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**STRUCTURE AND ELECTRONIC PROPERTIES OF
2D TRANSITION METAL DICHALCOGENIDES:
FIRST PRINCIPLES STUDY**

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Summary

Transition metal dichalcogenides monolayers are promising materials for many applications in electronics and optoelectronics. Exploration of their properties is performed both theoretically and experimentally. Although theoretically predicted structural properties are quite often in a good agreement with experimental results, the same is not always true for electronic properties. In TMD monolayers the excitons have large binding energies (~ 0.5 eV), thus the fundamental band gap differs significantly from the optical band gap. Widely used approximations in DFT (LDA, PBE, HSE) tend to yield optical band gaps deviating significantly from experimentally measured with PL. GW calculation of the fundamental band gap, could differ sometimes for more than 30 % from experimental one. Another important drawback of the available methods for the band gap calculation is the lack of correlation in the accuracy for 3D materials and for 2D structures. Thus an accurate theoretical exploration of electronic properties (and especially of the band gap) of emerging materials is a very challenging task.

The thesis focused (1) on implementing the general method for accurate band gap calculations (GVJ-2e), and on theoretical exploration of structural and electronic properties of (2) transition metal dichalcogenides (MoS_2 , MoSe_2 , WS_2 , WSe_2) in their bulk and monolayer forms and (3) $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy.

In the *first part* of the thesis the proposed *GVJ-2e method* for the band gap calculation is introduced within DFT framework. The GVJ-2e method is based solely on the total energy calculations and is adjustable parameters free. It was demonstrated that a non-local part of the exchange-correlation energy plays

a significant role in the accurate band gap calculation. The application of the method on traditional bulk semiconductors (ex. Si, Ge, C, etc.) and wide gap insulators (ex. Xe, Kr) demonstrated a good agreement of the theoretical band gap with experimental one. For GJVJ-2e method mean absolute error (MAE) is 0.08 eV which is the smallest among mean absolute errors given by other methods: 0.51 eV (GW), 0.14 eV (HSE), 0.52 eV (MBJLDA), and 2.26 eV (LDA) for considered materials.

In the *second part* of the thesis, structural and electronic properties of bulk and monolayer MoS₂, MoSe₂, WS₂, WSe₂ have been studied. The calculated relaxed lattice constants of bulk TMDs are in good agreement with experimental ones (deviate for less than 2 %). From the analysis of Kohn-Sham band structures has been shown that monolayer TMDs are direct gap semiconductors, while bulk TMDs are indirect gap semiconductors. The fundamental and optical band gaps of bulk and monolayer TMDs were calculated with GJVJ-2e method and both are in good agreement with experimental ones. Optical band gaps were calculated from GJVJ-2e fundamental band gaps with account of exciton binding energies. The mean absolute error (MAE) of GJVJ-2e method for the fundamental band gaps of bulk and monolayer TMDs is 0.06 eV, which is smaller than MAE of GW (0.23 eV) and G₀W₀ (0.09 eV). The accuracy of the calculated optical band gaps is higher than the results of hybrid functionals (MAE of 0.04 eV (GVJ-2e) and 0.11 eV (sX), 0.14 eV (TB-mBJ) and 0.17 eV (HSE)). Thus proposed GJVJ-2e method could be used for the band gap calculation not only of 3D materials but also 2D structures.

In the *third part* of the thesis, we analyzed in detail the formation, structural and electronic properties of monolayer $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy (the substitution rate x in the range from 0 to 1). First, we have analysed the free energy and energy of formation of the alloy, which revealed the presence of the region with positive energy of formation for substitution rates $x > 0.65$. Also we have shown that during nucleation of the alloy with higher probability will be obtained the structural configurations with equal occupation by substituting atoms of Se of top and bottom chalcogen planes. The study of the structural properties, including lattice constants, has revealed nonlinear dependency of the lattice constant on the substitution rate x . The study of the electronic properties demonstrated that the fundamental band gaps of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ calculated with GJV-2e method are in range of the fundamental band gaps of MoS_2 and MoSe_2 . The dependency of fundamental, optical and Kohn-Sham band gap is demonstrated to be nonlinear as well. The study shows that the electron and hole effective masses are smaller than a free electron mass and, similarly to MoS_2 and MoSe_2 monolayers, in the alloy electrons are lighter than holes. We have demonstrated that the physics of formation and properties of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy can be described with percolation theory and have determined the percolation thresholds (x_c) for the case of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ formation .

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Abbreviations

2D	Two dimensional
BSE	Bethe-Salpeter equation
B3LYP	Becke, 3 parameter, Lee-Yang-Parr functional
CBM	Conduction band minimum
CMOS	Complementary metal-oxide semiconductor
CVD	Chemical vapor deposition
DFT	Density functional theory
DOS	Density of states
FLAPW	Full-potential linearized augmented planewave method
GGA	Generalized gradient approximation
GGA+U	Generalized gradient approximation +U (Hubbard)
GW	GW approximation
HSE	Heyd–Scuseria–Ernzerhof functional
HOMO	Highest occupied molecular orbital
KS	Kohn-Sham
LCAO	Linear combination of atomic orbitals
LDA	Local density approximation
LSDA	Local spin density approximation
LT	Low temperature
MAE	Mean absolute error
MBJLDA	Modified Becke-Johnson and LDA potential
MAPD	Mean absolute percentage deviation

MX ₂	M: Mo, W; X: S, Se
PAW	Projector augmented wave
PBE	Perdew-Burke-Ernzerhof functional
pDOS	Projected density of states
PL	Photoluminescence
PVD	Physical vapor deposition
QP	Quasi particle
RT	Room temperature
STS	Scanning tunneling spectroscopy
sX	Screened exchange hybrid functional
TMD	Transition metal dichalcogenides
TB-mBJ	Tran-Blaha modified Becke-Johnson exchange potential approximation
USSP	Ultrasoft pseudopotential
VBM	Valence band maximum
XPS	X-ray photoelectron spectroscopy

Chapter 1. Introduction, Background and Motivation

1.1 Background: emerging devices and materials

Information processing technology is driving the semiconductor industry into a broadening range of new applications according to latest 2013 ITRS report [1], and device cost and performance will still be influenced by the dimensional and functional scaling of CMOS. Currently a lot of efforts have been put into research of III-V materials, for example Ge and others, in order to constantly improve the performance of devices. Apart from the development of novel materials, completely new devices have been reported recently. These new devices such as novel transistors operate on new principles like tunnelling (Tunnelling Field Effect Transistor) or spin manipulation which enables the device to operate at a very low power [2].

On the other hand, closer to year 2028 (which is the end of the 2013 ITRS period) two dimensional scaling might reach its fundamental limits. Thus the use of the third dimension (vertical stacking along the Z-axis) is being explored by logic and memory devices [1].

In order to develop new emerging devices, new materials are needed with properties that could potentially meet the needs for improved density, energy efficiency, and reliability. For device, examples of materials that could be considered are: p-III-V, n-Ge, carbon nanotubes, nanowires, graphene and other 2D materials, spin materials, and complex metal oxides according to ITRS reports [1].

The discovery of graphene in 2004 by K. Novoselov and A. Geim opened the era of 2D materials [3]. Graphene represents single layer of carbon atoms organized in honeycomb lattice [4]. Graphene possesses unique electronic properties [5]. Band structure of graphene reveals intersection of valence and conduction bands thus making band gap equal to zero. This special point is called the Dirac point and here effective mass of charge carriers equals to zero. This in its turn leads to huge electron mobilities reaching $200000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Charge transport in graphene could be described as ballistic even at room temperature. Nevertheless achieving band gap in graphene is mentioned among one of the challenges in recent ITRS reports.

Bulk forms of TMD materials were first investigated several decades back, the discovery of graphene renewed interest for two dimensional materials. Transition metal dichalcogenides (MoS_2 , MoSe_2 , WS_2 , etc.) were added into ITRS reports as potential alternate channel materials due to their 2D planar structure, sizable band gap and potential for high mobility [1]. The present research is focused on transition metal dichalcogenides (TMDs) including MoS_2 , MoSe_2 , WS_2 , WSe_2 (bulk and monolayer) and their structural and electronic properties. As well $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy based on TMDs is considered.

1.2 Motivation of the thesis

1.2.1 Theory: current band gap evaluation issues

Density functional theory (DFT) is the most extensively used method in theoretical computations of structural properties and ground state electronic properties of solid state. However, DFT band gap problem is known for a long time [6]. The Kohn-Sham band gap could vary significantly for different materials and the correlation between Kohn-Sham band gap and an experimental band gap is unclear. Kohn-Sham band gap could differ from an experimental band gap in some cases for 100% [7], [8]. Over the years there have been developed different approaches to overcome the above-mentioned issue. Methods with additional parameters have been introduced by Chan and Ceder [9]. Apart from the local density approximation (LDA) and the generalized gradient approximation (GGA) has been developed hybrid functionals (B3LYP, HSE, etc.) [10]. For TMDs the hybrid functionals tend to overestimate the band gap by more than 0.3 eV [16], [19]. In order to consider excited states, time dependent density functional theory has been developed [12]. Unfortunately, the results obtained by different methods have large variations of errors [11], [13]. More precise band gap values could be obtained from quasiparticles calculations energies using the many-body perturbation theory, e.g., within the *ab initio* GW [14], [15]. Nevertheless, for TMD monolayers GW tends to overestimate band gaps, while for some semiconductors quite accurate results could be obtained. As consequence, theoretical search for new materials with applications in electronics is significantly complicated.

1.2.2 Materials: band gaps of transition metal dichalcogenides

Bulk TMDs are layered structures with strong in-plane bonding and weak interactions between stacked planes. Such structure enables exfoliation of few layered structures from crystals. Significant interest for two dimensional TMDs has been stimulated by possible applications in nanoelectronics and optoelectronics. Pure TMDs include MoS₂, MoSe₂, WS₂, WSe₂. In both bulk and monolayer they have sizable band gaps which change from indirect (for bulk) to direct (for single layer) and thus enabling applications such as transistors, photodetectors and electroluminescent devices [30]-[34].

Table 1.1. Theoretical and experimental band gap values obtained for bulk TMD.

TMD	Theory <i>W. Li et al.^{a)}</i>				Experiment
	<i>TB-mBJ</i> (<i>Wien2k</i>)	<i>PBE</i>	<i>B3LYP</i>	<i>HSE06</i>	
MoS ₂	1.14	0.92	2.15	1.46	1.23 ^{b)}
MoSe ₂	1.03	0.94	-	1.36	1.09 ^{b), c)}
WS ₂	1.32	1.07	2.11	1.60	1.35 ^{b)}
WSe ₂	1.26	1.01	-	1.44	1.20 ^{b), c)}

^{a)} Ref. [16]; ^{b)} Ref. [17]; ^{c)} Ref. [22].

Although there are papers available with calculated electronic properties, these properties have significant variability in results. In TMD monolayers the excitons have large binding energies (~ 0.5 eV), thus fundamental band gap differs significantly from an optical band gap. For bulk materials, theoretical errors for band gap are ranging from 2% (TB-mBJ for WS₂) and for some

materials reaching up to 75% (B3LYP for MoS₂). Similar trends could be seen in the results obtained for TMD monolayers. For TMD monolayers, errors can range from 1% (PBE for WS₂) to 63% (GW for WS₂). Summary of results is represented in **Table 1.1** and **Table 1.2** for theoretical and experimental works performed till date. However, it is a common case for DFT to have such variation in results for band gap evaluations.

Table 1.2. Theoretical and experimental band gap values obtained for monolayer TMDs.

TMD 1L	Theory						Exp.
	<i>Y. Ding et al.^{a)}</i>				<i>F. A. Rasmussen et al.^{b)}</i>		
	<i>LDA</i>	<i>PBE</i>	<i>HSE</i>	<i>GW</i>	<i>LDA</i>	<i>G₀W₀</i>	
MoS ₂	1.86	1.67	2.25	2.66	1.58	2.48	1.74 ^{c)}
MoSe ₂	1.63	1.44	1.99	2.31	1.32	2.18	1.57 ^{d)} 1.48 ^{e)}
WS ₂	1.94	1.81	2.32	2.91	1.51	2.43	1.79 ^{c)} 1.97 ^{f)}
WSe ₂	1.74	1.55	2.10	2.51	1.22	2.08	1.65 ^{d)} 1.66 ^{f)}

^{a)} Ref. [19]; ^{b)} Ref. [20]; ^{c)} Ref. [21]; ^{d)} Ref. [22]; ^{e)} Ref. [23]; ^{f)} Ref. [27].

1.3 Objectives of thesis

Objectives of the thesis are split into two parts. The first part involves the advancements in theoretical approach for the band gap computation. The second part of objectives deals with novel 2D materials and their process of formation, structural and electronic properties predictions. The dissertation pursues following objectives:

1. Develop and implement the approach for an accurate band gap calculation within DFT framework (GVJ-2e method) for 2D materials (TMDs and their alloy).
2. Investigate the structural properties of bulk and monolayer TMDs (MoS_2 , MoSe_2 , WS_2 , WSe_2). Study electronic properties of bulk and monolayer MoS_2 , MoSe_2 , WS_2 , WSe_2 including fundamental band gaps and optical band gaps.
3. Investigate the process of monolayer $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy formation and its structural properties. Investigate the electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy including the fundamental and optical band gaps. Analyse Kohn-Sham band structures and estimate the electron and hole effective masses.

1.4 Thesis structure

The thesis comprises of seven chapters.

Chapter 1 states the thesis motivation, objectives and major outcomes.

Chapter 2 provides the literature review for TMD bulks and monolayers (MoS_2 , MoSe_2 , WS_2 , WSe_2), their heterostructures and alloys.

Chapter 3 provides the theoretical background including density functional theory (DFT), introduces standard approaches for band gap calculation. It also specifies which tools have been used.

Chapter 4 provides the overview of a proposed GJV-2e method for band gap calculation and its applications for bulk solids.

Chapter 5 contains the results of calculations of structural and electronic properties of bulk and monolayer MoS_2 , MoSe_2 , WS_2 , WSe_2 .

Chapter 6 describes the theoretical study of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy. The chapter presents the analysis of energy of formation, structural and electronic properties of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy for substitution rate x in range from 0 to 1.

Chapter 7 provides the conclusions and prospects for future work.

1.5 Thesis major outcomes

Major outcomes of the thesis are the following:

1. **Band gap calculation.** A new method for accurate band gap calculation is proposed (GVJ-2e method). GVJ-2e method is based on the total energy calculation and is adjustable parameters free. Thus GVJ-2e method doesn't have any inner limitations on the type and dimensionality of materials it could be applied to. It was demonstrated that a non-local part of the exchange-correlation energy plays a significant role in an accurate band gap calculation. The application of the method to traditional bulk semiconductors (ex. Si, Ge, C, etc.) and wide gap insulators (ex. Xe, Kr) demonstrated good agreement of the theoretical band gap with experimental one. The errors of GVJ-2e method in band gap calculations are smaller than errors of other widely used methods (GW, hybrid functional HSE, TB-mBJ functional).
2. **Bulk and monolayer MoS₂, MoSe₂, WS₂, WSe₂.** Structural and electronic properties of bulk and monolayer MoS₂, MoSe₂, WS₂ and WSe₂ have been studied. The calculated relaxed lattice constants of bulk TMDs are in good agreement with experimentally measured ones (deviate for less than 2 %). From the analysis of Kohn-Sham band structures has been shown that monolayer TMDs are direct gap semiconductors, while bulk TMDs are indirect gap semiconductors. The fundamental and optical band gaps of bulk and monolayer TMDs were calculated with GVJ-2e method and both are in good agreement with experimental results. Optical band gaps were calculated from GVJ-2e fundamental band gaps with

account of exciton binding energies. Thus we have obtained not only accurate band gaps for bulk TMDs (3D materials), but accurately determined the fundamental and optical band gaps of monolayer TMDs (2D materials). The mean absolute error (MAE) of GJVJ-2e method for fundamental band gaps of bulk and monolayer TMDs is 0.06 eV, which is smaller than MAE of GW (0.23 eV) and G_0W_0 (0.09 eV). The accuracy of optical band gaps calculated with GJVJ-2e method is higher than that of results obtained with hybrid functionals (compare MAE of 0.04 eV (GVJ-2e) and 0.11 eV (sX), 0.14 eV (TB-mBJ) and 0.17 eV (HSE)). Thus we confirm that the recently proposed GJVJ-2e method could be used for the band gap calculation not only of 3D materials but also 2D structures.

3. **MoS_{2(1-x)}Se_{2x} monolayer alloy.** We have performed analysis of the formation, structural and electronic properties of monolayer MoS_{2(1-x)}Se_{2x} alloy (the substitution rate x in the range from 0 to 1). First, we have analysed the free energy and energy of formation of the alloy, which revealed presence of the region with positive energy of formation for substitution rates $x > 0.65$. Also we show that during nucleation of the alloy with higher probability will be obtained the structural configurations with equal occupation by substituting atoms of Se of top and bottom chalcogen planes. The study of the structural properties including lattice constants, revealed nonlinear dependency of the lattice constant on the substitution rate x . The study of the electronic properties demonstrated that the fundamental band gap calculated with GJVJ-2e method of the MoS_{2(1-x)}Se_{2x} are in range of the fundamental bad gaps of MoS₂ and

MoSe₂. The dependency of fundamental, optical and Kohn-Sham band gaps are demonstrated to be nonlinear as well. The study of the electron and hole effective masses shows that both are smaller than a free electron mass and that in the alloy electrons are lighter than holes (similarly to MoS₂ and MoSe₂ monolayers) almost for entire range of substitution rates. We have analysed the physics of the formation and properties of the MoS_{2(1-x)}Se_{2x} with the percolation theory, which revealed presence of substitution rates x corresponding to the percolation thresholds.

Chapter 2. Literature Review

The current chapter reviews available theoretical and experimental results for structural and electronic properties of pure TMDs, vertical and in-plane heterostructures based on them, and TMD alloys.

2.1 Overview of 2D materials

2D materials represent an emerging class of materials which have thickness of one or few atomic layers [25], [26]. 2D materials could be distinguished into different classes, which include graphene family (graphene, hBN, fluorographene, BCN graphene oxide), 2D chalcogenides and 2D oxides [28]. They could have different electronic properties and could be found semiconducting (MoS_2 , WS_2 , etc.), metallic (TaS_2 , NbS_2 , etc.) and insulating (BN) materials and thus their band gaps could range from 0 up to 6 eV [29]. Transition metal dichalcogenides have attracted much attention owing to their rich physics and promising applications in electronic and optoelectronic devices [30]-[34]. Significant amount of effort has been invested into their synthesis exploration, characterization, fabrication of devices and theoretical exploration [35], [36]. The efficiency of various devices such as field effect transistors, hot electron transistors, photodiodes, phototransistors, and solar cells depends on the band gap [37]-[44]. Not only pure 2D materials have promising applications, but so are their heterostructures and alloys [45]-[50]. Recently Li et al. [50] reported the experimental observation of quasi-heterojunction bipolar transistors which

uses a monolayer of the lateral WSe₂–MoS₂ junctions (in-plane heterostructure) as the conducting p–n channel.

Transition metal dichalcogenides (TMDs) are layered materials with strong in-plane bonding and weak out-of-plane interactions (van der Waals forces). Chemical formula of TMDs is MX₂, where M stands for transitional metal and X is chalcogen atom [18]. Transitional metals include elements from groups IV-VI (Ti, Zr, Hf, V, Nb, Ta, Mo, W, etc.); chalcogen atoms are S, Se, Te. TMDs usually have layered structure with plane of metal atoms between two planes of chalcogen atoms (X-M-X). The structure X-M-X represents monolayer of TMD. The strong bonding holds metal and chalcogen planes together. As TMDs have very weak bonding between planes, it is possible to stack planes of different materials together. Thus vertical heterostructures could be created with different number of constituting monolayers.

Among all these materials we will focus on semiconducting TMDs which include MoS₂, WS₂, MoSe₂, WSe₂ (bulk and monolayer) and MoS_{2(1-x)}Se_{2x} monolayer alloy.

2.2 Pure Transition Metal Dichalcogenides (TMD)

2.2.1 Structural properties

Bulk MoS₂, WS₂, MoSe₂, WSe₂, MoTe₂ all exhibit hexagonal symmetry and correspond to space group P6₃/mmc. WTe₂ unlike others has orthorhombic symmetry and belongs to Pnm2₁ space group. Nevertheless in some papers electronic properties for WTe₂ with hexagonal symmetry are computed as well [19]. It should be mentioned that significant effort is put into theoretical study of

monolayers of TMD, while very few results are available for bulk form. Primitive cell of pure TMD from $P6_3/mmc$ space group contains two metal atoms and four chalcogen atoms.

