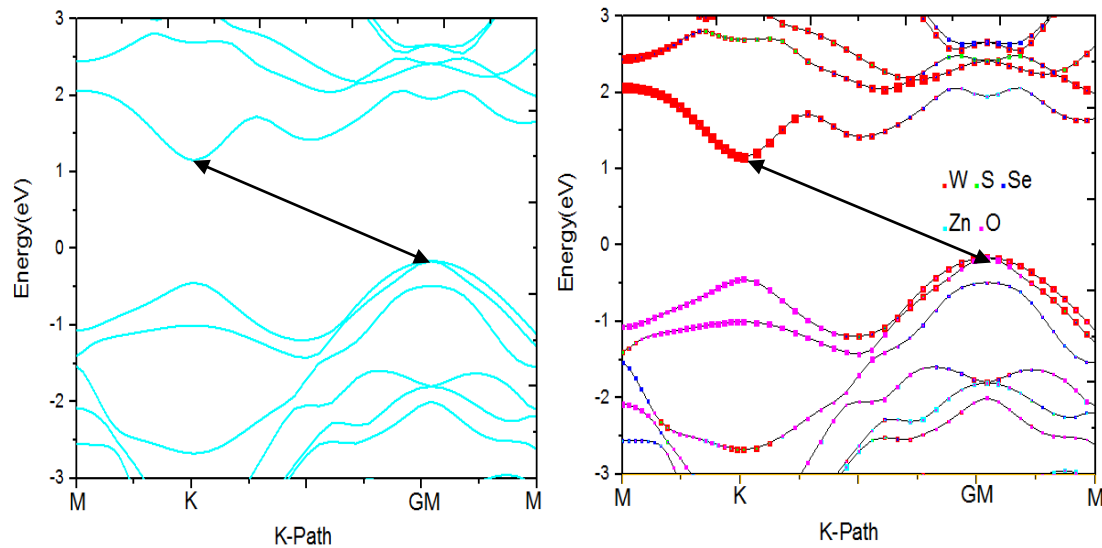


Figure 28 a) Plain band structure for configuration D b) projected band structure for configuration D

Heterostructure configuration D has indirect band with Band Gap of 1.3126eV.

As seen from figure 28, (a) and (b), CBM comes from contribution of W from WSe monolayer at K point and VBM comes from contribution of O from ZnO monolayer around GM point. The heterostructure is Type II band alignment since the CBM and VBM of the heterostructure are located in two different materials (the monolayers).

As discussed above under each plot, the four configurations (heterostructures) made from WS₂ monolayer and ZnO monolayer falls under type II band alignment.

In type-II materials, the CBM and VBM of the resultant structure are located in two different materials. The excitation of the wide-gap material is followed by the transfer of electrons, but not the holes. The opposite charge transfer occurs when the narrow-gap material is excited. The separation of the electrons and holes to different layers can increase their lifetime and is desirable for photovoltaics applications.

4.9 Planar Average Electrostatic potential of Heterostructures

The planar average electrostatic potential of the heterostructures is presented figures 29(a) upto figures 29(d).

The potential drops across ZnO/WS₂ heterostructures as indicated by different configurations A,B,C and D are found to be 6eV for all of them .This is the build-in electric field across the interface. The migration of photogenerated charges can be further improved by built-in electric field [37].

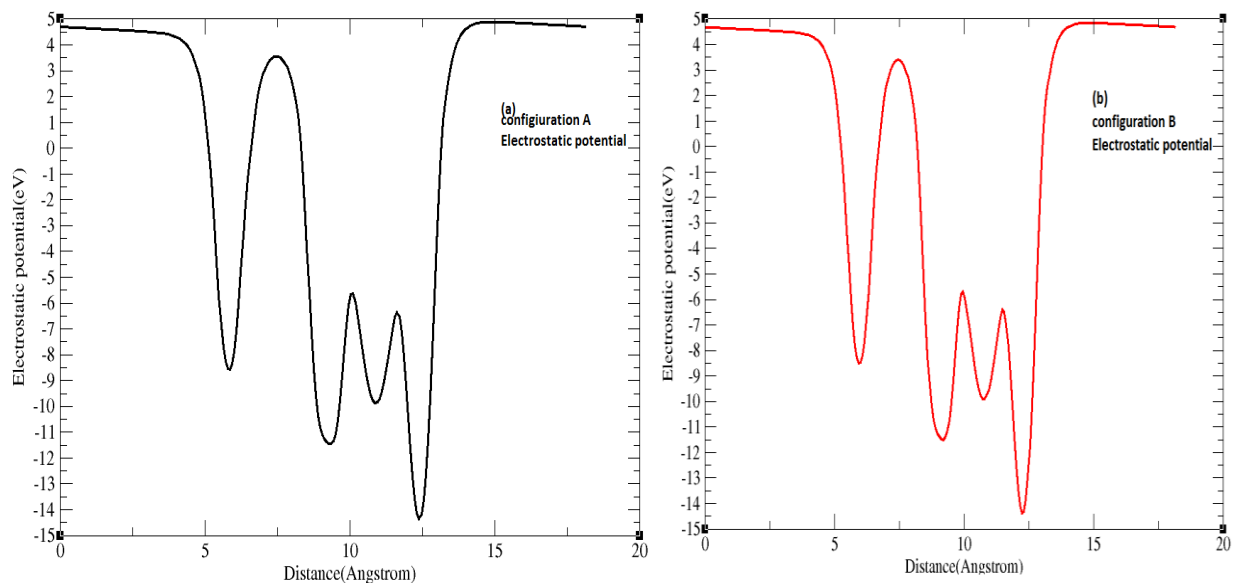


Figure 29(a) Average Electrostatic potential Configuration A b) Average Electrostatic potential Configuration B