MoS_2 shares common TMDs structure when metal layer is surrounded by two layers of sulphur. MoS_2 exists in three polytypes 1T (octahedral coordination of Mo atom), 2H (trigonal prismatic) and 3R (trigonal prismatic). 1T polytype is metastable and changes at 300°C , while 2H and 3R are thermodynamically stable polytypes. 2H and 3R polytypes share trigonal prismatic coordination of Mo atom, but differ in stacking order of monolayers in bulk structure. Present research is focused on 2H polytype which is the most abundant in Earth's crust [51]. Triangular prismatic coordination corresponds to Mo atoms with six bonds with sulphur atoms.

In unit cell of bulk MoS_2 Molybdenum atom is coordinated to six Sulphur atoms in a triangular prismatic way. MoS_2 is described by hexagonal symmetry with internal displacement $z=0.12$ [52].

Figure 2.1. (a) Bulk 2H- MoS_2 side view and top view of single MoS_2 monolayer (3×3 unit cells) [52]. (b) Top and side view of single-layer TMD with trigonal prismatic and octahedral (c) coordinations [53].

Figure 2.1 displays bulk and monolayer structures common for TMDs. WTe₂ in bulk is reported to have orthorhombic symmetry and Pnm2₁ space group [55]. **Figure 2.2** shows crystal structure of WTe₂ with orthorhombic symmetry. In **Table 2.1** summary of theoretical and experimental data for bulk TMD is represented.

Figure 2.2. Crystal structure of bulk WTe₂ (a) side view; (b) top view; (c) first Brillouin zone [58].

For TMD monolayer *c* constant determines the interlayer distance, so monolayer will be characterized by in-plane lattice constant *a* and theoretical results are displayed in **Table 2.2**. For WTe₂ results are calculated for hexagonal symmetry similarly to all the rest TMD.

Table 2.1. Experimental and theoretical lattice constants of bulk TMDs. Lattice constants are provided in Å.

TMD bulk	Symmetry	Theory	Experiment
MoS ₂	hexagonal	a = 3.173 c = 12.696 [PBE] ^{a)} a = 3.122 c = 11.986 ^{b)}	a = 3.160 c = 12.295 ^{a)}
MoSe ₂	hexagonal	a = 3.309 c = 13.323 [PBE] ^{c)}	a = 3.288 c = 12.900 ^{e)}
MoTe ₂	hexagonal	-	a = 3.530 c = 13.882 ^{g)}
WS ₂	hexagonal	a = 3.164 c = 12.473 [PBE] ^{a)}	a = 3.154 c = 12.362 ^{a)}
WSe ₂	hexagonal	a = 3.319 c = 13.729 [PBE] ^{c)}	a = 3.280 c = 12.950 ^{e)}
WTe ₂	orthorhombic	a = 6.34 b = 3.54 c = 14.44 ^{d)}	a = 6.282 b = 3.496 c = 14.07 ^{h)}

^{a)} Ref. [21]; ^{b)} Ref. [52]; ^{c)} Ref. [57]; ^{d)} Ref. [58]; ^{e)} Ref. [56]; ^{g)} Ref. [54]; ^{h)} Ref. [55].

Table 2.2. Theoretical in-plane lattice constants of monolayer TMDs with hexagonal symmetry. Lattice constants (a) are provided in Å.

TMD 1L	Gong et al. ^{a)}	Rasmussen et al. ^{b)}	Ding et al. ^{c)}	Kang et al. ^{d)}
MoS ₂	3.19 [PBE] 3.12 [LDA]	3.18 [PBE]	3.19 [PBE] 3.13 [LDA]	3.18 [PBE] 3.16 [HSE06]
MoSe ₂	3.33 [PBE] 3.25 [LDA]	3.32 [PBE]	3.33 [PBE] 3.25 [LDA]	3.32 [PBE] 3.29 [HSE06]
MoTe ₂	3.56 [PBE] 3.47 [LDA]	3.55 [PBE]	3.56 [PBE] 3.47 [LDA]	3.55 [PBE] 3.52 [HSE06]
WS ₂	3.19 [PBE] 3.13 [LDA]	3.19 [PBE]	3.19 [PBE] 3.13 [LDA]	3.18 [PBE] 3.16 [HSE06]
WSe ₂	3.32 [PBE] 3.25 [LDA]	3.32 [PBE]	3.32 [PBE] 3.25 [LDA]	3.32 [PBE] 3.29 [HSE06]
WTe ₂	3.56 [PBE] 3.48 [LDA]	-	3.56 [PBE] 3.47 [LDA]	3.55 [PBE] 3.52 [HSE06]

^{a)}Ref. [59]; ^{b)} Ref. [20]; ^{c)} Ref. [19]; ^{d)} Ref. [68].

2.2.2 Electronic properties

The interest for layered semiconductors exists for several decades. One of the first theoretical results was obtained by R. Coehoorn [60] in 1987 for bulk TMD materials. The band structures of compounds were calculated in self-consistent fashion with the augmented-spherical-wave method. It could be seen that MoS_2 , MoSe_2 , WSe_2 are indirect semiconductors with v-zone maximum at Γ point and c-zone minimum at K point (**Figure 2.3**). Experimental results of measuring photocurrents revealed band gaps matching solar spectrum and were obtained by K. Kam et al. [17]. The band gaps of MoS_2 and WS_2 are 1.23 eV and 1.35 eV correspondingly [17].

Figure 2.3. Scalar relativistic band structures of bulk MoS_2 , MoSe_2 , WSe_2 [60].

Several decades after when layered materials attracted interest theoretical and experimental research resumed. Kuk et al. [21] performed theoretical computations of electronic properties of bulk, multilayer and monolayers of MoS_2 , WS_2 . For first principles computations was used CRYSTAL09 implementation of DFT with generalized gradient approximation (GGA) of

exchange-correlation energy in Perdew-Burke-Ernzerhof (PBE) implementation. For monolayer BZ sampling was $8 \times 8 \times 1$. These calculations demonstrated transition from indirect to direct semiconductor with transition from bulk down to monolayer. The band gap value was greater for monolayer than bulk form of material. The similar trends were observed for WS_2 . **Figure 2.4** and **Figure 2.5** represent band structures. For bulk MoS_2 was obtained band gap of 1.2 eV which agrees well with experimental results; for bulk WS_2 band gap is 1.3 eV. For monolayer of MoS_2 and WS_2 theoretical direct band gaps are 1.8 eV and 1.9 eV respectively (experimental values are 1.74 eV and 1.79 eV).

Figure 2.4. Band structure of MoS_2 in bulk, multilayer and monolayer (GGA PBE). Arrow highlights the fundamental band gap [21].

Li et al. [62] obtained band gap for bulk MoS_2 equal to 0.79 eV with PBE functional of generalized gradient approximation. Matte et al. [62] obtained band gap for bulk MoS_2 equal to 1.1 eV and for monolayer 1.7 eV with same functional

but DZP basis set. Bulk WS_2 was demonstrated to possess indirect band gap of 1.32 eV using DFT with GGA PW (Perdew-Zunger) functional [63].

Figure 2.5. Band structure of WS_2 in bulk, multilayer and monolayer (GGA PBE). Arrow highlights the fundamental band gap [21].

Scalise et al. [64] has performed first principles investigation of strain on MoS_2 monolayer. It was shown that under 10% of tensile strain there occurs overlap of conduction and valence bands for MoS_2 monolayer.

Rasmussen et al. [20] performed theoretical computations of band structures for vast majority of TMD. All calculations were performed using projector augmented wave method within GPAW code implementation of DFT with plane waves basis set. GGA PBE was used for exchange-correlation energy approximation with 750 eV plane wave cutoff. For monolayers was used interlayer distance of 20 Å and 18x18x1 Monkhorst-Pack k-point sampling. Results are presented in **Table 2.3**.

By Ruppert et al. [24] has been obtained experimental value of direct band gap of MoTe₂ which is equal to 1.10 eV (see **Figure 2.6**). For MoTe₂ is observed transition from indirect semiconductor in bulk to direct semiconductor in monolayer. Lezama et al. [65] investigated change of band gap with decrease in number of monolayers. For MoTe₂ it has been found that it is direct semiconductor for monolayer and bilayer, trilayer has preliminary equal indirect and direct transitions, while tetralayer is indirect semiconductor. This behaviour differs from other TMDs, which are direct semiconductors only for monolayer.

Figure 2.6. Thickness-dependent photoluminescence (PL) spectra for MoTe₂ crystals on SiO₂/Si [24].

Structure of WTe₂ differs from other TMDs. While most of them are observed experimentally in structures with hexagonal symmetry, bulk WTe₂ has orthorhombic symmetry. Certain amount of calculations has been performed for monolayer WTe₂ with hexagonal symmetry [19] and it is semiconducting material in this configuration.

Gong et al. [59] has performed DFT computations for MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, WTe₂ with all having hexagonal symmetry. The calculations

were performed using VASP implementation with projector augmented wave (PAW) pseudopotential with both GGA PBE functional.

Kang et al. [66] performed calculations of band offsets using VASP package. Calculations were performed using GGA PBE functional and hybrid functional Heyd-Scuseria-Ernzerhof (HSE06). All calculations were performed for hexagonal cell, grid of 24x24x1 for monolayer and 24x24x5 for bulk. Interlayer distance was set to 10 Å to avoid interaction between adjacent images. Summary of results obtained by groups [59], [66] are presented in **Table 2.3**.

Table 2.3. *Theoretical band gaps of TMD monolayers with hexagonal symmetry obtained by different groups.*

TMD monolayer	MoS₂	MoSe₂	MoTe₂	WS₂	WSe₂	WTe₂
LDA ^{a)}	1.58	1.32	0.93	1.51	1.22	-
G ₀ W ₀ ^{a)}	2.48	2.18	1.72	2.43	2.08	-
PBE-SOC with GW corrections ^{b)}	1.59	1.32	0.94	1.54	1.32	0.74
PBE ^{c)}	1.59	1.33	0.94	1.55	1.25	0.75
HSE06 ^{c)}	2.02	1.72	1.28	1.98	1.63	1.03

^{a)} Ref. [20]; ^{b)} Ref. [59]; ^{c)} Ref. [68].

Lv et al. [58] performed calculations of band structure for bulk, monolayer and bilayer of WTe₂ with orthorhombic symmetry using implementation in ABINIT code. Calculations were performed within DFT with projector augmented wave (PAW) pseudopotential approach. Generalized gradient approximation (GGA) with the PBE functional was used for exchange-correlation energy. Calculation of the electronic properties included spin-orbit coupling. The plane-wave cutoff energy was set 600 eV and 8×4×1 Monkhorst-

Pack k mesh was used for Brillouin zone sampling [67]. Band structures and density of states are represented in **Figure 2.7** and **Figure 2.8**. It has been shown that bulk WTe_2 is semimetallic as DOS is very small at the Fermi energy level (E_F). Unlike results for hexagonal symmetry, for WTe_2 with orthorhombic symmetry was demonstrated small overlap of conduction and valence bands, which occurs along X- Γ close to Fermi level.

Figure 2.7. WTe_2 bulk with orthorhombic symmetry: (a) band structure; (b) total and partial density of states (DOS) [58].

Figure 2.8. WTe_2 monolayer with orthorhombic symmetry: band structure and total and partial DOS [58].

Komsa et al [68] performed computations of optical and fundamental band gaps of MoS_2 , MoSe_2 , MoTe_2 using GW first-principles calculation. For

bulk materials has been computed both direct and indirect transition. Results summary is represented in **Table 2.4**.

Table 2.4. Calculated optical and fundamental gaps for bulk and monolayer (1L) MoS_2 , MoSe_2 , MoTe_2 [68].

	MoS₂		MoSe₂		MoTe₂	
	Bulk	1L	Bulk	1L	Bulk	1L
<i>Optical transition A</i>						
BSE	1.86	1.80	1.55	1.64	1.08	1.17
<i>Fundamental gap</i>						
GW direct	2.00	2.97	1.66	2.41	1.15	1.79
GW indirect	1.30	3.26	1.11	2.97	0.88	2.49

2.3 In-plane and vertical heterostructures based on TMDs

Band gap engineering of TMD is important for their applications in photonics, optoelectronics, and nanoelectronics [69]. And creation of heterostructures is one of possible ways of band gap engineering [70]. Among the TMD based heterostructures could be considered vertical and in-plane heterostructures. Vertical heterostructures represent stacked layers of various 2D materials and some of them have been created experimentally [71].

Jung et al. [72] demonstrated facile chemical synthesis of vertical heterostructures based on two-dimensional (2D) transition metal dichalcogenides (TMDs). They have synthesized MoS_2/WS_2 and $\text{MoSe}_2/\text{WSe}_2$. For large area ($>1 \text{ cm}^2$) structures exhibit high uniformity of structural/chemical heterogeneity and show anisotropic carrier transport properties.

Song et al. [73] reported as well MoS₂/WS₂ heterostructures synthesis. Yu et al. [74] demonstrated synthesis of thin film of MoS₂/WSe₂ vertical structure. The heterostructure synthesis is scalable to a large area over 1 cm².

Bogaert et al. [75] showed that in-plane diffusion plays a significant role in the CVD of MoS₂/WS₂ lateral heterostructures. Thermodynamically driven TMD lateral heterostructure synthesis via two-step CVD growth is demonstrated. Also Bogaert et al. reported that the resulting structure of the heterostructures depends on the growth temperature: heterostructures grown at 650 °C consisted of a distinct MoS₂ core surrounded by area of Mo_{1-x}W_xS₂ alloy (Stage III-L), while more evenly distributed Mo_{1-x}W_xS₂ alloy throughout the entire crystal (Stage III-H) was obtained at higher growth temperatures of 680–710 °C (see **Figure 2.9**).

Figure 2.9. Growth stages of MoS₂/Mo_{1-x}W_xS₂ in-plane heterostructures [75].

The possibility of band gap engineering in 2D alloys was earlier predicted by Komsa et al [76]. It has been demonstrated that mixed MoS₂/MoSe₂/MoTe₂ compounds are thermodynamically stable at room temperature and thus could be obtained by chemical vapour deposition or exfoliation from the bulk material.

MoTe₂/MoS₂, MoS₂/MoSe₂, MoSe₂/MoTe₂, MoS₂/WS₂ are shown to be direct semiconductors with continuous band tuning. Band gaps of the MoS₂/MoSe₂ random alloys are in range from 1.65 eV to 2.0 eV. Band gaps of alloys containing Te are smaller and shift to the infrared region. In calculations has been used VASP implementation of DFT with GGA PBE functional and projector augmented wave formalism. Cutoff energy was 500 eV and k point sampling was 10x10x1. **Figure 2.10** shows the interface between MoS₂ and MoSe₂.

Figure 2.10. Top view and side view of the structures of MoS₂, MoS_{2x}Se_{2(1-x)} alloy, and MoSe₂ [76].

Gong et al. [77] reported a new strategy for growth of vertically stacked and in-plane heterostructures of WS₂/MoS₂. For WS₂/MoS₂ bilayer has been obtained direct band gap of 1.42 eV. For the in-plane heterostructures was revealed strong PL peak at 1.91 eV.

Kosmider et al. [78] performed DFT calculations of band structures of MoS₂/WS₂ bilayer and obtained direct band gap of 1.2 eV. Calculations were performed using VASP package, plane wave cutoff was 400 eV, with PBE and HSE functionals. For PBE calculations was used 6x6x1 mesh, and for HSE

5x5x1. For bilayer MoS₂/WS₂ using PBE was obtained direct (1.25 eV) and indirect (1.22 eV) band gap. Using HSE direct and indirect band gaps were 1.60 eV and 1.68 eV respectively, which are smaller than corresponding band gaps for bilayers of pure materials.

Figure 2.11. Illustration of the interaction of states close to band-edges around Γ and K points [79].

Komsa et al. [79] performed calculations for different vertical heterostructures containing two monolayers where one monolayer is MoS₂ and the other is WS₂, MoSe₂, MoTe₂, BN, or graphene sheets. In this work lattice constants of monolayers were retained unstrained in bilayer structure. It has been shown that when TMD monolayer is paired with BN or graphene, electronic structure resembles that of two independent monolayers. In order to maximize photoemission, v-band maximum and c-band minimum should both reside at the same k point and should be localized to the same monolayer (could be seen for MoS₂/BN in **Figure 2.11**). It is expected that MoTe₂/WSe₂ and MoSe₂/WS₂ will fulfil this condition.

Wei et al. [80] have studied the formation of one-dimensional interfaces (in-plane heterostructures of monolayer TMDs) in case of MoS₂/WS₂ from the first principles. For MoS₂/WS₂ in-plane heterostructures have been observed type-II band alignments with small band offset for the v-band maximum and a relatively large band offset for the c-band minimum. **Figure 2.12** illustrates MoS₂/WS₂/MoS₂ in-plane heterostructures (the interface between materials).

Figure 2.12. MoS₂/WS₂/MoS₂ in-plane heterostructures top and side view [80].

Recently Chiu et al. [81] reported synthesis of atomically sharp interfaces based on in-plane artificial lattices of WS₂/WSe₂/MoSe₂ at reduced growth temperatures. Such in-plane heterostructures (WSe₂/MoS₂) are of particular interest as they are a prototype of p–n diode that integrates two field-effect transistors of different polarity.

2.4 TMD monolayer alloys

The TMD alloys represent another way of band gap engineering. For TMD materials, depending on the chemical composition of the alloy, two main types can be specified. The first type of alloys is characterized by the presence of two different atoms of metal (Mo_(1-x)W_xS₂ and Mo_(1-x)W_xSe₂ [82], [83]). Photoluminescence characterization of Mo_(1-x)W_xS₂ monolayer alloys has shown the continuously tuned emission from 1.82 eV (reached at x=0.20) to 1.99 eV

(reached at $x=1$) [84], [85]. Moreover centimeter-scale and high-quality $\text{Mo}_{0.5}\text{W}_{0.5}\text{Se}_2$ alloy films were obtained on both a rigid SiO_2/Si substrate and a flexible polyimide (PI) substrate [86].

Figure 2.13. (a) Normalized PL RT of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ films with different substitution rate. (b) Variation of the photon energy of the PL emission peak as function of substitution rate x (obtained from XPS). The black line illustrates the variation between the values obtained from DFT calculations (DFT with PBE GGA) [87].

For the second type of alloys two different chalcogen atoms present in alloy ($\text{MoS}_{2(1-x)}\text{Se}_{2x}$ [87]-[91] and $\text{WS}_{2(1-x)}\text{Se}_{2x}$ [82]). **Figure 2.13** (a) demonstrates the dependency of the PL RT of chemical composition of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy. Measured optical band gap of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ranges from 1.9 eV to 1.5 eV [87]. Also Mann et al. [87] calculated optical band gaps with DFT using PBE GGA approximation for the exchange correlation energy. **Figure 2.13** (b) illustrates that optical band gaps are underestimated by PBE GGA.

Figure 2.14. (a) PL spectrum of the complete composition $\text{MoS}_2(1-x)\text{Se}_{2x}$ nanosheets and a typical PL mapping of a single ternary nanosheets (the inset, scale bar, 7 μm) excited with a 488 argon ion laser. (b) Measured band gaps as a function of substitution rate [95].

Tuneable composition $\text{MoS}_2(1-x)\text{Se}_{2x}$ alloy with controlled morphology and large domain size was obtained with physical vapor deposition (PVD) [92], [93]. Also ultrathin $\text{MoS}_2(1-x)\text{Se}_{2x}$ alloy nanoflakes with monolayer or few layer thicknesses were prepared through a high-temperature solution method [94]. Li et al. reported a simple one-step chemical vapor deposition approach for the simultaneous growth of alloy $\text{MoS}_2(1-x)\text{Se}_{2x}$ triangular nanosheets with complete composition tunability [95]. **Figure 2.14** illustrates the variation in the optical band gap of $\text{MoS}_2(1-x)\text{Se}_{2x}$ monolayer alloy with the change of composition [95]. In both **Figure 2.13** (a) and **Figure 2.14** (a) the slight change in the PL peak width could be also noticed.

Further continuous lateral growth of composition graded bilayer $\text{MoS}_2(1-x)\text{Se}_{2x}$ alloys along single triangular nanosheets was demonstrated by an improved chemical vapor deposition approach [96]. Li et al. reported that the change in composition within single triangular nanosheets from $x = 0$ to $x = 0.68$

leads to the band gap variation from 1.82 eV (680 nm) to 1.64 eV (755 nm) [96]. Wu et al. reported the synthesis of $\text{WS}_{2x}\text{Se}_{2(1-x)}$ nanosheets and $\text{WS}_2\text{-WS}_{2x}\text{Se}_{2(1-x)}$ lateral heterostructures by one-step CVD approach. Wu et al. optically tuned the composition along the nanosheets via precise control of evaporation sources [97]. These results highlight the possibility of the band gap engineering within nanosheets of TMD alloy. Also vertical heterostructures including pure TMD monolayers and alloys were synthesized (ex. $\text{MoS}_2\text{-MoS}_{2(1-x)}\text{Se}_{2x}$ [98] and $\text{Mo}_{1-x}\text{W}_x\text{S}_2\text{-WS}_2$, and $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ alloyed bilayer heterostructures [99]).

Figure 2.15. Internal E_{mix} and free F_{mix} energies of $\text{MoS}_2/\text{MoSe}_2/\text{MoTe}_2$ monolayer alloy per primitive cell. MoS_2 , $\text{MoS}_{2(1-x)}\text{Se}_{2x}$, MoSe_2 effective band structures [76].

The stability and the band gap of $\text{MoS}_2/\text{MoSe}_2/\text{MoTe}_2$ alloys have been studied theoretically [76], [100], [101]. Komsa et al. have calculated effective band structures of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy which illustrates the presence of the band gap with c-band minimum and v-band maximum around K-point (see **Figure 2.15**). Their calculation of the energy of mixing and of the free energy reveals that both are negative for the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy [76].

Kutana et al. also have studies electronic properties of $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ and $\text{MoS}_{2x}\text{Se}_{2(1-x)}$ alloys with DFT and LSDA [102]. The reported values of the calculated $\text{MoSe}_{2(1-x)}\text{S}_{2x}$ alloy band gaps range from 1.62 eV to 1.86 eV (see **Figure 2.16**).

Figure 2.16. $\text{MoSe}_{2(1-x)}\text{Se}_{2x}$ and $\text{Mo}_{1-x}\text{W}_x\text{S}_2$ monolayer alloys optical band gaps as a function of concentration x . The band gap values in the thermodynamic ground states are shown with big triangles [102].

The band gaps of alloys were estimated within density functional theory (DFT) with PBE approximation for exchange-correlation energy and range from 1.65 eV to 2.0 eV [76]. However, it is well known that the PBE GGA and GGA+U underestimate the band gap of bulk TMDs for about 30 % [103] - [107], and for the detailed theoretical study of TMD alloys the application of more sophisticated method is needed.

Chapter 3. Theoretical Background and Methodology

In the current chapter, main theoretical concepts of Density Functional Theory (DFT) such as Hohenberg-Kohn theorems and Kohn-Sham formalism are introduced. Existing methods for band gap evaluation are discussed. Quantum Espresso package is described as it will be used for computations.

3.1 Theoretical background: Density Functional Theory (DFT)

In theoretical physics, one of the basic problems is how to represent the structure and dynamics of complex many-electron system. Solid state is a complex system comprising electrons and nuclei. Nuclei motion takes much longer on time scale comparing with electron scales, which is due to fact that nuclei are 1000 times heavier than electrons. So electrons may be considered to be at their instantaneous ground state while the nucleus moves. In Born-Oppenheimer approximation nuclei are considered not moving and electrons are moving in effective potential [108]. System could be described by non-relativistic and time-independent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (3.1)$$

Or the description of electrons in a periodic materials could be represented in the following form:

$$(\hat{T} + \hat{U}(\mathbf{r}))\Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \quad (3.2)$$

where Hamiltonian contains kinetic part and background potential $\hat{U}(\mathbf{r})$. In crystalline the potential $\hat{U}(\mathbf{r})$ has the same periodicity ($\mathbf{R}$) as the lattice ($\hat{U}(\mathbf{r}) = \hat{U}(\mathbf{r} + \mathbf{R})$) [109]. Bloch's theorem states that the eigenfunctions of the Schrödinger equation for a periodic potential are the product of a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ and a function $u_{\mathbf{k}}(\mathbf{r})$, which has the same periodicity as the periodic potential ($u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R})$):

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}). \quad (3.3)$$

Thus electronic wave function in a crystal has following properties:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})}u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}). \quad (3.4)$$

3.1.1 Hohenberg-Kohn theorems

There are several key pillars of DFT and Hohenberg-Kohn theorem is one of them. First standard Hamiltonian describing system of N interacting particles should be considered:

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{W}, \quad (3.5)$$

where $\hat{T}$ is kinetic energy operator, $\hat{V}_{ext}$ interaction with external sources (time-independent potential) $v_{ext}(\mathbf{r})$, and particle interaction $\hat{W}$ [110].

Solving stationary Schrödinger equation, many-body eigenstates $|\Psi_{\mathbf{k}}\rangle$ could be obtained:

$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle, \quad (3.6)$$

where Hamiltonian is given by (3.5). Among the solutions of equation (3.6) will exist $|\Psi_0\rangle$ which describes ground state. Let us introduce ground state density n_0 as:

$$n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle. \quad (3.7)$$

Fundamental statements of Hohenberg–Kohn (HK) theorem could be formulated [111].

Statement 1

External potential, ground state (non-degenerate) and ground state density determine each other uniquely ($|\Psi_0\rangle$, n_0 and v_{ext}). The ground state is a unique functional of ground state density, denoted as $|\Psi[n]\rangle$ [111]. Ground state could be obtained from this functional when as density is used ground state density n_0 :

$$|\Psi_0\rangle = |\Psi[n_0]\rangle. \quad (3.8)$$

Here should be mentioned, that explicit form of external potential is not needed to derive ground state $|\Psi_0\rangle$ from corresponding ground state density n_0 . The form of ground state density functional depends strongly on the interaction between the particles constituting the many-body particle system. Thus, it will be the same for atoms, molecules and solids (they share Coulomb interaction). On the other hand, geometry (which is specific for system under consideration) is incorporated into the structure of density. As follows, the dependence of ground state functional from density is extremely complicated.

Statement 2

As follows from the statement 1, ground state energy is also density functional [113]. Total energy functional is represented in the following way to highlight that universal part $F[n]$ is completely independent from external potential term:

$$E[n] = \langle \Psi[n] | \hat{H} | \Psi[n] \rangle = \int v_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n] \quad (3.9)$$

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle. \quad (3.10)$$

Statement 3

Minimum principle could be formulated for total energy functional: if n_0 denotes the ground state density by external potential to v_{ext} , than for all densities n'_0 (3.11) functional $E[n_0]$ will be minimal.

$$n'_0 \neq n_0. \quad (3.11)$$

Restricted domain of the functional $E[n]$ constitutes only ground state densities, which are derived from Schrödinger equation.

3.1.2 Kohn-Sham equations

For the system described with Hamiltonian (3.5), from HK theorem it follows that all ground state characteristics could be obtained if ground state density is known. Unfortunately, Hohenberg-Kohn theorem doesn't provide explicit form of $E[n]$ or $F[n]$. Connection between existence theorems established

previously and mapping of system of interacting particles onto system with noninteracting particles is performed within Kohn-Sham (KS) formalism [112].

To obtain the Kohn-Sham equations, first should be considered system of noninteracting electrons (KS system):

$$\hat{H}_s = \hat{T} + \hat{V}_s, \text{ where } \hat{V}_s = \int v_s(\mathbf{r}) \hat{n}(\mathbf{r}) d\mathbf{r}. \quad (3.12)$$

The ground state of noninteracting system is denoted as $|\Phi_0\rangle$ and could be represented as Slater determinant:

$$\hat{H}_s |\Phi_0\rangle = E_{s,0} |\Phi_0\rangle \quad (3.13)$$

$$\Phi_0(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_1(\mathbf{r}_1\sigma_1) & \dots & \phi_N(\mathbf{r}_1\sigma_1) \\ \dots & \dots & \dots \\ \phi_N(\mathbf{r}_1\sigma_1) & \dots & \phi_N(\mathbf{r}_N\sigma_N) \end{pmatrix}, \quad (3.14)$$

which includes the energetically lowest solutions ϕ_i of the single-particle Schrödinger equation,

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right\} \phi_i(\mathbf{r}\sigma) = \varepsilon_i \phi_i(\mathbf{r}\sigma). \quad (3.15)$$

The ground state density associated with Equation (3.15) could be represented in the following way:

$$n_{0s}(\mathbf{r}) = \sum_i \sum_{\sigma=\uparrow,\downarrow} \Theta_i |\phi_i(\mathbf{r}\sigma)|^2. \quad (3.16)$$

In Equation (3.16) Θ_i is an occupation function which denotes the standard step function, which is 1 for $\varepsilon_i \leq \varepsilon_F$ and 0 for $\varepsilon_i > \varepsilon_F$. The eigenvalues ε_i are assumed to be ordered as

$$\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N = \varepsilon_F < \varepsilon_{N+1} \leq \dots, \quad (3.17)$$

where ε_F is Fermi energy of the system.

Hohenberg-Kohn theorem could be applied to KS system of noninteracting particles. Thus, its ground state is unique functional of ground state density by definition:

$$|\Phi_0\rangle = |\Phi[n_{0s}]\rangle \quad (3.18)$$

As in KS system there is no interaction between particles, the form of ground state functional $|\Phi[n]\rangle$ will differ from that of functional $|\Psi[n]\rangle$ (3.8) which describes interacting system. Ground state energy functional of Kohn-Sham system could be constructed in the following way:

$$E_s[n] = \langle \Phi[n] | \hat{T} + \hat{V}_s | \Phi[n] \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle + \int v_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (3.19)$$

For noninteracting system, kinetic energy functional could be expressed in the way:

$$\hat{T}_s[n] = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle. \quad (3.20)$$

Kohn-Sham system is an auxiliary noninteracting system with a Hamiltonian of the form (3.12). The ground state density $n_0(\mathbf{r})$ should be simultaneously ground state density of initial system of interacting particles (with external potential v_{ext}) and of this auxiliary system (having single-particle potential v_s) to enable mapping between these two systems. If the assumptions are correct, than ground

state density of the initial system of interacting particles could be represented using single-particle orbitals ϕ_i of the noninteracting system,

$$n_0(\mathbf{r}) \equiv n_{0s}(\mathbf{r}) = \sum_i \sum_{\sigma=\uparrow,\downarrow} \Theta_i |\phi_i(\mathbf{r}\sigma)|^2. \quad (3.21)$$

Equation (3.21) establishes sophisticated link between interacting density and single-particle orbitals, in contrast to Equation (3.16) which specifies direct form of density of noninteracting system.

The nature of interacting system must be incorporated into the structure of potential v_s . The total energy functional $E[n]$ needs to be decomposed in a suitable fashion to obtain functionals v_s

$$E[n] = T_s[n] + E_H[n] + E_{ext}[n] + E_{xc}[n]. \quad (3.22)$$

In Equation (3.22) second and third terms are energy functionals describing classical interaction within system of N particles and interaction with external potential correspondingly. Hartree term $E_H[n]$ and $E_{ext}[n]$ are given by Equations (3.23) and (3.24):

$$E_H[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r}', \quad (3.23)$$

$$E_{ext}[n] = \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}. \quad (3.24)$$

Equation (3.22) defines the exchange-correlation (xc) energy as density functional. All the complicated many-body effects and interactions, which are not included into T_s , E_H and E_{ext} , are incorporated in exchange-correlation functional. Such decomposition (3.22) of total energy functional isolates terms,

which usually dominate over xc-energy: simple density functionals E_H and E_{ext} ; T_s exact handling will be discussed further. Often qualitatively correct electronic structure of system could be obtained even if exchange-correlation energy is not taken into account. It could be assumed that majority of many-particle systems could be described with sufficient accuracy if approximated exchange-correlation energy is considered.

Similarly to functionals $T_s[n]$, $E_H[n]$, $E_{ext}[n]$, $F[n]$, $E_{XC}[n]$ is a universal functional as well. Therefore, all systems, which share Coulomb particle-particle interaction, will share the same exchange-correlation functional. If an approximated form of xc-functional was derived for some model system with Coulomb interaction, than this xc-functional can legitimately be applied for all other systems with Coulomb interactions. The potential $v_s(\mathbf{r})$ could be represented in the following way:

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{XC}[n](\mathbf{r}), \quad (3.25)$$

where v_H is Hartree potential,

$$v_H[n](\mathbf{r}) = \int w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r}' = \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (3.26)$$

and the exchange-correlation potential v_{XC} is defined as

$$v_{XC}[n](\mathbf{r}) = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}. \quad (3.27)$$

The effective potential v_s is determined by density according to Equation (3.25).

Density is determined by the solutions ϕ_i via Equation (3.22). Single-particle

Equations (3.15) include potential v_s and are nonlinear. And the Kohn-Sham equations are:

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + v_{ext}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc}[n](\mathbf{r}) \right\} \phi_i(\mathbf{r}\sigma) = \varepsilon_i \phi_i(\mathbf{r}\sigma) \quad (3.28)$$

and the solution should be obtained in self-consistent way.

In conclusion, Kohn-Sham system is auxiliary system and both ϕ_i and ε_i , which present in (3.28), are mathematical objects, which don't have any known, directly observable meaning [113], except two cases:

1. physical density n , which describes real system of interacting particles, is constructed from Kohn-Sham orbitals ϕ_i (see Eq. 3.21) [113];
2. ionization energy is equal to the magnitude of highest occupied ε_i (when the latter is measured relatively to the vacuum level) [113].

Although ground state density n and energy are reproduced when initial interacting system is mapped on to the KS system, this doesn't enforce that both systems share the same ground state (and ground state functionals). Ground state of interacting system is only approached by KS ground state when particle-particle interactions are considered infinitely small. In Kohn-Sham scheme complexity of initial problem of interacting particles is reduced, as consequence only limited information could be obtained about initial system.

Nonetheless, such limited information about electronic charge distribution and energies could be enough to find an answer on many structural questions.

3.1.3 LDA and GGA approximations of exchange-correlation functional

Unfortunately, true form of the exchange-correlation functional is unknown. Various approximations have been developed for this energy functional. The first is local density approximation (LDA). Uniform (heterogeneous) electron gas has been studied for long time and one of important properties is that it has constant electron density all over space. So, the exchange-correlation potential is approximated in every point in space as known xc-potential from the heterogeneous electron gas for the electron density observed at that point in space [114]. This approximation provides way to completely define and solve Kohn-Sham equations. Approximation of exchange-correlation functional only includes local density. It is important to remember that solution for Kohn-Sham equations won't be solutions of the true Schrödinger equation due to the assumptions made.

The second well know class of approximations developed after LDA is generalized gradient approximation (GGA). In this approach, exchange-correlation energy functional utilizes not only density but also includes local gradient of density. Although more physical information about the system is included in GGA than in LDA, it is tempting to consider that it will give results that are more accurate. Unfortunately, this is not always true, as quite often GGA overcorrects LDA.

There are different implementations of LDA and GGA exchange-correlation functionals. Perdew–Burke–Ernzerhof functional (PBE) and Perdew–Wang functional (PW91) [115] are most widely used GGA functionals for

computations involving solids. We will use Perdew-Zunger (PZ) LDA functional and PBE GGA implementation in calculations.

3.1.4 Hybrid exchange-correlation functionals overview

Becke made a conclusion [141], [116] that GGA exchange and correlation should be mixed with a fraction of exact exchange. Thus following form of hybrid functional is suggested:

$$E_{xc}^{hyb} = aE_x^{exact} + (1 - a)E_x^{GGA} + E_c^{GGA}. \quad (3.29)$$

It should be noted, that mixing coefficient a is not equal to or close to 1. Equation (3.29) can be rewritten in the following form:

$$E_{xc}^{hyb} = E_x^{exact} + (1 - a)(E_x^{GGA} - E_x^{exact}) + E_c^{GGA}. \quad (3.30)$$

PBE0 is one of the introduced hybrid functionals [117], [118], [119], [139] and is based on the PBE exchange-correlation functional [115]. PBE0 functional assumes the following form of the exchange-correlation energy:

$$E_{xc}^{PBE0} = aE_x^{exact} + (1 - a)E_x^{PBE} + E_c^{PBE}, \quad (3.31)$$

where $a=1/4$ is determined by perturbation theory [139]. Exchange energy in PBE0 is equal determined according to the Equation (3.32).

$$E_x^{PBE0} = aE_x^{HF} + (1 - a)E_x^{PBE} \quad (3.32)$$

Heyd-Scuseria-Ernserhof introduced another hybrid functional (HSE) [137] focusing on Equation (3.32) and via splitting all terms in short-range (SR) and long-range (LR) components. Thus Equation (3.32) takes form:

$$\begin{aligned} E_x^{PBE0} = & aE_x^{HF,SR}(w) + aE_x^{HF,LR}(w) \\ & + (1 - a)E_x^{PBE,SR}(w) + (1 - a)E_x^{PBE,LR}(w) \end{aligned} \quad (3.33)$$

Thus a screened Coulomb potential hybrid density functional of the form Equation (3.34) is obtained:

$$E_{xc}^{wPBEh} = aE_x^{HF,SR}(w) + (1 - a)E_x^{PBE,SR}(w) + E_x^{PBE,LR}(w) + E_c^{PBE}, \quad (3.34)$$

where w is an adjustable parameter governing the extent of short-range interactions.

It is considered that hybrid functionals are perhaps the most accurate density functionals in use for quantum chemical calculations.

3.1.5 Band Gap

The difference between the binding energy of the most weakly bound electron in the ground state of the material (insulator or semiconductor) and binding energy of the most weakly bound electron in the ground state of the system obtained by adding one electron defines the fundamental band gap E_g [110]. In the case, when neutral system contains N particles, $N+1$ or $N-1$ particle corresponds to charged system:

$$E_g = -\{[E_0^N - E_0^{N-1}] - [E_0^{N+1} - E_0^N]\}, \quad (3.35)$$

where band gap is always positive value. While the most weakly bound electron of the neutral system belongs to highest occupied band (valence band), the $(N+1)$ -th electron occupies the lowest empty band (conduction band). And from this behaviour follows the name band gap. For noninteracting systems (KS systems) band gap could be obtained from the following equation:

$$\Delta_s = \varepsilon_{N+1} - \varepsilon_N, \quad (3.36)$$

due to the identity of ionization energies with the orbital energies $E_0^N - E_0^{N-1} = \varepsilon_N$. System with N particles corresponds to system with neutral charge $Z=0$ and systems with N-1 and N+1 correspond to charge $Z=+1$ and $Z=-1$, thus Equation (3.35) could be rewritten in the following way:

$$E_g = E_{Z=+1} + E_{Z=-1} - 2E_{Z=0}, \quad (3.37)$$

where $E_{Z=+1}, E_{Z=-1}, E_{Z=0}$ corresponds to ground state energy of system with total charge $Z=+1, Z=-1, Z=0$. As total energy of the system will be computed using approximation LDA or GGA PBE, than Equation (3.37) takes form:

$$E_g^{(LDA)} = E_{Z=+1}^{(LDA)} + E_{Z=-1}^{(LDA)} - 2E_{Z=0}^{(LDA)}, \quad (3.38)$$

$$E_g^{(PBE)} = E_{Z=+1}^{(PBE)} + E_{Z=-1}^{(PBE)} - 2E_{Z=0}^{(PBE)}. \quad (3.39)$$

In the similar fashion approximation could be explicitly shown in Equation (3.36):

$$E_g^{(KS, LDA)} = \Delta_s^{(LDA)} = \varepsilon_{N+1}^{(LDA)} - \varepsilon_N^{(LDA)}, \quad (3.40)$$

$$E_g^{(KS, PBE)} = \Delta_s^{(PBE)} = \varepsilon_{N+1}^{(PBE)} - \varepsilon_N^{(PBE)}. \quad (3.41)$$

It should be highlighted, that Equations (3.38-3.39) are based on ground state total energies, while Equations (3.40-3.41) are based on Kohn-Sham energy eigenvalues.

3.2 Tools overview

3.2.1 *Concept of the supercell and slab model*

In order to perform DFT calculation one should describe system under investigation. This could be done by defining a collection of atoms, such that translation in three dimensions would reconstruct crystal structure.

First, one needs to define the volume, and this could be achieved by setting vectors along each direction. Second, the positions of atoms included in this volume should be provided. As result, these two steps completely define crystal. The vectors together with atom positions inside the specified cell are called supercell. One of the most basic inputs into DFT computation is definition of supercell. The choice of supercell is not unique. Supercell, which contains the minimum number of atoms sufficient to completely define crystal structure, is called primitive cell [114].

In order to study two dimensional materials, one should consider a model in which material is infinite along two dimensions and is finite along the third one. In order to have such structure, periodic boundary conditions are needed only along two dimensions. But in most computational codes it is impossible to eliminate periodic boundary conditions along the third dimension, so slab approach has been created in order to work around this. The key idea is to add vacuum space into supercell, so only part of volume of supercell is filled with atoms. Series of stacked slabs of material separated by vacuum occurs when supercell is translated along all three dimensions (see **Figure 3.1**). Sufficient amount of vacuum should be specified between the slabs, so that in vacuum

electron density of material will be equal to zero. Thus, slabs of material will not have an effect on each other [114].

Figure 3.1. Schematic view of slab model.

3.2.2 Quantum ESPRESSO package

Different packages are available for investigation of electronic properties of solid state with DFT such as Quantum Espresso, VASP, Gaussian, Crystal09 and others. In the present research will be used Quantum Espresso package which is an implementation of density functional theory, with use of plane waves and pseudopotentials. Quantum Espresso is an integrated suite of open-source computer codes for electronic-structure calculations and materials modelling at the nanoscale [130], [131], [132]. Quantum Espresso also provides an extensive list of pseudopotentials for the calculations.