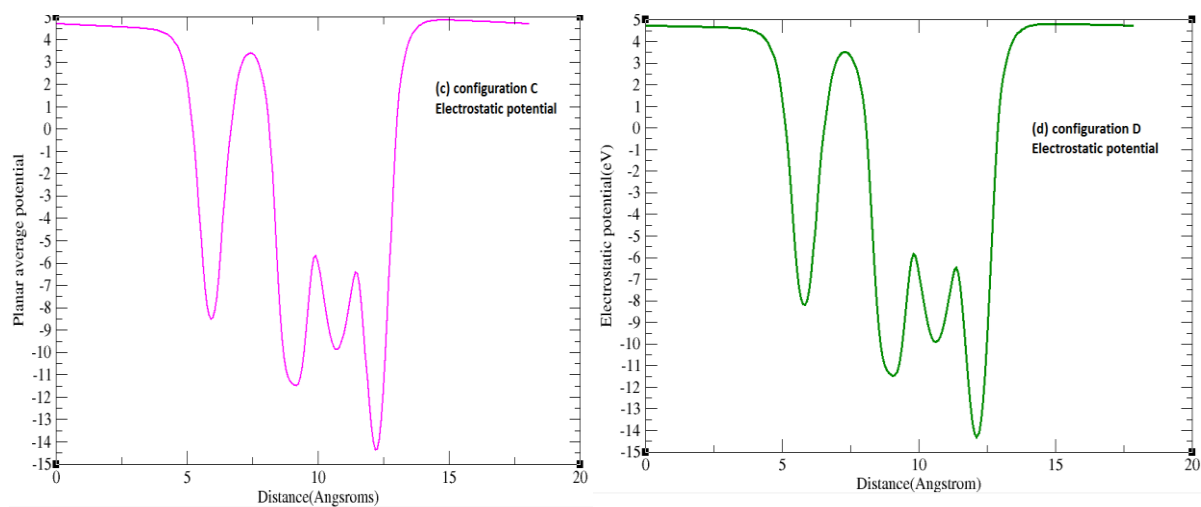


Figure 29 c) Average Electrostatic potential Configuration C d) Average Electrostatic potential Configuration D

4.10 Electronic properties for the heterostructures

As shown in table 4, work function (Φ), Ionization energy (I), electron affinity (χ) and vacuum level (E_{VAC}) of the heterostructures were obtained using VASP calculation. The work function is the minimum energy needed to remove an electron from a solid to a point in the vacuum immediately outside the solid surface. It represents the energy barrier to free space that prevents an electron at the Fermi level from escaping the solid [29].

Table 4 Different electronic properties of Heterostructures done by VASP

Configurations (Heterostructures)	VBM (eV)	CBM (eV)	EF(eV)	EG(eV)	χ (eV)	I(eV)	E_{VAC} (eV)	Φ (eV)= E_{VAC} -EF
A	-0.79	0.9205	-0.60476	1.7106	-3.963	-5.673	4.883	5.48776
B	-0.7666	0.8582	-0.65674	1.625	-3.986	-5.610	4.844	5.50074
C	-0.7429	0.8891	-0.60791	1.6319	-3.979	-5.611	4.868	5.47592
D	-0.6178	0.6948	-0.45875	1.3126	-4.119	-5.431	4.813	5.27175

The values of work function indicated in Table 4, are the calculated values taking the difference between vacuum level and Fermi level [12].

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In summary, we systematically examined the electronic structures of ZnO / WSSe vdW heterostructures and their respective monolayers using GGA-PBE with vdW corrections. We found binding energy of -1.024 Ry, -1.030 Ry, -1.0309 Ry and -1.0276 Ry for configurations A, B, C and D respectively. The negative binding energies indicate that the heterostructures and corresponding monolayers considered for Four ZnO / WSSe are stable. The other result we get was lattice mismatch of 0.388%, 0.338%, 0.322% and 0.229% for configurations A, B, C and D respectively. Since those lattice mismatches are very small value of almost less than 0.5%, therefore, the heterostructures can be formed and feasible.

The structures of the bands show that three heterostructures are indirect semiconductors and one is a direct gap in the bands. All four heterostructures are in accordance with type-II band alignment. Moreover, three configurations B, C and D exhibit indirect band gaps of 1.6248eV, 1.6319eV and 1.3126eV, respectively. But the other configuration A has direct band gap of 1.7106eV. The vdW heterostructures based on ZnO and Janus WSSe are seen as a promising candidate for Photovoltaic devices on the basis of interesting results obtained and Configuration A is preferred compared to other configurations since it is with direct band.

5.2 Recommendation

In this study modeling and simulation has been done by using density functional theory with the software package QUANTUM ESPRESSO and VASP. The electronic exchange – correlation energy is handled using Perdew–Burke–Ernzerhof (GGA-PBE) generalized-gradient approximation. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) with the approach of Grimme (DFT-D2) is adopted to correct the weak Van der Waals like interaction between layers of heterostructures. From those electronic calculations outstanding results are obtained. But due to shortage of time, optical properties and checking efficiency and performance of solar cells are not performed. So we recommend continuing with those parameters to fully tell the efficiency of solar cells theoretically.

In addition it is also good to do theoretical modeling and electronic calculations by using Heyd Scuseria-Ernzerhof (HSE06) hybrid functional approximation to get more improved results on electronic properties.

These days computational material engineering has grown very well, so it is better to bring experimental works and computational modeling aspects together to see and examine application of Janus transition metal dichalcogenides for solar cells and improve their overall efficiency and performance.

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