One of the advantages of Quantum Espresso is that it supports various platforms and hardware configurations. It is possible to execute the Quantum Espresso codes on large clusters and on personal workstations. Quantum Espresso package could make use of OpenMPI library which enables execution

of computation on multiple processors. Also various operating systems are supported and codes could be successfully run under Windows, Linux, and Mac OS. In present research Quantum Espresso was run on personal workstation with Linux environment and on NTU High Performance Cluster (HPC) with Linux environment. In both cases OpenMPI library is utilized. The full Quantum Espresso distribution contains two core packages for the calculation of electronic-structure properties:

- PWscf (PW) : Plane-Wave Self-Consistent Field,
- CP (CPV): Car-Parrinello Molecular Dynamics [130].

On top of that additional packages could be installed on demand. All the supplementary scripts for data preparation, analysis and post processing were created using shell and python (including data classification algorithm).

3.2.3 Pseudopotentials

Quantum Espresso package uses plane waves and pseudopotentials, which correspondingly were used in present research. Chemical bonding and physical properties of materials are dominated by valence electrons, while contribution of core electrons is smaller [157]. Concept of pseudopotentials has been introduced to lower computational burden due to the core electrons. Pseudopotential replaces the electron density from a chosen set of core electrons with a smoothed density chosen to match various important physical properties of the true ion core. Thus in a frozen core calculation the properties of core electrons are fixed and approximated. In all-electron calculations frozen core concept is not applied.

Pseudopotentials should be transferable. Thus pseudopotential which was developed considering an isolated atom of an element, later can be reliably and without any adjustments used in calculations with different chemical environments. Different types of pseudopotentials has been developed including norm-conserving [188], [189], ultrasoft (USPP) [190] and projector augmented wave (PAW) [128]. Ultrasoft pseudopotentials require much lower cutoff energies than others. Nevertheless USPP construction for each atom needs a number of empirical parameters to be provided.

Blöchl [128] has originally introduced PAW method. Later Kresse and Joubert [191] has adapted it for plane-wave calculations and derived a formal relationship between USPP and PAW. Moreover they have performed tests to compare the accuracy and efficiency of PAW and USPP with relaxed core all electron methods which are in good agreement. Such tests were performed on different molecules (H_2 , H_2O , Li_2 , N_2 , F_2 , BF_3 , SiF_4) and bulks (Si, V, Li, Ca, CaF_2 , Fe, Co, Ni). PAW produces more reliable results than ultrasoft pseudopotentials in materials with strong magnetic moments or with atoms that have large differences in electronegativity.

It is a big advantage of the PAW method, that it is formally exactly equivalent to all-electron methods (with a frozen core) but is computationally comparable to doing pseudopotential calculations. In pseudopotential approaches, projecting out the core region is handled by a static projection kernel, while in PAW this projection kernel is dynamically updated during the SCF-cycle via an expansion of the core region in a local atomic basis set [128], [129].

3.3 Percolation theory

Percolation theory is the simplest model to describe phase transitions. Percolation process was introduced by Broadbent and Hammersley [152]. Initially they described process in which fluid spreads randomly through medium. In this case terms fluid and medium are quite general, and for example fluid could refer to electrons migrating in medium (atomic lattice). It should be mentioned the difference between diffusion process and percolation process. In the diffusion process fluid particles determine where to spread in the medium, while in the percolation process medium defines the where the particle will spread.

Figure 3.2. *Percolation on sites and percolation on bonds.*

There are two typical percolation problems on *sites* and on *bonds* (see **Figure 3.2**) [153]. In the percolation bonds problem there are some occupied (with probability p) and vacant (with probability $1-p$) bonds. As it could be seen from **Figure 3.2**, there exists some bond percolation threshold p_{cb} . At percolation threshold the topology of the network changes significantly and connected path

from A to B occurs. In the site percolation problem there are some sites are occupied (with probability p) and some are vacant (with probability $1-p$). In the similar fashion there exists p_{cs} at which A and B are connected. In general, the following relationship $p_{cb} \leq p_{cs}$ is true. For some 2D and 3D lattices values of the percolation thresholds have been calculated (see **Table 3.1**).

Table 3.1. Percolation thresholds (on sites p_{cs} and bonds p_{cb}) for some 2D and 3D lattices. Z is the coordination number of lattice. Values are provided from ref. [153].

Lattice type	Z	p_{cb} (bonds)	p_{cs} (sites)
2D lattice			
Honeycomb	3	0.6527	0.6962
Square	4	0.5	0.5927
Traingular	6	0.3473	0.5
3D lattice			
Diamond	4	0.3886	0.4299
Simple cubic	6	0.2488	0.3116
BCC (body-centered cubic)	8	0.1795	0.2464
FCC (face-centered cubic)	12	0.198	0.119

Percolation theory has been applied to many problems in physics, for example to theory of the electric conductivity of strongly inhomogeneous media [154]. Shklovski and Efros described main results of hopping conductivity, dependencies of temperature and concentration, magnetoresistance and theory of the conductivity of films [154]. It is also reported that around percolation threshold some critical behavior will be observed. Hoshen and Kopelman has applied percolation theory to exciton transfer problem in binary and ternary

mixed crystals (via migration and trapping) [155]. In the present thesis percolation theory is used for the in-depth analysis of energy of formation, structural and electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy.

Chapter 4. GVJ-2e Method for Band Gap Calculation

This chapter provides overview of the recently proposed GVJ-2e method for band gap calculation within DFT framework. Results of the band gap calculation for bulk solids with GVJ-2e method are discussed. The GVJ-2e method is used as main method for band gap calculation of bulk and monolayer TMDs and their alloy in the following chapters.

4.1 Towards accurate theoretical predictions of properties

Density functional theory (DFT) [133] is a method of choice for theoretical exploration of solids. The approximation of the exchange-correlation energy plays a key role in DFT computations. So, various approximations of the exchange-correlation energy have been developed starting with local density approximation (LDA) and generalized gradient approximation (GGA) [121], [134], [135], which allow accurate prediction of many ground state properties including structural properties and stability. Unfortunately, the same is not always true for the electronic properties, where the lack of correlation between experimental and theoretical results could be found as the band gap could be significantly underestimated, and errors can reach even 40% [136]. The latter essentially complicates the theoretical search for new materials with desired electronic properties.

In order to improve the efficiency and accuracy of theoretically obtained electronic properties, hybrid functionals (HSE [126], [137], [138], PBE0 [139],

B3LYP [140], [141]) and screened exchange (sX) hybrid functionals [142] have been developed. As another attempt to improve the prediction of electronic properties by DFT, LDA+U has been developed in which physics of Hubbard model was incorporated into density functionals [143]-[145]. Also the modified version of Becke-Johnson exchange potential [146] has been developed by Tran and Blaha [10], which contains adjustable parameters. On the other hand, theoretically sophisticated way to solve the band gap problem was suggested by Green's function based methods as in GW approach [56], [147]. Nevertheless, although quite often GW (or G_0W_0) becomes the method of choice, it is known to be quite computationally expensive method, as is the use of hybrid functionals in DFT.

Along with experimental exploration of the TMDs, theoretical investigation of TMDs has been performed to contribute to the search for new materials with desirable electronic properties. The use of LDA for TMD monolayers leads to band gap values underestimated for about 30 % [148]. Similarly PBE [115] GGA and GGA+U underestimate band gap for about 30 % [103], [104], [105], [106], [107], while B3LYP overcorrects band gap values for about 0.7 eV [104]. It has been shown that for bulk TMDs PBE performs better than hybrid PBE0, the latter of which tends to overestimate the band gap for about 1 eV [104]. When HSE hybrid functional was used, band gaps for both bulk and monolayer TMDs were overestimated for about 0.2 eV [100], [104]. Very similar performance has been shown with the use of screened exchange functional (sX) [149]. GW (or G_0W_0) is also used to compute electronic properties and band gaps of TMD. Although GW produces satisfactory results for bulk forms [68], [103],

[150], it usually significantly overestimates band gaps for monolayers for about 0.5 eV [148], [151]. The large errors make it difficult to predict the electronic properties of new materials precisely with current calculation methods.

4.2 Band gap calculation with GVJ-2e method

As it has been discussed in **Chapter 3** if one considers energy functional $E[n]$ in the form (3.22) exchange-correlation part should be approximated. Although various functionals has been developed (local, generalized gradient, hybrid approximations) [120], still theoretical results do not always correlate with experiment.

We recently has proposed a new method for band gap calculation (GVJ-2e), which produces band gaps in good agreement with experimental results [122], [123]. The main expression for band gap calculation has been derived using total energy functionals of charge density only, which are represented as a sum of kinetic energy, interaction with external field, Hartree and exchange-correlation terms. The fundamental band gap is defined as the difference between the first ionization potential (I) and the first electron affinity (A) [122], [123]:

$$E_g = A_e^\infty(N) - A_e^\infty(N+1) = E_{N+1}^{(0)} + E_{N-1}^{(0)} - 2E_N^{(0)}, \quad (4.1)$$

where $A_e^\infty(N), A_e^\infty(N+1)$ are works on the transfer of one electron from HOMO of a crystal (with N or $N+1$ electrons, respectively) to infinity; $E_{N-1}^{(0)} = E_N^{(0)} + A_e^\infty(N)$, $E_N^{(0)} = E_{N+1}^{(0)} + A_e^\infty(N+1)$, $E_N^{(0)}$ is the total energy of a neutral ($Z=0$) crystal with N electrons.

Figure 4.1. Schematic drawing of ensembles both containing two systems (each ensemble with total charge 0). Each system is a supercell with total charge Z .

In order to compute a band gap through Equation (4.1), one should select an approximation for the exchange-correlation energy functional, the analytical expression of which is not available. The local density approximation (LDA) [126] is one of the most widely used, and it has demonstrated satisfactory results for the ground state properties of solids. However, when electronic properties, and especially the band gap, are considered, results do not always correlate with the experiment. Germanium is an example, where computation of the band gap with LDA approximation for the exchange-correlation energy fails, as the calculated band gap turns out to be about 0 eV [122].

In our analysis we expressed the band gap using works to transfer two electrons from HOMO of a crystal (with N or $N+2$ electrons) to infinity: $A_{2e}^{\infty}(N)$ and $A_{2e}^{\infty}(N+2)$. In this case the Equation (4.1) takes the following form:

$$E_g = 0.5(A_{2e}^{\infty}(N) - A_{2e}^{\infty}(N+2)) = 0.5(E_{N+2}^{(0)} + E_{N-2}^{(0)} - 2E_N^{(0)}), \quad (4.2)$$

$$E_g^{(LDA)} = 0.5(E_{N+2}^{(LDA)} + E_{N-2}^{(LDA)} - 2E_N^{(LDA)}). \quad (4.3)$$

It is important to note that the Equation (4.3) is more accurate in LDA approximation in comparison with the traditionally used Equation (4.1) [122]. On the grounds of Equation (4.2) we considered two ensembles with the total charge equal to zero (see **Figure 4.1**). The first ensemble consists of two neutral supercells, while the second contains charged supercells with the total charges +2 and -2. For these ensembles we considered difference between true (exact) total energy functionals and approximated (LDA):

$$\Delta_{xc}^{\infty} = (E_{ens.2} - E_{ens.1})^{(0)} - (E_{ens.2} - E_{ens.1})^{(LDA)}, \quad (4.4)$$

$$E_{ens.2} - E_{ens.1} = E_{Z=+2} + E_{Z=-2} - 2E_{Z=0} \quad (4.5)$$

where E_Z is the total energy of the supercell, calculated in the charge state Z and for a given approximation of the exchange-correlation energy. We decomposed the exact exchange-correlation energy as a sum of the local E_{xc}^{LDA} and nonlocal parts and used Equation (4.5) for the ensembles. As a result, we have obtained the nonlinear equation for the exact band gap as a sum of the band gap, calculated in LDA approximation of the exchange-correlation energy, and two correction terms:

$$E_g^{(0)} = E_g^{(LDA)} + \frac{\Delta_{xc}^{\infty}}{2} - \frac{E_{(1,0)}^{(\infty,xc)}}{2} \left(1 + \exp\left(-\frac{E_g^{(0)}}{E_0}\right) \right), \quad (4.6)$$

where $E_g^{(0)}$ is the band gap, E_0 is used for the dimensionless energy in the exponent (in the following calculations is taken equal $E_0 = 1$ eV). The $E_g^{(LDA)}$ is the band gap calculated according to the Equation (4.3), where the total energies for neutral and charged systems are calculated in LDA approximation (LDA2e). The correction terms Δ_{xc}^{∞} and $E_{(1,0)}^{(\infty,xc)}$ are determined by a nonlocal part of the

exchange-correlation energy. The correction term $E_{(1,0)}^{(\infty,xc)}$ describes a nonlocal part of the exact exchange-correlation energy of interaction of the pair electrons at HOMO with the rest of the neutral system (pair of electrons (1) in **Figure 4.1**) with all electrons in lower energy bands and can be represented in the following form:

$$E_{(1,0)}^{(\infty,xc)} = \left\{ E_{Z=0}^{(0)} - E_{Z=0}^{(LDA)} \right\} - \left\{ E_{Z=2}^{(0)} - E_{Z=2}^{(LDA)} \right\} \quad (4.7)$$

Here we should emphasize the fact that the exact form of the exchange-correlation energy is not available and could only be approximated. So errors, in the calculation of the exact value of the band gap $E_g^{(0)}$ are determined by the precision of calculation Δ_{xc}^{∞} and $E_{(1,0)}^{(\infty,xc)}$, and stem from two main approximations, namely the use of pseudopotentials and approximation of the exchange-correlation energy. In Equations (4.3), (4.4), (4.6) and (4.7) all the quantities included are the total energies of neutral ($Z=0$) and charged systems ($Z=+2$ and $Z=-2$). It should be noted that the correction terms introduced in Equations (4.4), (4.7) essentially are not fixed values and they are calculated for each material separately. And thus they could be used in further analysis of the contribution of non-local exchange-correlation energy for each material.

The final Equation (4.6) obtained for band gap is based on the DFT total energy calculation only, doesn't contain any adjustable parameters and consequently is less expensive computationally comparing to the GW method. From the final Equation (4.6) it follows immediately why $E_g^{(LDA)}$ defined by Equation (4.3) will not be equal to exact band gap value. Significantly, the final

Equation (4.6) is parameter free and all terms are expressed through total energy differences.

4.3 Applications of GVJ-2e method

4.3.1 Bulk solids

In the **Table 4.1** detailed results of the band gap computation with GVJ-2e method are represented for bulk semiconductors and insulators. We have purposely considered semiconductor with a narrow band gap (Ge) and dielectric with wide band gap (Kr). As one can see from **Table 4.1** for all investigated materials calculated band gaps are in a good agreement with experimental ones. Correction terms Δ_{xc}^{∞} and $E_{(1,0)}^{(\infty,xc)}$, account for the nonlocal part of the exchange-correlation energy and substantially affect the calculated value of the band gap. As follows from the definition, the $E_{(1,0)}^{(\infty,xc)}$ value should not vary for isostructural semiconductors and this was confirmed for Si, Ge, and C results demonstrated in **Table 4.1**. Comparison of the calculated LDA band gap according to the Equations (3.38) and (4.3) (LDA and LDA2e columns in **Table 4.1**) clearly shows that the Equation (4.3) gives more accurate results. Really, for germanium Equation (3.38) gives band gap equal to 0, while Equation (4.3) gives LDA2e band gap value of 0.89 eV.

As one can see from the **Table 4.1** for all investigated materials band gaps calculated with our method are in a good agreement with experimental ones. Moreover, theoretical band gaps obtained with proposed GVJ-2e method have in

general smaller deviation from experiment than band gaps obtained using other theoretical methods (GW, HSE, MBJLDA) (see **Figure 4.2**).

Table 4.1. Calculated band gaps with GVJ-2e method (Eq. (4.6)), LDA2e band gap value (Eq. (4.3)) and correction terms. Band gap values referenced from literature are LDA, GW, MBJLDA, HSE and experimental. All values are in eV.

Solid	GVJ-2e	LDA2e	$0.5\Delta_{xc}^{\infty}$	$E_{(1,0)}^{(\infty,xc)}$	LDA ^{a)}	GW ^{b)}	MBJ LDA ^{a)}	HSE ^{c)}	Exp. ^{c)}
Si (A4)	1.28	0.87	0.65	0.38	0.47	1.41	1.17	1.28	1.17
Ge (A4)	0.78	0.89	0.20	0.43	0.00	0.95	0.85	0.56	0.74
C (A4)	5.39	4.5	1.11	0.43	4.11	6.18	4.93	5.49	5.48
BN (B3)	6.3	5.3	1.2	0.4	4.39	7.14	5.85	5.98	6.25
Xe (A1)	9.82	6.12	0.067	-7.27	5.78	-	8.52	-	9.8
Kr (A1)	11.74	7.0	2.86	-3.86	6.76	-	10.83	-	11.6

^{a)} LDA and MBJLDA ref. [10]; ^{b)} GW ref. [125]; ^{c)} Exp. results ref. [126], [127].

We have evaluated mean absolute error (MAE) and mean absolute percentage deviation (MAPD) for the methods presented in **Table 4.1** for investigated solids. And for proposed GVJ-2e method MAE is 0.08 eV which is the smallest among mean absolute errors given by other methods: 0.51 eV (GW), 0.14 eV (HSE), 0.52 eV (MBJLDA), and 2.26 eV (LDA). Mean absolute percentage deviation (MAPD) for GVJ-2e method is even more impressive and is 3 %, while other methods have 19 % (GW), 10 % (HSE), 9 % (MBJLDA), and 50 % (LDA) (see **Figure 4.3**).

Figure 4.2. Comparison of theoretical and experimental band gap. The values GJVJ-2e and LDA2e are calculated according to Equations (4.6), (4.3). Values GW, LDA, MBJLDA, HSE are taken from **Table 4.1**.

Figure 4.3. Mean absolute error (MAE) of GJVJ-2e, LDA2e, GW, LDA, HSE, MBJLDA methods for selected solids.

4.3.2 Bulk and monolayer TMDs

The final form of the Equation (4.6) has been obtained with the assumption for the limit of nonlocal part of the exchange-correlation energy between the two outer pairs of electrons of system with $N+2$ electrons:

$$\lim_{E_g \rightarrow 0} E_{(12, Eg)}^{(\infty, xc)} = E_{(12, 0)}^{(\infty, xc)} \approx E_{(1, 0)}^{(\infty, xc)}.$$

The term $E_{(12, Eg)}^{(\infty, xc)}$ describes a nonlocal part of the exchange-correlation energy between (1) and (2) pairs of electrons in the system with $N+2$ electrons. It has been demonstrated [122] that such approximation gives good results for band gap computation for such 3D materials as C, Si, Ge, LiF, BN and as well for wide gap insulators (Xe, Kr). In general case, the limit of $E_{(12, Eg)}^{(\infty, xc)}$ when $E_g \rightarrow 0$ depends on the orbitals to which electron pairs (1) and (2) belong. Unlike monoatomic semiconductors (Si, Ge) for which band orbitals are formed by s and p orbitals, for TMD materials different set of orbitals (s, p, d) is involved in calculation of the nonlocal part of the exchange-correlation energy and as a consequence the general expression for the nonlocal part of the exchange-correlation energy and PAW [128], [129] pseudopotentials have been used. Thus, we have used the following approximation of the limit

$$\lim_{E_g \rightarrow 0} E_{(12, Eg)}^{(\infty, xc)} = E_{(12, 0)}^{(\infty, xc)} \approx E_{(1, 0)}^{(\infty, xc)} \text{ for TMD materials.}$$

It should be emphasized that the accuracy of the band gap calculation is determined by the accuracy of calculation Δ_{xc}^∞ and $E_{(1, 0)}^{(\infty, xc)}$, while the last is determined by the approximation used for the exchange-correlation energy and used pseudopotentials. There are two approaches for calculating correction terms, the one is a molecular cluster method without using the pseudopotentials, and the other is a crystal supercell

method. In this study, all calculations are made within the framework of a supercell method.

4.4 Conclusions

A general approach is introduced for calculating the band gap of solids (GVJ-2e method). The application of the method for band gap calculations to the narrow-gap semiconductors (Ge) and insulators with very wide band gap (Kr) has shown that the method predicts the band gap with good agreement with experimental results. Theoretical band gaps obtained with proposed method have in general smaller deviation from experiment than band gaps obtained with other widely used theoretical methods (GW, HSE, MBJLDA).

The crucial role of the nonlocal part of the exchange-correlation energy in accurate determination of a band gap of semiconductors and insulators has been demonstrated.

GVJ-2e method proposes a new approach for band gap calculation within DFT, however it doesn't develop a new approximation of exchange-correlation energy but uses an existing ones. GVJ-2e method is based on the DFT total energy calculation only and doesn't introduce any adjustable parameters. As well, computational costs for accurate band gap calculation with proposed method are comparable with one of LDA.

Chapter 5. Structure and Electronic Properties of Bulk and Monolayer TMDs

The current chapter contains results of the theoretical study of structural and electronic properties of bulk and monolayer MoS₂, MoSe₂, WS₂, WSe₂. First convergence tests with respect to kinetic energy cutoff and number of k points are performed. In order to obtain theoretical lattice constants for bulk (a and c) and monolayer (a) TMDs relaxation calculations are performed. Electronic properties of bulk and monolayer TMDs are calculated and included band gap value, band diagram and projected density of states.

5.1 Introduction

We have considered the following semiconducting TMDs: MoS₂, MoSe₂, WS₂, WSe₂. In structural information of material could be included information about symmetry, space group, lattice constants, bond length, and atomic positions. TMDs such as MoS₂, MoSe₂, WS₂, WSe₂ possess the hexagonal symmetry with the space group P6₃/mmc (194 space group). The TMD monolayer (1L) contains three atomic planes in the configuration when two chalcogen (S or Se) planes sandwich the plane of metal atoms (Mo or W). Bulk TMD is formed when monolayers are stacked together with weak inter-plane (van der Waals) but strong intra-plane interactions. **Figure 5.1** plots the structure of bulk and monolayer TMD. There are several structural polytypes of MoS₂ monolayer 2H (hexagonal symmetry, Mo atom in trigonal prismatic coordination) and 1T (tetragonal symmetry, Mo atom in octahedral coordination)

[156]. We will consider 2H polytype. A primitive cell of bulk TMD contains 6 atoms (2 metal atoms and 4 chalcogen atoms), while monolayer primitive cell contains 3 atoms (1 metal atom and 2 chalcogen atoms). The structure of bulk TMD is described by two lattice constants a and c . The structure of monolayer TMDs is also described with a and c , but c in this case contains the interlayer distance.

Figure 5.1. Monolayer TMD (MX_2) primitive cell (a) and supercell (b). Bulk TMD primitive cell (c) and supercell (d). Metal atoms (M) – grey color, chalcogen atoms (X) – yellow color.

Quantum Espresso [130]-[132] implementation of the DFT was used for the computation of structural and electronic properties of bulk and monolayer TMDs. We used PZ LDA [121] and PBE GGA [115] approximations of the exchange-correlation energy and pseudopotentials (PAW). For all calculations using Quantum Espresso package, lattice constants, atomic positions and symmetry are necessary input data to describe structural properties of the material under investigation. Although there is experimental data on lattice constants, prior running computations of electronic properties, optimal structural properties should be found for each functional used (LDA or GGA). This needs to be done,

as relaxed lattice values minimize the total energy functional and thus one will obtain ground state energy. In case, one would try to use experimental lattice constants, the final energy value will not correspond to the minimum and moreover there will be non zero forces and stress acting on material and affecting electronic properties.

The kinetic energy cutoff is another important input for calculations and it relates to the atomic composition of material and pseudopotential used. The number of k points is also an important parameter for DFT calculation, which depends on the symmetry and dimensionality of the system.

To model structural and electronic properties of considered materials first two main convergence tests should be performed. These two convergence tests include the kinetic energy cutoff convergence and convergence with respect to the number of k points. Convergence tests are a series of calculations with variation of the kinetic energy cutoff value (or k points number) in order to find the optimal value.

First convergence tests are performed to find optimal values of the kinetic energy cutoff and k points (primitive cells for bulk and monolayer TMDs are used). After that the relaxation calculations for lattice constants and atomic positions will be performed. For a monolayer prior to relaxation calculations appropriate interlayer distance will be determined.

Kinetic energy cutoff and mesh in k space are necessary parameters of DFT computations in Quantum Espresso package. Convergence tests with respect to the kinetic energy cutoff and with respect to k-points have been performed. For bulk and monolayer MoS₂ and MoSe₂ 40 Ry cutoff is used in

subsequent calculations, while 50 Ry cutoff is used for WS₂ and WSe₂. Resulting k points meshes of $12 \times 12 \times 3$ (bulk TMDs) and $10 \times 10 \times 1$ (monolayer TMDs) are used in further calculations. The details of convergence tests are described in **Appendix A**.

5.2 Calculation set up for bulk and monolayer TMDs

5.2.1 Interlayer distance relaxation for TMD monolayers

TMD monolayer is described with a slab concept when DFT is used with plane waves and pseudopotentials. Due to the use of plane waves and periodical boundary conditions we will have the translational symmetry along all directions, although TMD monolayer doesn't need it along the z direction. So even though it could not be eliminated, it is desirable to treat a monolayer as there are no other images of a monolayer. In order to do that, the distance between layers should be enough for monolayers not to interact with each other. For this purpose the relaxation computation of interlayer distance was performed for PZ LDA and PBE GGA functionals.

Figure 5.2 illustrates the dependency of the total energy per atom versus interlayer distance for MoS₂ monolayer. The similar dependencies occur also for MoSe₂, WS₂, WSe₂ monolayers. For LDA and GGA approximations the variation of the total energy per atom is less than 0.001 eV when the interlayer distance is greater than 7 Å. In subsequent calculations of monolayer TMD properties we will use 10 Å interlayer distance.

Figure 5.2. Total energy per atom versus interlayer distance for MoS_2 monolayer (PZ LDA and PBE GGA).

5.2.2 Calculations set up summary

So in all subsequent calculations of structural and electronic properties we will use calculation parameters presented in **Table 5.1**.

Table 5.1. The general calculation parameters.

Parameter	Value
Kinetic energy cutoff, Ry	40 Ry (MoS_2 , MoSe_2) 50 Ry (WS_2 , WSe_2)
Mesh in k space	$12 \times 12 \times 3$ mesh for bulk TMDs $10 \times 10 \times 1$ mesh for monolayer TMDs
Interlayer distance for monolayer calculations	10 Å for monolayer TMDs

5.3 MoS_2 , MoSe_2 , WS_2 , WSe_2 bulk and monolayer structural properties

So first, we obtain relaxed values for the lattice constants and afterwards we relax atomic positions in order to obtain the final structure. We used uneven

real space mesh for the lattice constants relaxation, having more points around the corresponding experimental value for each material. In this way for bulk TMDs we performed the relaxation of both a and c lattice parameters, while for TMD monolayers only the lattice parameter a was further relaxed. We assume that theoretical value of the lattice parameter is in the vicinity of experimental one, which makes such relaxation approach relevant. In the relaxation of lattice structures of bulk TMDs van der Waals contribution was not included. **Figure 5.3** plots the relaxation of lattice parameters a and c for bulk MoS₂ obtained in PZ LDA and PBE GGA approximations and pseudopotentials. Similar dependencies of the total energy per atom versus a lattice parameter are observed for bulk MoSe₂, WS₂, WSe₂ (and for monolayer TMDs).

We are interested in theoretical value of the lattice constant which will minimize the total energy. The total energy functional dependence as a function of a lattice constant is very close to a quadratic function [157] around the minimum. Taylor expansion is the simplest approach to obtain its analytical form around minimum. We find the relaxed lattice constant as value for which the first derivative of the total energy turns to zero. Such lattice constant, producing the minimum of the total energy in current approximation, is considered as the theoretical lattice constant of material within used approximation. Both lattice constants (a and c) for bulk TMDs and the lattice constant a for TMD monolayers are obtained in this fashion for PZ LDA and PBE GGA approximations.

Figure 5.3. Lattice parameters a and c relaxation (bulk MoS_2).

Table 5.2. Lattice constants (a and c) and bond length of bulk TMDs.

Experimental values of lattice constants are taken from literature MoS_2 , MoSe_2 , WS_2 [60], WSe_2 [163]. All values are given in Å.

Bulk	PZ LDA			PBE GGA			Experiment	
	a	c	Bond length	a	c	Bond length	a	c
MoS_2	3.136	12.312	2.390	3.195	12.334	2.416	3.160	12.295
MoSe_2	3.269	12.979	2.516	3.335	12.989	2.547	3.288	12.900
WS_2	3.133	12.392	2.389	3.189	12.397	2.415	3.153	12.323
WSe_2	3.264	13.012	2.516	3.327	13.013	2.547	3.280	12.950

The calculated values of the relaxed lattice parameters and experimental ones are presented in **Table 5.2**. From **Table 5.2** follows that PZ LDA tends to give lattice constants smaller than experimental ones, while PBE GGA lattice

constants are bigger. These results are in agreement with the fact that LDA tends to over bind atoms and thus underestimate lattice constants for 1-2 % and GGA overcorrects lattice constants and gives overestimated values. Nevertheless, the deviation of the relaxed lattice parameters a and c for both PZ LDA and PBE GGA is mostly within 1% when compared to the experimental ones.

Table 5.3. *Structural properties of TMD monolayer including lattice parameter a and bond length. All values are in Å.*

1L	PZ LDA		PBE GGA	
	a	Bond length	a	Bond length
MoS ₂	3.133	2.386	3.195	2.420
MoSe ₂	3.263	2.511	3.336	2.551
WS ₂	3.130	2.386	3.202	2.421
WSe ₂	3.257	2.512	3.339	2.553

For monolayer TMDs was performed relaxations of the lattice constant a and atomic positions in PZ LDA and PBE GGA. In calculation for monolayer TMDs we used 10 Å interlayer distance. **Table 5.3** contains relaxed lattice constants a and bond lengths of monolayer MoS₂, MoSe₂, WS₂, WSe₂. Comparison of the relaxed lattice constant a of monolayer TMDs with bulk reveals that in PZ LDA lattice constant a of monolayer decreases together with the bond length, which means that the lattice is more compressed (for about 0.2% comparing to the relaxed lattice constant of bulk). For PBE GGA lattice constant a and bond length of monolayer increases comparing to bulk, which shows that lattice is more expanded (for about 0.4% comparing to the relaxed lattice constant of bulk). In all subsequent computations for TMD monolayers corresponding relaxed lattice parameters are used.

Lattice constants describe the volume of a supercell or primitive cell. But in order to completely describe material under investigation one needs atomic positions. And with obtained theoretical values of the lattice constants we performed the relaxation computation to obtain the relaxed atomic positions for PZ LDA and PBE GGA approximations.

As result for PZ LDA and PBE GGA approximations we obtained theoretical values for lattice constants and atomic positions for bulk and monolayer TMDs. This data is essential to perform electronic properties computations of bulk and monolayer TMDs.

5.4 MoS₂, MoSe₂, WS₂, WSe₂ bulk and monolayer electronic properties

After the relaxed lattice parameters and atom positions has been obtained, the electronic properties of bulk and monolayer TMDs could be calculated. We will consider the band gap, band diagram, projected density of states (pDOS) and charge density as part of electronic properties study. The calculation of electronic properties will be performed using determined previously number of k points and cutoff energy.

5.4.1 Bulk and monolayer TMDs band diagrams and Kohn-Sham band gaps

First, we will obtain Kohn-Sham band diagram and Kohn-Sham band gap value (from Kohn-Sham energy eigenvalues) using the primitive cell of bulk TMDs which contains 6 atoms. We also calculate the projected density of states

and charge density for bulk TMD primitive cell. In order to obtain Kohn-Sham band diagram one should run set of computations in Quantum Espresso package and after that build and analyze the band structure. **Figure 5.4** presents band diagrams of bulk MoS₂, MoSe₂, WS₂, WSe₂ calculated using PZ LDA approximation for bulk TMD primitive cell with total charge $Z = 0$. In the similar way we have calculated band diagrams of monolayer TMDs which are presented in **Figure 5.5**. Band diagrams are calculated along high-symmetry points in Brillouin zone using path Γ -M-K- Γ (similarly to [164], [21]).

We calculated the electronic band structures for bulk and monolayer TMDs. Bulk MoS₂, MoSe₂, WS₂ and WSe₂ are indirect band gap semiconductors with the valence band maximum (VBM) and conduction band minimum (CBM) located at G point and middle of K-G line in k-space, respectively. At the same time MoS₂, MoSe₂, WS₂ and WSe₂ monolayers are direct band semiconductors with both VBM and CBM located at K point (see **Figure 5.4** and **Figure 5.5**). With the transition from bulk to monolayer, the transition from indirect to direct band gap semiconductor is observed.

Figure 5.4. Band diagrams of bulk MoS₂, MoSe₂, WS₂, WSe₂ (PZ LDA).

Figure 5.5. Band diagrams of monolayer MoS₂, MoSe₂, WS₂ and WSe₂ (PZ

LDA). VBM – dark red, CBM – blue; Fermi level – grey dashed line.

The calculation of Kohn-Sham (KS) band gaps was also performed for bulk and monolayer TMDs. For bulk materials using LDA (or PBE) we obtained the following KS band gaps 0.83 eV (0.89 eV) for MoS₂, 0.81 eV (0.83 eV) for MoSe₂, 0.95 eV (1.01 eV) for WS₂, 0.92 eV (0.95 eV) for WSe₂. The Kohn-Sham band gap obtained in LDA (or PBE) approximation for bulk TMD tend to underestimate the experimental band gap for about 0.34 eV (28 %) for LDA and 0.30 eV (25 %) for PBE GGA. Nevertheless for monolayers LDA (or PBE) KS band gaps of MoS₂ 1.84 eV (1.65 eV), MoSe₂ 1.60 eV (1.42 eV), WS₂ 1.97 eV (1.74 eV), WSe₂ 1.73 eV (1.51 eV) are much closer to the experimental values.

5.4.2 Projected density of states of bulk and monolayer TMDs

Figure 5.6 and **Figure 5.7** depict the projected density of states (pDOS) of bulk and monolayer TMDs, respectively. PDOS was calculated using PZ LDA approximation of the exchange-correlation energy functional and pseudopotential for the bulk and monolayer primitive cell. Projected DOS for each atom are obtained as sum of respective pDOS on linear combination of atomic orbitals (LCAO). For both bulk and monolayer TMDs *c*-band and *v*-band are dominated by *d* states of metal atoms comparing to the number of states from more localized *s* and *p* metal states. And in the similar way there are more *p* states of chalcogen atoms in *c*-band and *v*-band comparing to more localized *s* states.

Figure 5.6. Projected density of states of bulk MoS_2 , MoSe_2 , WS_2 , WSe_2 (PZ LDA).

Figure 5.7. Projected density of states of TMD monolayers (PZ LDA).

The density of states of the conduction band is formed largely by d states from metal atoms (Mo or W), which agree with published data [161]. It could be noticed that c -band contains more metal states (dominated by Mo_d and W_d) than chalcogen states. Closer to v -band maximum the numbers of metal and chalcogen states are comparable, while for lower energy values more chalcogen states presents. It could be noticed from **Figure 5.7** that in TMD monolayer metal states depend on the particular chalcogen of the compound. For example Mo states in MoS_2 are more similar to W states in WS_2 than with MoSe_2 .

It could be also noticed that pDOS of monolayers is more sharp and contains more peaks comparing to the bulk TMDs. On the scale of energy monolayer peaks are located at lower energies than pDOS peaks of bulk TMDs. For both bulk and monolayer TMDs prominent band gap could be seen on pDOS figures, which agrees well with band diagrams data [160].

Density of energy states is obtained by differentiation of the number of quantum states (η) with respect to energy [158]. Thus the integration of density of states will produce corresponding number of quantum states. Number of quantum states could be used as measure to quantitevely compare pDOS of bulk and monolayer TMDs.

Figure 5.8 displays the distribution of the number of quantum states per 3 atoms (MX_2) between metal and chalcogen orbitals for bulk and monolayer TMDs. Number of quantum states is obtained by integration of pDOS in valence band. As it could be seen in bulk and monolayer TMDs there are more states of metal character than chalcogen. With transition from bulk to monolayer total number of quantum states remains constant.

Figure 5.8. Number of quantum states in bulk and monolayer TMDs (provided for 3 atoms MX_2).

5.4.3 Bulk and monolayer TMDs charge densities

Figure 5.9 displays the charge density bulk MoS₂, MoSe₂, WS₂, WSe₂ (see **Figure 5.10** for TMD monolayers). The analysis of the charge density for bulk TMDs confirms that the path of maximal density exists between metal and chalcogen atoms' nuclei (i.e. the atomic interaction line). The presence of maximal density path which is usually referred as bond path is an indicator of chemical bonding [159].

Along the maximal density path for bulk MoS₂ and MoSe₂ $\Delta n(r)$ is in range from 0.03 to 0.15, while for WS₂ and WSe₂ $\Delta n(r)$ is in range from 0.07 to 0.25. Around chalcogen atom nucleus the charge density distribution is not spherical, but is elongated towards nucleus of metal atom. For bulk and monolayer TMDs occurs charge transfer from metal atoms to chalcogen atoms. From **Figure 5.9** could be seen that there is secondary path with increased charge density along chalcogen-chalcogen line between the two layers (inter-plane interaction). The minimal change charge density along inter-plane chalcogen-

chalcogen line is about 0.008, which is much smaller than minimal charge density change along metal-chalcogen line (within layer) [160].

Figure 5.9. Charge density of bulk TMDs (PZ LDA).

Figure 5.10. Charge density of TMD monolayers (PZ LDA).

Along the maximal density path for monolayer MoS₂ and MoSe₂ $\Delta n(r)$ is in range from 0.02 to 0.11, while for WS₂ and WSe₂ $\Delta n(r)$ is in range from 0.07 to 0.21. Also in TMD monolayers charge density decreases outside of monolayer. With transition from bulk to monolayer TMD charge density within

the layer increases, comparing to one of bulk. This confirms the fact that with the reduction of dimensionality of the system to 2D, electrons are confined along the z dimension.

5.4.4 Bulk and monolayer TMDs fundamental and optical band gaps

The fundamental band gap is defined as the difference between the first ionization potential and the first electron affinity (see details in **Chapter 3** and **Chapter 4**). From the experimental point of view it is also possible to determine the optical band gap - the band gap is determined on the basis of the photoluminescence spectra. For the case when binding energy of the exciton is small in comparison with the width of the forbidden band, the optical band gap practically coincides with the fundamental band gap. It is known that in monolayer TMDs exciton binding energies are bigger than 0.01 eV [178] and thus they cannot be omitted from consideration.

In **Chapter 4** we have provided more details on the main equations for the band gap calculation within GVJ-2e method. For the bulk and monolayer TMDs (MoS₂, MoSe₂, WS₂, WSe₂) we have calculated the band gaps using GVJ-2e method according to the nonlinear Equation (4.6).

In order to use nonlinear Equation (4.6) for the band gap calculation, first total energies of bulk and monolayer TMDs has been calculated for three total charges ($Z=0$; $+2$; -2). Based on the calculated total energies correction terms has been obtained from Equation (4.4) and Equation (4.7), and LDA2e band gap was calculated according to the Equation (4.3). Thus all quantities in the main

nonlinear Equation (4.6) for the fundamental band gap are known, except for the fundamental band gap ($E_g^{(0)}$) itself for which Equation (4.6) was solved numerically.

With the GJVJ-2e approach first we obtained the fundamental band gap (E_g^{QP}), from which optical band gap (E_g^{PL}) has been calculated using the equation $E_g^{PL} = E_g^{QP} - E_{exc.binding}$. The exciton binding energies ($E_{exc.binding}$) were obtained from the Bethe-Salpeter equation (BSE) [178], as there exists variability in experimental values of exciton binding energy in monolayer TMDs. The results for the fundamental band gap (GVJ-2e QP) and optical band gap (GVJ-2e PL) are provided in **Table 5.4**, **Table 5.5** and **Table 5.6**. In **Table 5.4** we present the comparison of the theoretically obtained values for GVJ-2e fundamental band gap with the experimentally obtained fundamental band gap from the scanning tunnelling spectroscopy (STS). In the tables we also provide results of GW and G_0W_0 band gap calculations which are compared with STS QP gap values.

From **Table 5.4** follows that the fundamental band gaps obtained with GVJ-2e method (GVJ-2e QP) for TMD monolayers are in good agreement with STS QP experimentally obtained values (the mean absolute error (MAE) is 0.10 eV and mean absolute percentage deviation (MAPD) is 4 %).

In **Table 5.4** for each TMD monolayer in brackets the percentage deviation from experimental value is provided. The comparison of QP gaps with experimental STS data for TMD monolayers for GW yields MAE of 0.42 eV (MAPD 18 %) and for G_0W_0 method MAE is about 0.09 eV (MAPD 3 %).

Table 5.4. TMD monolayers fundamental band gaps: theoretical – obtained from GW and G_0W_0 ; calculated with GJVJ-2e method (Equation (4.6)); experimental – obtained from STS measurement. BSE are the theoretical exciton binding energies in TMD 1L. All values are in eV.

1L	G_0W_0 & GW	Exciton BSE	GVJ-2e QP	Exp.
MoS ₂	2.48 ^{a)} 2.97 ^{b)}	0.501 ^{c)}	2.39 (2%)	2.40 ^{d)} 2.5 ^{e)}
MoSe ₂	2.18 ^{a)} 2.41 ^{b)}	0.465 ^{c)}	2.12 (3%)	2.18 ^{f)}
WS ₂	2.43 ^{a)}	0.481 ^{c)}	2.52 (8%)	2.73 ^{g)}
WSe ₂	2.08 ^{a)}	0.442 ^{c)}	2.01 (5%)	2.12 ^{h)}

^{a)} G_0W_0 Ref. [148]; ^{b)} GW Ref. [68]; ^{c)} BSE Ref. [178]; ^{d)} Ref. [172]; ^{e)} Ref. [179]; ^{f)} Ref. [180]; ^{g)} Ref. [181]; ^{h)} Ref. [182].

Table 5.5. Theoretically obtained fundamental band gaps with GJVJ-2e method (GVJ-2e QP, Eq. (4.6)), calculated optical band gap values (GVJ-2e PL), LDA2e band gaps (Eq. (5.2)), and correction terms Δ_{xc}^∞ and $E_{(1,0)}^{(\infty,xc)} - E_{(2,0)}^{(\infty,xc)}$ for bulk and monolayer MoS₂, MoSe₂, WS₂, WSe₂.

TMD		LDA2e QP	Δ_{xc}^∞	$E_{(1,0)}^{(\infty,xc)} - E_{(2,0)}^{(\infty,xc)}$	GVJ-2e QP (GVJ-2e PL)
MoS₂	Bulk	1.14	0.02	-0.05	1.19
	1L	2.66	-0.17	0.33	2.39 (1.89)
MoSe₂	Bulk	1.05	0.01	-0.02	1.07
	1L	2.26	-0.08	0.17	2.12 (1.66)
WS₂	Bulk	1.30	0.04	-0.08	1.37
	1L	2.78	-0.16	0.33	2.52 (2.04)
WSe₂	Bulk	1.19	0.03	-0.05	1.24
	1L	2.13	-0.07	0.14	2.01 (1.57)

In **Table 5.5** both fundamental and optical band gaps obtained with GJVJ-2e method are provided together with the calculated correction terms. The absolute values of correction terms for TMD are greater than the absolute values for bulk TMDs, which could be attributed to the dimensionality reduction of the

system as correction terms describe the nonlocal part of exchange-correlation energy.

As it follows from **Table 5.4**, **Table 5.5** and **Table 5.6**, GVJ-2e method allows obtaining the band gap values correlating well with the experimentally obtained band gap for both bulk and monolayer TMDs. For bulk and monolayer TMDs, the GVJ-2e method demonstrates MAE of 0.04 eV and MAPD of about 3% for optical gap evaluation; for the GVJ-2e fundamental band gap MAE is 0.06 eV (MAPD is 3 %).

The comparison of the theoretical and experimental optical and fundamental band gaps is demonstrated in **Figure 5.11**. The theoretical set of band gaps includes values calculated with GVJ-2e method and well-accepted HSE, TB-mBJ, sX, GW, G_0W_0 methods.

There exists variability in the published experimental values (including our own values obtained from the PL measurement) for the band gap of TMD monolayers (as listed in **Table 5.5**) [165]-[177]. The experimentally obtained band gaps are 1.87 – 1.92 eV (MoS_2), 1.55 – 1.58 eV (MoSe_2), 1.98 – 2.05 eV (WS_2), 1.6 – 1.66 eV (WSe_2) [165]-[177]. It should be noted that PL band gaps obtained theoretically with GVJ-2e method are 1.89 eV (MoS_2), 1.66 eV (MoSe_2), 2.04 eV (WS_2), 1.57 eV (WSe_2), which agree well with both experimental results obtained in our research group and the experimental results published by other groups.

Figure 5.11. Comparison of the experimental and theoretical optical (PL) and fundamental (QP) band gaps for bulk and monolayer TMDs. Calculated theoretical band gaps include GJVJ-2e PL, GJVJ-2e QP and LDA2e QP. The band gaps referenced from literature include HSE, TB-mBJ, sX, GW, G_0W_0 (Table 5.6). Experimental band gap values are taken from Table 5.4 and Table 5.6.

In order to compute the band gap according to Equation (4.6), one first needs to compute the LDA band gap. It is important to underline that the equation for LDA2e (Equation (4.3)) should be used. Equation (4.3) produces LDA2e band gap, which usually has better correlation with experiment than LDA band gaps obtained with Equation (3.38) [122]. Calculated LDA2e band gap values for bulk and monolayer TMDs are presented in Table 5.5. For monolayers, the following values are available from the literature for the LDA band gap: 1.58 eV (MoS_2), 1.32 (MoSe_2), 1.51 eV (WS_2), and 1.22 eV (WSe_2) [148]. Thus the mean absolute error for TMD monolayer of LDA band gap is 0.37 eV, while for LDA2e this error is about 0.21 eV (compare with LDA2e mean absolute error for bulk TMDs of 0.03 eV).

Table 5.6. Theoretically obtained fundamental band gaps (GVJ-2e QP), calculated GVJ-2e PL values, for bulk and monolayer MoS₂, MoSe₂, WS₂, WSe₂. Experimental values and theoretical band gaps obtained with other methods (GW, G₀W₀, HSE, TB-mBJ, sX) are referenced from the literature. PL measured experimental band gaps are provided for TMD monolayers. All values are given in eV.

TMD		GW & G ₀ W ₀	HSE	TB- mBJ	sX	GVJ-2e QP (GVJ-2e PL)	Exp.
MoS ₂	bulk	1.23 ^{a)} 1.30 ^{b)}	1.46 ^{d)}	1.11 ^{d)}	1.35 ^{g)}	1.19	1.23 ^{h)}
	1L	2.48 ^{c)} 2.97 ^{b)}	2.02 ^{e)}	1.62 ^{f)}	1.88 ^{g)}	2.39 (1.89)	1.89 ⁱ⁾ 1.87, 1.9, 1.92 ^{j)} 1.87 ^{q)}
MoSe ₂	bulk	1.11 ^{b), a)}	1.36 ^{d)}	1.02 ^{d)}	1.16 ^{g)}	1.07	1.09 ^{h)}
	1L	2.18 ^{c)} 2.41 ^{b)}	1.72 ^{e)}	1.40 ^{f)}	1.71 ^{g)}	2.12 (1.66)	1.56 ^{k)} 1.55, 1.57, 1.58 ^{l)} 1.52 ^{q)}
WS ₂	bulk	1.30 ^{a)}	1.60 ^{d)}	1.31 ^{d)}	1.44 ^{g)}	1.37	1.35 ^{h)}
	1L	2.43 ^{c)}	1.98 ^{e)}	1.74 ^{f)}	2.13 ^{g)}	2.52 (2.04)	2.01 ^{m)} 1.98, 2.02, 2.05 ⁿ⁾ 1.99 ^{q)}
WSe ₂	bulk	1.19 ^{a)}	1.44 ^{d)}	1.20 ^{d)}	1.33 ^{g)}	1.24	1.20 ^{h)}
	1L	2.08 ^{c)}	1.63 ^{e)}	1.43 ^{f)}	1.82 ^{g)}	2.01 (1.57)	1.66 ^{o)} 1.6, 1.64, 1.65 ^{p)} 1.62 ^{q)}

^{a)}GW Ref. [103]; ^{b)}GW Ref. [68]; ^{c)}G₀W₀ Ref. [148]; ^{d)}HSE for 1L TMDs Ref. [100]; ^{e)}HSE and TB-mBJ for bulk TMDs Ref. [104]; ^{f)}TB-mBJ for 1L TMDs Ref. [107]; ^{g)}sX Ref. [149]; ^{h)}Bulk TMDs experimental band gaps from Ref. [162]; ⁱ⁾MoS₂ 1L exp. Ref. [166]; ^{j)}MoS₂ 1L exp. Refs. [170], [171], [172]; ^{k)}MoSe₂ 1L exp. Ref. [167]; ^{l)}MoSe₂ 1L exp. Refs. [171], [173], [174]; ^{m)}WS₂ 1L exp. Ref. [168]; ⁿ⁾WS₂ 1L exp. Refs. [169], [175], [176]; ^{o)}WSe₂ 1L exp. Ref. [169]; ^{p)}WSe₂ 1L exp. Refs. [165], [177], [173]; ^{q)}Our experimentally obtained band gaps [123].

The comparison of the band gap calculated with GVJ-2e and LDA2e methods reveals that a nonlocal part of the exchange-correlation energy plays a crucial role for the precision of band gap calculations. The latter is implemented by means of including the correction terms. Quite often, the correction terms have

magnitudes, which are comparable with magnitude of the band gap. Contribution of nonlocal part of exchange-correlation energy is greater for MoS₂ and WS₂, than for MoSe₂ and WSe₂.

Figure 5.12. Calculated band gap mean absolute errors (MAE) for widely used methods (GW, G₀W₀, HSE, TB-mBJ, sX) and proposed GVJ-2e method for bulk and monolayer TMDs. Also MAE for LDA2e QP band gap is displayed. Mean absolute percentage deviations (MAPD) are provided in %.

We have evaluated as well other well-accepted methods presented in **Table 5.4** and **Table 5.6** and obtained the following results for MAE (and MAPD) on bulk and monolayer TMDs: GW 0.23 eV (10%), G₀W₀ 0.09 eV (3%), HSE 0.17 eV (13 %), TB-mBJ 0.14 eV (9 %), sX 0.11 eV (8 %) (see **Figure 5.12**). These results clearly demonstrate that the recently proposed method GVJ-2e implements a way to compute band gap values with much smaller average errors MAE 0.06 eV (3%) for GVJ-2e QP gaps and of 0.04 eV (3%) for PL band gaps. Although the precision of the GVJ-2e method overcomes the precision of hybrid functionals and GW methods, the GVJ-2e computational costs are comparable with one of LDA/GGA calculation. From **Figure 5.12** follows that

LDA2e calculation could be also used for qualitative analysis of the fundamental band gap for new materials, as the accuracy of LDA2e is comparable with accuracy of GW methods.

It is interesting to compare the behavior of the methods for the calculated band gap values for 3D (bulk) and 2D (monolayer) TMDs. GW and G_0W_0 methods tend to give a more accurate band gap values for bulk TMDs, while larger errors occur for monolayers. The similar behavior is demonstrated by TB-mBJ functional, while opposite trend occurs for HSE which turns out to give better results for 2D structures. Proposed GVJ-2e method works equally well for both bulk and monolayer forms of TMDs.

5.5 Conclusions

In this chapter structural and electronic properties of bulk and monolayer MoS_2 , MoSe_2 , WS_2 , WSe_2 (TMDs) have been studied. For the fundamental band gap calculation GVJ-2e method was applied to the bulk TMDs (3D representative with layered structure) and monolayer TMD (2D structure).

Structural properties

The calculated relaxed lattice constants of bulk MoS_2 , MoSe_2 , WS_2 , WSe_2 are in good agreement with experimentally obtained values and deviate for about 1-2%. As expected relaxed lattice constant (a) for monolayers slightly differs from the value for bulk TMD ($\sim 0.5\%$).

Electronic properties

For bulk and monolayer TMDs a detailed analysis of the electronic properties including fundamental and optical band gaps, Kohn-Sham band structures, Kohn-Sham band gaps, projected density of states and spatial charge distribution has been performed.

The analysis of Kohn-Sham band structures of bulk MoS₂, MoSe₂, WS₂, WSe₂ confirms the fact that mentioned TMDs are indirect band gap semiconductors with v-band maximum and c-band minimum) located at G point and middle of K-G line in k-space, respectively. Unlike bulk TMDs, monolayer TMDs are direct band gap semiconductors with v-band maximum and c-band minimum located at K point. Thus TMD semiconducting monolayers, in contrast to bulk analogs, are direct-band semiconductors.

The calculated Kohn-Sham band gaps of bulk TMDs using PZ LDA and PBE GGA which underestimated band gap for about 25-30 %. For monolayer TMDs Kohn-Sham band gaps are in much closer agreement with experiment.

The analysis of the projected density of states (pDOS) of bulk and monolayer TMDs have shown that pDOS of the conduction band is formed largely by *d* states from metal atoms (Mo or W). Around the v-band maximum the number of metal and chalcogen states are comparable. Such behavior is true for both bulk and monolayer TMDs.

The width of the fundamental and optical band gap for a number of bulk TMD semiconductors and their two-dimensional analogues is calculated with GJVJ-2e method. For bulk TMDs, the calculated band gaps are 1.19 eV (MoS₂), 1.07 eV (MoSe₂), 1.37 eV (WS₂), 1.24 eV (WSe₂). For monolayer TMDs, the

calculated fundamental (and optical) band gaps are 2.39 eV (1.89 eV) for MoS₂, 2.12 eV (1.66 eV) for MoSe₂, 2.52 eV (2.04 eV) for WS₂, and 2.01 eV (1.57 eV) WSe₂.

The optical band gap of TMD monolayers is calculated from the values of the fundamental band gap with account of exciton binding energies. The obtained optical band gaps of TMD monolayers are in good agreement with the experimental ones obtained from the analysis of the photoluminescence spectra. The agreement between the calculated and experimental optical band gaps confirms the fact that the experimentally observed luminescence spectra are caused by the recombination of excitons characterizing the band gap of two-dimensional materials.

Similar to the case of conventional semiconductors and wide gap dielectrics, the calculated band gap for bulk and monolayer TMDs are in good agreement with the experimental ones. Although the precision of the GJVJ-2e for TMD monolayers is close to one of G₀W₀ method, on both bulk and monolayer TMDs the GJVJ-2e method has the smallest error of all. Thus the mean absolute error (MAE) of fundamental band gaps for bulk and monolayer TMDs obtained with GJVJ-2e method is 0.06 eV, which overcomes MAE of GW (0.23 eV) and G₀W₀ (0.09 eV) methods. For the GJVJ-2e optical band gaps (calculated from GJVJ-2e fundamental band gaps) MAE is 0.04 eV, which is lower than MAE of other widely used methods such as HSE 0.17 eV, TB-mBJ 0.14 eV, and sX 0.11 eV.

In agreement with the case of conventional semiconductors, the accuracy of the calculated band gaps is largely affected by a nonlocal part of the exchange-correlation energy.

Chapter 6. TMD Based Alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$: Results and Discussion

In this chapter the results of the study of structure and electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy are presented.

6.1 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy configurations and energy of formation

The $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy is synthesized by substitution of certain number of S atoms with Se which corresponds to the substitution rate x . To model the process of alloy synthesis and its microscopic properties, we used a MoS_2 supercell with 12 atoms which corresponds to 4 Mo atoms and 8 S atoms. Successive substitution of Sulphur atoms by Selenium in the initial MoS_2 supercell correspond to the substitution rates of 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%. It is clear that for the same substitution rate Se atoms could occupy different positions in MoS_2 matrix. **Figure 6.1** presents MoS_2 matrix (MoS_2 monolayer) with labels for each S atom specified depending on the position. Further each alloy configuration will be named according to occupied positions by Se atoms.

Quantum Espresso [130]-[132] implementation of the DFT is used for the computation of structural and electronic properties of monolayer alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$. We used PAW pseudopotentials and PZ LDA [121] and PBE GGA [115] approximations of the exchange-correlation energy. Brillouin zone was sampled

using Monkhorst-Pack approach and $10 \times 10 \times 1$ mesh was used for a monolayer alloy [67]. The kinetic energy cutoff was set to 40 Ry.

Figure 6.1. MoS_2 matrix with labels assigned to each Sulphur atom. $\text{MoS}_{1.75}\text{Se}_{0.25}$ alloy configuration with Se at $t1$ position.

For each Se substitution configuration of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy first, full relaxation of atomic positions and the lattice parameter (a) is performed. The obtained atomic positions and the relaxed lattice parameter have been used in all subsequent computations.

So **Figure 6.1** shows structure of $\text{MoS}_{1.75}\text{Se}_{0.25}$ alloy with Se atom at $t1$ position, which corresponds to the substitution rate $x=0.125$. The relaxed lattice parameters of $\text{MoS}_{1.75}\text{Se}_{0.25}$ are 6.288 Å (LDA) and 6.415 Å (PBE).

6.1.1 $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy ($x=0.25$)

For the substitution rate of 25% we replace two S atoms with Se in MoS_2 matrix of 12 atoms. In this case Se atoms could occupy different positions in the supercell. There exists 7 not equivalent configurations according to the symmetry of the supercell, namely $t1b3$, $t1b4$, $t1b1$, $t2b3$, $t1t4$, $t1t2$, $t2t3$. We consider the following types of the supercell configurations: Se atoms are distributed between top and bottom Sulphur planes (configurations $t1b3$, $t1b4$, $t2b3$ and ‘stacking’

t1b1); Se atoms are concentrated at one of the planes (*t1t2*, *t1t4*, *b2b4*). **Figure 6.2** illustrates some of the possible configurations of $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy.

Figure 6.2. The supercell of $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy ($x=0.25$) with various Se atoms positions. Mo atoms are grey, S atoms are yellow, Se atoms are blue.

Table 6.1 presents the relaxed lattice parameter of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($x=0.25$) alloy for different Se atoms positions. The lattice parameter of relaxed MoS_2 and MoSe_2 monolayers differs in about 5%. The alloy lattice parameter deviates from MoS_2 1L lattice parameter for about 1-1.5% for all configurations. Such deviation corresponds to about 17% shift (LDA) of the alloy lattice parameter from the lattice parameter of MoS_2 1L towards the lattice parameter of MoSe_2 1L (18% for PBE). The shift was calculated according to Equation (6.1). For $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy monolayer using Boltzmann probability averaging gives lattice parameters 6.311 Å (PZ LDA) and 6.441 Å (PBE GGA). Boltzmann probabilities are calculated according to the following equation $P_i = P_0 \exp\left(-\frac{E_i}{kT}\right)$, where

$$P_0 = \left(\sum_j \exp\left(-\frac{E_j}{kT}\right) \right)^{-1}.$$

$$\text{shift}(a) = \frac{a^{\text{MoS}_{2(1-x)}\text{Se}_{2x}} - a^{\text{MoS}_2}}{a^{\text{MoSe}_2} - a^{\text{MoS}_2}} \quad (6.1)$$

Table 6.1 The relaxed lattice parameter (a) for MoS_2 , MoSe_2 , $\text{MoS}_{1.5}\text{Se}_{0.5}$ for all studied structural configurations of monolayers. Boltzmann probabilities of each configuration. All lattice parameters are given in Å for the cell with 12 atoms.

1L	PZ LDA	PBE GGA	Probability
MoS₂	6.266	6.390	
MoS_{1.5}Se_{0.5}	6.311	6.441	
<i>t1b3</i>	6.311	6.441	0.191
<i>t1b4</i>	6.311	6.441	0.191
<i>t2b3</i>	6.311	6.439	0.189
<i>t1b1</i>	6.311	6.441	0.143
<i>t1t4</i>	6.312	6.442	0.098
<i>t1t2</i>	6.312	6.442	0.094
<i>b2b4</i>	6.312	6.445	0.094
MoSe₂	6.526	6.672	

We analyzed the formation energy of $\text{MoS}_{1.5}\text{Se}_{0.5}$ supercell with different positions of Se atoms to study the structure of alloy. The formation energy of the particular configuration of alloy is calculated according to Equation (6.2).

$$E_{\text{formation}} = E^{\text{MoS}_{2(1-x)}\text{Se}_{2x}} - (1-x)E^{\text{MoS}_2} - xE^{\text{MoSe}_2} \quad (6.2)$$

Figure 6.3 shows the formation energy of $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy for different positions of Se atoms in the supercell. Negative value of the formation energy points the energetically more favorable configurations. Configurations *t1b3*, *t1b4* and *t2b3* have the lowest formation energy. These configurations correspond to Se atoms located at top and bottom chalcogen planes. Configuration *t1b1* (stacking of Se atoms on top of each other) have higher formation energy but still negative. This configuration is the most ordered from the configurations with Se atoms located in two planes. The configurations in which both Se atoms are located at the same plane (*t1t4*, *t1t2*, *b2b4*) have positive formation energy. The latter makes them less likely to appear during the synthesis of $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy.

Figure 6.3. $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy formation energy for different Se atoms positions (calculated in PBE GGA). Energy values are provided for supercell with 12 atoms. Atoms on the figure: grey – Mo, yellow – S, blue – Se.

Although it was previously reported that for the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ system, the variation in formation energies is small (few meV), and there is no preference for any particular configuration [76], we conclude that configurations *t1b3*, *t1b4*, and *t2b3* are energetically more favorable. In a real $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy all these configurations will be observed with different probabilities. We calculated the partial distribution function for all configurations in a real alloy (see **Table 6.1**). Most of positions of Se atoms in a real alloy correspond to the configuration with Se atoms distributed between top and bottom layers.

6.1.2 $\text{MoS}_{1.25}\text{Se}_{0.75}$ alloy ($x=0.375$)

$\text{MoS}_{1.25}\text{Se}_{0.75}$ alloy (substitution rate 37.5%) contains 3 Se and 5 S atoms in the cell of 12 atoms. With allowance for the symmetry, the realization of 14 structures with different positions of the Se atoms in the supercell is possible (namely *t1b3b1*, *t2b3b1*, *t3b3b1*, *t4b3b1*, *t1b3b2*, *t2b3b2*, *t3b3b2*, *t4b3b2*,

$t1b1b4$, $t2b1b4$, $t3b1b4$, $t4b1b4$, $t1t2t3$, $t1t3t4$). Possible configuration types include: more atoms at the bottom plane (ex. $t1b3_b4$, $t1b3_b2$, $t1b3_b1$); more atoms at the top plane (ex. $t1b3_t2$, $t1b3_t4$, $t1b3_t3$).

Figure 6.4. The supercell of MoS_{1.25}Se_{0.75} alloy (x=0.375) with various Se atoms positions. Mo atoms are grey, S atoms are yellow, Se atoms are blue.

Table 6.2. The relaxed lattice parameter (a) for MoS₂, MoSe₂, MoS_{1.25}Se_{0.75} for some structural configurations of monolayers. Boltzmann probabilities of each configuration. All lattice parameters are given in Å for the cell with 12 atoms.

1L	PZ LDA	PBE GGA	Probability
MoS₂	6.266	6.390	
MoS_{1.25}Se_{0.75}	6.347	6.488	
$t1b3_b4$	6.347	6.487	0.166
$t1b3_b2$	6.346	6.487	0.167
$t1b3_t4$	6.346	6.487	0.164
$t1b3_t2$	6.346	6.486	0.164
$t1b3_t3$	6.348	6.488	0.126
$t1b3_b1$	6.348	6.489	0.126
$t1t2_t3$	6.349	6.489	0.045
$b1b3_b4$	6.349	6.489	0.043
MoSe₂	6.526	6.672	

Figure 6.4 displays some supercell configurations of MoS_{1.25}Se_{0.75} alloy, including two configurations with ‘stacking’ of Se atoms ($t1b3_b1$, $t1b3_t3$). The

case when all Se atoms concentrate at either top or bottom chalcogen planes correspond to *t1t2_t3* and *b1b3_b4* configurations. **Table 6.2** contains relaxed lattice parameters for some supercell configurations of $\text{MoS}_{1.25}\text{Se}_{0.75}$ monolayer alloy.

Figure 6.5 presents the formation energy of $\text{MoS}_{1.25}\text{Se}_{0.75}$ alloy for different positions of Se atoms. $\text{MoS}_{1.25}\text{Se}_{0.75}$ alloy supercell configurations *t1b3_b4*, *t1b3_b2* and *t1b3_t2* have the lowest formation energy, while alloy supercell configurations including pair of Se atoms one on top of the other (*t1b3_t3* and *t1b3_b1*) have slightly higher formation energy. The configurations in which all Se atoms are located at the same plane (*t1t2_t3*, *b1b3_b4*) have positive formation energy. The latter makes them less likely to appear during the synthesis of $\text{MoS}_{1.25}\text{Se}_{0.75}$ alloy.

Figure 6.5. $\text{MoS}_{1.25}\text{Se}_{0.75}$ alloy formation energy for different Se atoms positions (calculated in PBE GGA). Energy values are provided for cell with 12 atoms. Atoms on the figure: grey – Mo, yellow – S, blue – Se.

6.1.3 MoS_1Se_1 alloy ($x=0.5$)

MoS_1Se_1 alloy (substitution rate 50%) contains equal number of S and Se atoms. With allowance for the symmetry, the realization of 18 structures with different positions of the Se atoms in the supercell is possible (namely $t1b1b2b3$, $t2b1b2b3$, $t3b1b2b3$, $t1b2b3b4$, $t2b2b3b4$, $t4b2b3b4$, $t1t2b1b2$, $t2t3b1b2$, $t3t4b1b2$, $t2t4b1b2$, $t1t4b1b2$, $t1t4b1b4$, $t2t4b1b4$, $t2t3b1b4$, $t2t3b2b3$, $t2t4b2b3$, $t1t4b2b3$, $t1t2t3t4$). Possible configuration types include equal distribution of Se atoms between top and bottom planes ($b1t3_b4t2$, $t1b3_b4t2$, $t1b3_b4t3$, $t1b3_b4t4$, $t1b3_b1t3$, $t1b4_b1t4$, $t2b3_b2t3$); unequal distribution between top and bottom chalcogen planes ($t1b3_b4b2$, $t1b3_b4b1$).

Figure 6.6. The supercell of MoS_1Se_1 alloy ($x=0.5$) with various Se atoms positions. Mo atoms are grey, S atoms are yellow, Se atoms are blue.

Figure 6.6 shows MoS_1Se_1 alloy configurations including the configuration $t1t2_t3t4$ when all Se atoms are concentrated at the top chalcogen plane (SMoSe). SMOSe configuration has the plane of metal atoms (Mo) surrounded by two different chalcogen planes (S and Se), unlike other configurations when chalcogen planes contain both chalcogens (S and Se). **Table**

6.3 contains the relaxed lattice parameter for configurations of MoS_1Se_1 monolayer alloy supercell.

Figure 6.7. MoS_1Se_1 alloy formation energy for different Se atoms positions (calculated in PBE GGA). Energy values are provided for cell with 12 atoms. Atoms on the figure: grey – Mo, yellow – S, blue – Se.

Figure 6.7 presents the formation energy of MoS_1Se_1 alloy for different positions of Se atoms. MoS_1Se_1 alloy configurations with equal distribution of Se atoms between top and bottom chalcogen planes are more energetically favorable (similarly to the case of $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy) and include following configurations $t1b3_b4t2$, $b1t3_b4t2$, $t1b3_b4t3$, $t1b3_b4t4$. Among these configuration the lower formation energy corresponds to the configurations without a ‘stacking’ pair of Se atoms (ex. $t1b3_b4t2$ and $b1t3_b4t2$). Configurations when Se atoms are unequally distributed between the chalcogen planes have positive energy of formation and will less likely occur in real alloy. The SMoSe configuration has the highest positive formation energy.

Table 6.3. The relaxed lattice parameter (*a*) for MoS₂, MoSe₂, MoS₁Se₁ for some structural configurations of monolayers. Boltzmann probabilities of each configuration. All lattice parameters are given in Å for the cell with 12 atoms.

1L	PZ LDA	PBE GGA	Probability
MoS₂	6.266	6.390	
MoS₁Se₁	6.364	6.508	
<i>t1b3_b4t2</i>	6.335	6.494	0.155
<i>b1t3_b4t2</i>	6.358	6.492	0.152
<i>t1b3_b4t3</i>	6.371	6.515	0.125
<i>t1b3_b4t4</i>	6.371	6.515	0.125
<i>t1b3_b1t3</i>	6.372	6.516	0.095
<i>t1b4_b1t4</i>	6.372	6.515	0.095
<i>t2b3_b2t3</i>	6.373	6.515	0.095
<i>t1b3_b4b2</i>	6.372	6.514	0.083
<i>t1b3_b4b1</i>	6.373	6.517	0.064
<i>t1t2_t3t4</i>	6.362	6.496	0.011
MoSe₂	6.526	6.672	

6.1.4 MoS_{0.75}Se_{1.25} alloy (x=0.625)

MoS_{0.75}Se_{1.25} alloy (substitution rate 62.5%) contains more Se atoms (5) than S atoms (3). With allowance for the symmetry, the realization of 14 structures with different positions of the Se atoms in the supercell is possible (namely *t2t3t4b2b4*, *t3t1t4b2b4*, *t1t2t4b2b4*, *t1t2t3b2b4*, *t2t3t4b1b4*, *t1t3t4b1b4*, *t1t2t4b1b4*, *t1t2t3b1b4*, *t2t3t4b2b3*, *t1t3t4b2b3*, *t1t2t4b2b3*, *t1t2t3b2b3*, *t4b1b2b3b4*, *t2b1b2b3b4*). Possible supercell configurations include only an unequal distribution of Se atoms between the top and bottom planes: more Se atoms at the bottom plane (*t1b3_b4t2_b2*, *t1b3_b4t2_b1*, *t1b3_b4b2_b1*, *b1b2_b3b4_t2*) and more atoms of Se at the top plane (*t1b3_b4t2_t4*,

$t1b3_b4t2_t3$, $t1b3_b4t3_t4$, $t1b3_t3b2_t2$). The configurations $t1b3_b4b2_b1$ and $b1b2_b3b4_t2$ have the bottom chalcogen plane fully occupied by Se atoms. **Figure 6.8** shows $\text{MoS}_{0.75}\text{Se}_{1.25}$ alloy configurations and **Figure 6.9** displays the formation energy of $\text{MoS}_{0.75}\text{Se}_{1.25}$ alloy for different positions of Se atoms. $\text{MoS}_{0.75}\text{Se}_{1.25}$ alloy configurations with more Se atoms at the top plane have lower formation energy ($t1b3_b4t2_t4$, $t1b3_b4t2_t3$), while the configurations $t1b3_b4b2_b1$ and $b1b2_b3b4_t2$ with completely occupied bottom plane by Se atoms have positive energy of formation.

Figure 6.8. The supercell of $\text{MoS}_{0.75}\text{Se}_{1.25}$ alloy ($x=0.625$) with various Se atoms positions. Mo atoms are grey, S atoms are yellow, Se atoms are blue.

Table 6.4 contains the relaxed lattice parameter for configurations of $\text{MoS}_{0.75}\text{Se}_{1.25}$ monolayer alloy and also the lattice constant Boltzmann average value for the alloy.

Table 6.4. The relaxed lattice parameter (a) for MoS_2 , MoSe_2 , $\text{MoS}_{0.75}\text{Se}_{1.25}$ for some structural supercell configurations of monolayers. Boltzmann probabilities of each configuration. All lattice parameters are given in Å for the cell with 12 atoms.

1L	PZ LDA	PBE GGA	Probability
MoS₂	6.266	6.390	
MoS_{0.75}Se_{1.25}	6.397	6.542	
<i>t1b3_b4t2_t4</i>	6.396	6.541	0.169
<i>t1b3_b4t2_t3</i>	6.396	6.541	0.169
<i>t1b3_b4t2_b1</i>	6.397	6.541	0.156
<i>t1b3_b4t2_b2</i>	6.396	6.542	0.156
<i>t1b3_b4t3_t4</i>	6.397	6.543	0.132
<i>t1b3_t3b2_t2</i>	6.397	6.543	0.132
<i>b1b2_b3b4_t2</i>	6.399	6.544	0.045
<i>t1b3_b4b2_b1</i>	6.399	6.544	0.041
MoSe₂	6.526	6.672

Figure 6.9. $\text{MoS}_{0.75}\text{Se}_{1.25}$ alloy formation energy for different Se atoms positions (calculated in PBE GGA). Energy values are provided for cell with 12 atoms. Atoms on the figure: grey – Mo, yellow – S, blue – Se.

6.1.5 MoS_{0.5}Se_{1.5} alloy (x=0.75)

MoS_{0.5}Se_{1.5} alloy (substitution rate 75%) contains 6 Se atoms and 2 S atoms in the cell. With allowance for the symmetry, the realization of 7 structures with different positions of the Se atoms in the supercell is possible (namely *t2t3t4b2b3b4*, *t2t3t4b1b3b4*, *t2t3t4b1b2b3*, *t1t3t4b1b2b4*, *t2t3b1b2b3b4*, *t1t4b1b2b3b4*, *t1t3b1b2b3b4*). Configurations with equal distribution of Se atoms (*t1b3_b4t2_t4b2*, *t1b3_b4t2_b2t3*, *t1b3_b4t2_t4b1*) have negative energy of formation while configuration *t1b3_b4t4_b1t3* (all Se atoms are stacked on top of each other) has positive energy of formation. Configurations with more Se atoms at top or bottom plane have positive energy of formation (*t1b3_b4t2_t4t3*, *t1b3_b4t2_b2b1*, *t1b3_b4t4_b1b2*).

Figure 6.10. The supercell of MoS_{0.5}Se_{1.5} alloy (x=0.75) with various Se atoms positions (also is provided S atom position in the name of configuration). Mo atoms are grey, S atoms are yellow, Se atoms are blue.

Figure 6.10 shows the supercell of MoS_{0.5}Se_{1.5} alloy configurations and Table 6.5 contains relaxed lattice parameters for each supercell configuration of

MoS_{0.5}Se_{1.5} monolayer alloy and also the lattice constant Boltzmann average value for the alloy. **Figure 6.11** plots energy of formation of MoS_{0.5}Se_{1.5} alloy configurations.

Table 6.5. The relaxed lattice parameter (*a*) for MoS₂, MoSe₂, MoS_{0.5}Se_{1.5} for all studied structural configurations of monolayers. Boltzmann probabilities of each configuration. All lattice parameters are given in Å for the cell with 12 atoms.

1L		PZ LDA	PBE GGA	Probability
MoS₂		6.266	6.390	
MoS_{0.5}Se_{1.5}		6.410	6.549	
<i>t1b3_b4t2_t4b2</i>	<i>S{b1t3}</i>	6.410	6.550	0.191
<i>t1b3_b4t2_b2t3</i>	<i>S{b1t4}</i>	6.410	6.549	0.188
<i>t1b3_b4t2_t4b1</i>	<i>S{b2t3}</i>	6.409	6.548	0.187
<i>t1b3_b4t4_b1t3</i>	<i>S{b2t2}</i>	6.411	6.550	0.144
<i>t1b3_b4t2_t4t3</i>	<i>S{b1b2}</i>	6.411	6.550	0.097
<i>t1b3_b4t2_b2b1</i>	<i>S{t3t4}</i>	6.411	6.550	0.097
<i>t1b3_b4t4_b1b2</i>	<i>S{t2t3}</i>	6.410	6.550	0.096
MoSe₂		6.526	6.672

Figure 6.11. MoS_{0.5}Se_{1.5} alloy formation energy for different Se atoms positions (calculated in PBE GGA). Energy values are provided for the cell with 12 atoms.

Atoms on the figure: grey – Mo, yellow – S, blue – Se.

6.1.6 $\text{MoS}_{0.25}\text{Se}_{1.75}$ alloy ($x=0.875$)

$\text{MoS}_{0.25}\text{Se}_{1.75}$ alloy (substitution rate 87.5%) contains 7 Se atoms and only 1 S atom (see **Figure 6.12**). The relaxed lattice constants of $\text{MoS}_{0.25}\text{Se}_{1.75}$ are 6.499 Å (PZ LDA) and 6.643 Å (PBE GGA).

$\text{MoS}_{0.25}\text{Se}_{1.75}$ ($x=0.875$)

$t1b3 \ b4t2 \ t4b2 \ b1$
($S\{t3\}$)

Figure 6.12. $\text{MoS}_{0.25}\text{Se}_{1.75}$ alloy ($x=0.875$) configuration. Mo atoms are grey, S atoms are yellow, Se atoms are blue.

6.1.7 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy structural properties summary

To quantitatively describe peculiarities of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy structure we introduce parameter of asymmetric occupation of top and bottom S planes with Se atoms. The parameter of asymmetric occupation is defined by the following equation:

$$s = |n_t - n_b|, \quad (6.3)$$

where n_t and n_b are the numbers of Se atoms in top and bottom planes correspondingly. The parameter of asymmetric occupation s is an integer number in range $[0; 4]$ for considered alloy supercells (see **Table 6.1** - **Table 6.5**). For each asymmetry parameter s we have calculated normalized Boltzmann probability $\tilde{P}(s)$, which characterizes the probability of occurrence in the alloy of the structure with asymmetry parameter s .

Figure 6.13. The normalized probability $\tilde{P}(s)$ as a function of the asymmetry parameter s for $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy.

Figure 6.13 plots the dependency of $\tilde{P}(s)$ versus parameter of asymmetry (s). Such dependency ($\tilde{P}(s)$) reveals that in most of the cases will be synthesized the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with symmetric distribution of Se atoms between top and bottom chalcogen planes (parameter of asymmetry $s \approx 0$).

Let's analyze the change in energy of formation of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy as function of substitution rate x . **Figure 6.14** shows Boltzmann average of the energy of formation of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy for each considered substitution rate. With transition from MoS_2 to MoSe_2 , the energy of formation is positive in the range of substitution rates of S atoms $0.8 < x < 1$ (corresponds to $0 < x_{\text{Se}} < 0.2$ for Se atoms substitution rate). In this region of substitution rate ($0.8 < x_s < 1$) S atoms are relatively far away from each other and their interaction is low. In the specified region of high substitution rate $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy could be considered

as MoS₂ monolayer heavily doped with Se. The increase of the energy of formation for the substitution rates of $0.8 < x < 1$ is attributed to the fact that absolute value of total energy per atom is higher in MoS₂ than in MoSe₂. For the substitution rate x from 0.8 to 0.5 (for Se atoms this corresponds to the range $0.2 < x_{Se} < 0.5$) the energy of formation drops quickly. The energy of formation becomes negative and reaches minimum at substitution rate $x \sim 0.5$.

Figure 6.14. Boltzmann average of the energy of formation of MoS_{2(1-x)}Se_{2x} alloy. Dependency of energy of formation derivative on substitution rate x .

Thus the alloy MoS_{2(1-x)}Se_{2x} will form at such substitution rates of Se atoms ($x \sim 0.5$). Indeed let us consider a square lattice with S atoms at lattice sites. During doping Se atoms substitute S atoms. According to the percolation theory [183], a connected set of lattice sites occupied by Se atoms occurs when substitution rate of Se atoms reaches X_c (the percolation threshold). According to the percolation theory, physical properties of the system abruptly change around the percolation threshold X_c . **Figure 6.14** also shows the dependency of the calculated derivative of MoS_{2(1-x)}Se_{2x} alloy energy of formation on substitution rate x .

The energy of formation derivative reaches its maximum at $X_c \approx 0.4$ ($x_{Se} \approx 0.4$), which corresponds to $x_S = 1 - x_{Se}$ (60%) S atoms substituted by Se. The calculated percolation threshold value falls between the two theoretical threshold values for site percolation problem $X_{c1} \approx 0.57$ on square lattice and $X_{c2} \approx 0.3$ on cubic lattice. The shift of the calculated percolation threshold towards the theoretical percolation threshold on cubic lattice is attributed to the fact that in 2D alloy $MoS_{2(1-x)}Se_{2x}$ atoms of Se(S) occupy two separate in space planes (top and bottom).

Figure 6.15. The dependency of the width (at half-height) of PL line of the complete composition $MoS_{2(1-x)}Se_{2x}$ nanosheets. Data is extracted from literature [95].

Due to the fact that $MoS_{2(1-x)}Se_{2x}$ energy of formation is negative with the minimum at $x \sim 0.5$, for the substitution rates $0.25 < x < 0.5$ synthesis of non-uniform alloy is possible due to nucleation of large areas having a local substitution rate of $x \sim 0.5$. This agrees well with experimental results [95]. The

dependency of the PL line width of the complete composition $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ is displayed in **Figure 6.15**. For substitution rates $0.25 < x < 0.5$ the width of PL lines of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy increases significantly relatively to the PL line width of MoS_2 and MoSe_2 . **Figure 6.15** illustrates that PL peak width of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy for almost all substitution rates is greater than PL peak width of MoS_2 monolayer.

Figure 6.16. $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ lattice constant shift depending on substitution rate x calculated using PZ LDA and PBE GGA (dashed line corresponds to linear dependency). Derivative of lattice constant versus substitution rate.

Let us consider the variation of lattice constant (a) of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy. We have calculated the lattice parameters for each configuration for different substitution rates. As it was shown a different distribution of Se atoms in the supercell will be observed in the resulting alloy with some probability. **Figure 6.16** plots the shift of average Boltzmann lattice parameter of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ for the substitution rate ranging from 0 to 1. The dashed line displays linear variation of a . The lattice parameter shifts have been calculated using Equation (6.1). From **Table 6.6** follows that the lattice parameter shift in % is smaller than the

corresponding substitution rate in %. Thus increase of Se substitution rate doesn't produce the change of the lattice constant on the same value. Relaxed lattice parameter increases slower than Se substitution rate increases. Although the lattice constant depends on substitution rate, it varies slightly for different alloy configurations within certain substitution rate.

Table 6.6. The Boltzmann average relaxed lattice parameter (a) for MoS_2 , MoSe_2 , $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayers. All lattice parameters are given in Å for the cell with 12 atoms.

1L	x, %	PZ LDA		PBE GGA	
		a	Shift, %	a	Shift, %
MoS₂	0 %	6.266	0 %	6.390	0 %
MoS _{1.75} Se _{0.25}	12.5 %	6.288	8 %	6.415	9 %
MoS _{1.5} Se _{0.5}	25 %	6.311	17 %	6.442	18 %
MoS _{1.25} Se _{0.75}	37.5 %	6.347	31 %	6.488	35 %
MoS ₁ Se ₁	50 %	6.364	38 %	6.508	42 %
MoS _{0.75} Se _{1.25}	62.5 %	6.397	50 %	6.542	54 %
MoS _{0.5} Se _{1.5}	75 %	6.410	55 %	6.549	56 %
MoS _{0.25} Se _{1.75}	87.5 %	6.499	90 %	6.643	90 %
MoSe₂	100 %	6.526	100 %	6.672	100 %

Similarly to the analysis of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy the derivative of formation energy, the analysis of the derivative of the lattice constant is interesting. **Figure 6.16** also visualizes the dependency of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ lattice constant rate of change with substitution rate (derivative plot is based on **Table 6.6**). From the lattice constant derivative we have obtained following values of the percolation thresholds $X_c(\text{Se}) \approx 0.25$ (for Se atoms sublattice) and $X_c(\text{S}) \approx 0.2$ (for S atoms sublattice). The values of $X_c(\text{S})$ and $X_c(\text{Se})$ are close to the theoretical percolation threshold value for bond percolation problem on cubic lattice $X_c \approx 0.25$. This result

emphasizes that $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy lattice constant is governed by the bond length during substitution of S with Se (or Se with S), while the alloy itself is a quasi 2D structure.

We have also analyzed thermodynamic stability of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy. The Gibbs free energy is defined as $G = H - TS$, where H is the enthalpy of mixing, T is the temperature and S is the entropy. When two components form a solution change of free energy on mixing is $\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}}$ [184]. The change enthalpy on mixing is equal to the calculated value of the energy of formation (as in case of different redistributions of atoms between top and bottom planes $\Delta p = 0$ and $\Delta V = 0$). The variation of the entropy on mixing is defined according to:

$$\Delta S_{\text{mixing}} = k_B \ln p = k_B \ln \left(\frac{n_0!}{n_A! n_B!} \right), \quad (6.4)$$

where p is the number of distinguishable arrangements of atoms, n_A and n_B is the number of atoms of element A and element B. Using Stirling's approximation $\ln(n!) = n \ln(n) - n$:

$$\Delta S_{\text{mixing}} = -k_B [x \ln x + (1-x) \ln(1-x)], \quad (6.5)$$

where x is the substitution rate of Se in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy. **Figure 6.17** visualizes the variation of the free energy on mixing (ΔG_{mixing}), change of the entropy on mixing ($T\Delta S_{\text{mixing}}$) and the energy of formation on mixing.

For $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy the energy of formation is small but negative for the substitution rates less than 67%. Thus formation of alloy is favorable for the substitution rates smaller than 67%. The entropy change on mixing promotes the

formation of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy for all substitution rates, as the change of free energy on mixing is negative for all substitution rates from 0% to 100%, which agrees with the free energy reported by [76]. Thus such alloys could be obtained experimentally for ex. using CVD [95].

Figure 6.17. Change of free energy on mixing (ΔG_{mixing}), change of entropy on mixing ($T\Delta S_{\text{mixing}}$), energy of formation of alloy ($E_{\text{formation}}$) of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with substitution rate 0-100%.

6.2 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy electronic properties

6.2.1 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy fundamental and optical band gaps

In the previous chapter we have demonstrated that monolayer TMDs (MoS_2 , MoSe_2 , WS_2 , WSe_2) are semiconducting materials with direct band gap. The calculated fundamental and optical band gaps with GJVJ-2e method are in a good agreement with experimental ones obtained from STS and PL experiments.

So for the calculation of electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy we will utilize the same approach.

We calculate the fundamental band gaps of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with different substitution rates and with different positions of Se atoms using GJVJ-2e method according to Equation (4.6). **Table 6.7** contains calculated GJVJ-2e fundamental band gap of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy for the substitution rate of S atoms with Se in range 0 - 1. The fundamental band gap not only depends on the substitution rate but is also sensitive to relative positions of Se atoms in MoS_2 matrix. For each substitution rate in alloy we have calculated Boltzmann average values of the fundamental band gap and correction terms (see **Table 6.7**).

In order to evaluate the influence of relative distribution of Se atoms on the fundamental band gap and the lattice parameter we have calculated the shifts according to the Equation (6.6) and Equation (6.1).

$$\text{shift}(E_g) = \frac{E_g^{\text{MoS}_{2(1-x)}\text{Se}_{2x}} - E_g^{\text{MoS}_2}}{E_g^{\text{MoSe}_2} - E_g^{\text{MoS}_2}} \quad (6.6)$$

Figure 6.18. Calculated fundamental band gap shift of $\text{MoS}_{1.5}\text{Se}_{0.5}$ (GVJ-2e QP band gap) and lattice parameter shift (PZ LDA) from MoS_2 values towards MoSe_2 .

Let's consider $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with $x=0.25$. From **Figure 6.18** and **Table 6.1** could be noted that lattice constant of the $\text{MoS}_{1.5}\text{Se}_{0.5}$ is almost independent from Se atoms positions for particular substitution rate, while the band gap is very sensitive to Se atoms positions. The case when Se atoms are located on a single plane corresponds to the band gap of about 2.32 eV, while the distribution of Se atoms between planes corresponds to band gap values close to 2.37 eV. The configurations where both Se atoms are concentrated at one plane (*t1t4* and *t1t2, b2b4*) have a higher band gap shift towards MoSe_2 band gap. For TMD monolayers the experimental fundamental band gap are 2.40 eV, 2.5 eV for MoS_2 , and 2.18 eV for MoSe_2 [172], [179], [180]. We have obtained Boltzmann average value of the fundamental band gap 2.35 eV for $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy, using the calculated probability distribution function (**Table 6.7**). As expected the calculated GJV-2e fundamental band gap of $\text{MoS}_{1.5}\text{Se}_{0.5}$ alloy lies in the range between MoS_2 and MoSe_2 band gaps. The similar trends are observed for substitution rates x from 0 to 1.

Table 6.7. Calculated fundamental band gap (GVJ-2e QP), LDA2e band gap, and correction terms ($E_{(1,0)}^{(\infty,xc)} - E_{(2,0)}^{(\infty,xc)}$ and Δ_{xc}^{∞}) of $MoS_{2(1-x)}Se_{2x}$ alloy.

1L	GVJ-2e QP	LDA2e	$E_{(1,0)}^{(\infty,xc)} - E_{(2,0)}^{(\infty,xc)}$	Δ_{xc}^{∞}
MoS₂	2.39	2.66	0.33	-0.17
MoS_{1.75}Se_{0.25} (x=0.125)	2.37	2.61	0.30	-0.15
<i>tl</i>	2.37	2.61	0.30	-0.15
MoS_{1.5}Se_{0.5} (x=0.25)	2.35	2.56	0.26	-0.13
<i>tlb3</i>	2.37	2.57	0.26	-0.13
<i>tlb4</i>	2.37	2.57	0.26	-0.13
<i>t2b3</i>	2.37	2.57	0.25	-0.13
<i>tlb1</i>	2.34	2.55	0.25	-0.13
<i>tlt4</i>	2.33	2.53	0.26	-0.13
<i>tlt2</i>	2.33	2.53	0.26	-0.13
<i>b2b4</i>	2.32	2.53	0.27	-0.13
MoS_{1.25}Se_{0.75} (x=0.375)	2.28	2.50	0.29	-0.14
<i>tlb3_b4</i>	2.28	2.51	0.29	-0.14
<i>tlb3_b2</i>	2.29	2.51	0.29	-0.14
<i>tlb3_t4</i>	2.29	2.51	0.29	-0.14
<i>tlb3_t2</i>	2.29	2.51	0.29	-0.14
<i>tlb3_t3</i>	2.26	2.49	0.29	-0.14
<i>tlb3_b1</i>	2.26	2.49	0.29	-0.14
<i>tlt2_t3</i>	2.23	2.46	0.29	-0.14
<i>b1b3_b4</i>	2.23	2.46	0.28	-0.14
MoS₁Se₁ (x=0.50)	2.27	2.44	0.21	-0.11
<i>b3b4_tlt2</i>	2.33	2.44	0.14	-0.07
<i>b1b4_t2t3</i>	2.33	2.46	0.17	-0.08
<i>tlb3_b4t3</i>	2.25	2.45	0.24	-0.12
<i>tlb3_b4t4</i>	2.25	2.45	0.24	-0.12
<i>tlb3_b1t3</i>	2.22	2.42	0.24	-0.12
<i>tlb4_b1t4</i>	2.22	2.42	0.24	-0.12
<i>t2b3_b2t3</i>	2.22	2.42	0.24	-0.12
<i>tlb3_b4b2</i>	2.26	2.45	0.24	-0.12
<i>tlb3_b4b1</i>	2.23	2.43	0.25	-0.12
<i>tlt2_t3t4 (SMoSe)</i>	2.23	2.39	0.19	-0.10
MoS_{0.75}Se_{1.25} (x=0.625)	2.24	2.37	0.16	-0.08
<i>tlb3_b4t2_t4</i>	2.25	2.39	0.18	-0.09
<i>tlb3_b4t2_t3</i>	2.25	2.39	0.18	-0.09
<i>tlb3_b4t2_b1</i>	2.26	2.36	0.12	-0.06
<i>tlb3_b4t2_b2</i>	2.26	2.35	0.11	-0.06
<i>tlb3_b4t3_t4</i>	2.21	2.38	0.20	-0.10
<i>tlb3_t3b2_t2</i>	2.21	2.38	0.20	-0.10
<i>b1b2_b3b4_t2</i>	2.21	2.37	0.19	-0.10
<i>tlb3_b4b2_b1</i>	2.23	2.33	0.13	-0.06
MoS_{0.5}Se_{1.5} (x=0.75)	2.23	2.32	0.12	-0.06
<i>tlb3_b4t2_b2t4</i>	2.24	2.33	0.11	-0.06
<i>tlb3_b4t2_b2t3</i>	2.24	2.33	0.11	-0.06
<i>tlb3_b4t2_b1t4</i>	2.24	2.33	0.11	-0.05
<i>tlb3_b4t4_b1t3</i>	2.20	2.31	0.14	-0.07
<i>tlb3_b4t2_t3t4</i>	2.22	2.32	0.12	-0.06
<i>tlb3_b4t2_b2b1</i>	2.22	2.32	0.12	-0.06
<i>tlb3_b4t4_b1b2</i>	2.22	2.32	0.12	-0.06
MoS_{0.25}Se_{1.75} (x=0.875)	2.12	2.30	0.23	-0.11
<i>tlb3_b4t2_b2t4_b1</i>	2.12	2.30	0.23	-0.11
MoSe₂	2.12	2.26	0.17	-0.08

Figure 6.19 plots the dependency of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy fundamental band gap on the substitution rate which is nonlinear. The analysis of the derivative of the fundamental band gap shows that it has two peaks at $x \approx 0.8$ ($X_c(\text{S})$) and $x \approx 0.25$ ($X_c(\text{Se})$) which is very similar to the behavior of the lattice constant derivative.

Figure 6.19. $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy fundamental band gap (QP GVJ-2e) dependency on substitution rate. Absolute value of the derivative of fundamental band gap.

We provide the calculation of the fundamental band gap (see **Figure 6.20**) which should be compared with an experimentally obtained band gap via STS measurement. Unfortunately only limited STS measurements are available for pristine TMD monolayers. Usually from experiment an optical band gap is available (determined from photoluminescence (PL)). It was shown previously [76] that the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy band gaps are mostly in the red part of a visible spectrum (1.65–2.0 eV). For example, PBE calculations [101] give the value of $\text{MoS}_{1.5}\text{Se}_{0.5}$ band gap 1.63 eV, which differs from the experimentally obtained value of 1.79 eV [185] on 0.16 eV (9%).

Figure 6.20. $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy Boltzmann average fundamental band gap for each substitution rate (GVJ-2e QP). Interpolation lines based on experimental and theoretical MoS_2 and MoSe_2 fundamental band gaps (Exp. line and Theory line). $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ fundamental band gap of each configuration for considered substitution rates (GVJ-2e QP conf.) and Boltzmann average for each substitution rate (GVJ-2e QP av.).

We also estimate the optical band gap for $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy at low temperature using $E_g^{PL} = E_g^{QP} - E_{exc.binding}$ equation, where $E_{exc.binding}$ is the exciton binding energy. The theoretical exciton binding energy has been calculated on the basis of BSE theory and equals to 0.501 eV and 0.465 eV for MoS_2 and MoSe_2 monolayers respectively [178]. For the alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ BSE exciton binding energy is not available. So in our case, to estimate the exciton binding energy for $\text{MoS}_{2(1-x)}\text{Se}_2$ alloy, we use the following interpolation equation:

$$E_{exc.binding}^{alloy} = (1 - x)E_{exc.binding}^{MoS_2} + xE_{exc.binding}^{MoSe_2}. \quad (6.7)$$

The interpolated values of $E_{exc.binding}^{alloy}$ for each considered substitution rate of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy are given in **Table 6.8**. Thus for $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy the optical band gap at low temperature ranges from 1.89 eV to 1.65 eV.

It was previously demonstrated that PL spectra of $\text{MoS}_2/\text{MoSe}_2$ depend on temperature [171]. Namely, the intensity of the PL peak increases both for MoS_2 and MoSe_2 and the peak position shifts to lower energy with increasing temperature.

Table 6.8. Fundamental band gap (GVJ-2e QP), exciton binding energy ($E_{exc.binding}$), optical band gap at low temperature (GVJ-2e PL LT) and room temperature (GVJ-2e PL RT), band gap temperature shift ($\Delta E_g^{T,alloy}$) for $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy for substitution rate x . All band gap values are in eV.

1L	x	GVJ-2e QP	$E_{exc.binding}$	GVJ-2e PL LT	$\Delta E_g^{T,alloy}$	GVJ-2e PL RT
MoS_2	0	2.39	0.501	1.89	0.0475	1.84
$\text{MoS}_{1.75}\text{Se}_{0.25}$	0.125	2.37	0.4965	1.87	0.0516	1.82
$\text{MoS}_{1.5}\text{Se}_{0.5}$	0.25	2.35	0.492	1.86	0.0557	1.80
$\text{MoS}_{1.25}\text{Se}_{0.75}$	0.375	2.28	0.4875	1.79	0.0598	1.73
MoS_1Se_1	0.50	2.27	0.483	1.78	0.0639	1.72
$\text{MoS}_{0.75}\text{Se}_{1.25}$	0.625	2.24	0.4785	1.76	0.0679	1.69
$\text{MoS}_{0.5}\text{Se}_{1.5}$	0.75	2.23	0.474	1.76	0.0720	1.68
$\text{MoS}_{0.25}\text{Se}_{1.75}$	0.875	2.12	0.4695	1.65	0.0761	1.58
MoSe_2	1	2.12	0.465	1.65	0.0802	1.57

To estimate the theoretical PL band gap values at room temperature we need to estimate the temperature PL band gap shift. The analytical expression for $E_g(T)$ is lacking, though the origin of the band gap temperature dependence is known [171]. We estimate the PL band gap shift with temperature according to the Equation $\Delta E_g^T = E_g^{LT} - E_g^{RT}$, based on average experimental values of PL for room and low temperature measurements. For MoS_2 and MoSe_2 PL band gap

shifts with temperature are $\Delta E_g^T=0.0475$ eV and $\Delta E_g^T=0.0802$ eV, respectively. For $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy we interpolated the value of PL band gap shift in a similar way to Equation 6.7 and the values are provided in **Table 6.8**. The band gap at room temperature equals $E_g^{RT} = E_g^{LT} - \Delta E_g^T$. The calculated values of the optical band gap at 0 K (PL LT) and room temperature (PL RT) are presented in **Table 6.8**. In **Table 6.8** are provided fundamental band gaps GVJ-2e QP which are Boltzmann average for each alloy substitution rate over considered configurations.

Figure 6.21. Calculated optical band gaps at low and room temperature of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy (GVJ-2e PL LT and GVJ-2e PL RT). Lines are interpolation based on the calculated and experimental optical band gap values of optic of MoS_2 and MoSe_2 (Exp. and Theory lines).

Figure 6.21 plots the dependency of calculated optical band gap at low (and room) temperature over substitution rate (GVJ-2e PL LT and GVJ-2e PL RT). **Figure 6.21** also contains two interpolation lines based on the calculated and experimental optical band gaps of MoS_2 and MoSe_2 . The dependency of the optical band gap of substitution rate is more complex than a linear dependency.

We have also considered the variation of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy optical band gap of substitution rate in the percolation theory framework. **Figure 6.22** illustrates theoretical dependency of the absolute rate of band gap change of the alloy as a function of substitution rate x . From this dependency percolation thresholds $X_c(\text{Se}) \approx 0.25$ and $X_c(\text{S}) \approx 0.2$ were obtained. Calculated percolation threshold values correlate well both with theoretical value $X_c(\text{theory}) = 0.25$ and with percolation threshold values calculated from structural properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy.

Figure 6.22. The rate of optical band gap change as function of substitution rate x . Derivative of experimental PL data is built based on data from ref. [95]. Derivative of theoretical optical band gap is built from calculated PL RT values. $X_c(\text{S})$, $X_c(\text{Se})$ – percolation thresholds for sublattices of S and Se atoms.

For the substitution rates $x < X_c(\text{Se})$ ($x < 0.25$) and $x > 1 - X_c(\text{S})$ ($x > 0.8$) the substitution rate of Se and S atoms correspondingly is low to form connected sublattice. Thus for these substitution rates the rate of band gap change is quite high. For the substitution rates $X_c(\text{Se}) < x < 1 - X_c(\text{S})$ ($0.25 < x < 0.8$)

Se atoms form connected sublattice, and the rate of band gap change is almost constant. For such substitution rates we can consider $\text{MoS}_{2(1-x)}\text{Se}_x$ as a true alloy.

Figure 6.22 also plots the rate of experimental band gap change of $\text{MoS}_{2(1-x)}\text{Se}_x$ alloy as function of substitution rate x . This dependency is calculated using results from PL measurement from literature [95]. It should be highlighted that the peculiarities of both theoretical and experimental dependencies are very similar.

6.2.2 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy projected density of states

We calculate the projected density of states (pDOS) for alloy configurations with minimal energy of formation for each substitution rate. **Figure 6.23** displays projected density of states for each substitution rate. The increase in the substitution rate of Se atoms changes projected density of states of chalcogen and metal states. **Figure 6.23** illustrates that there are more Mo states in the c-band than states of chalcogen. At the same time in the valence band closer to its maximum both metal and chalcogen states input significantly. Such behavior agrees with published band structure by Komsa et al. [76].

Figure 6.23 Projected density of states of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with x ranging from 0 (MoS_2) to 1 (MoSe_2) calculated using PZ LDA.

Figure 6.24 displays the total number of quantum states of S and Se atoms versus the substitution rate x . Unlike the dependency of band gap, the total number of quantum states doesn't have any peculiarities at the percolation

thresholds. Such behavior is explained with the general theorem of quantum mechanics that the total number of quantum states is an invariant and does not depend on the spatial distribution of atoms in the supercell. With the increase of Se atoms in the alloy corresponding number of quantum states increases, while the total number of quantum states from S decreases (as the number of S atoms decreases).

Figure 6.24. Relative number of quantum states per S and Se atoms in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy as function of substitution rate x .

6.2.3 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy band diagrams and Kohn-Sham band gap

Figure 6.25 plots the band diagrams calculated for $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy for different substitution rates (Fermi level is indicated with grey dashed line).

Figure 6.25. $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ 1L alloy Kohn-Sham band diagrams (PZ LDA).

$\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy monolayer is a direct band gap semiconductor and has c-band minimum and v-band maximum located at K point of Brillouin zone similarly to TMD monolayers. Thus substitution of S with Se in the monolayer doesn't lead to the change of band extremum positions in k space and the type of transition. The latter agrees with experimental PL data [95], [185].

Figure 6.26. Kohn-Sham band gap (PBE GGA). Absolute value of derivative of Kohn-Sham band gap as function of substitution rate x . $X_c(S)$ and $X_c(Se)$ are percolation thresholds for sub lattice of S and Se atoms correspondingly.

The calculated values of Kohn-Sham band gap with PZ LDA and PBE GGA underestimate optical band gap for about 0.10 eV and 0.25 eV correspondingly. The calculation of Kohn-Sham band gap variation with substitution rate change reveals its non-linear character (see **Figure 6.26**). Similarly to the case of structural parameters of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy, the rate of Kohn-Sham band gap variation is described with the percolation theory. Determined value $X_c(S, Se) \approx 0.2$ of the percolation threshold is close to the values obtained from analysis of structural parameters and band gap calculated using GVJ-2e method. **Table 6.9** contains calculated Kohn-Sham band gaps of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy.

Table 6.9. Kohn-Sham direct band gap of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy.

1L	x	PZ LDA	PBE GGA
MoS ₂	0	1.817	1.657
MoS _{1.75} Se _{0.25}	0.125	1.784	1.627
MoS _{1.5} Se _{0.5}	0.25	1.753	1.604
MoS _{1.25} Se _{0.75}	0.375	1.721	1.55
MoS ₁ Se ₁	0.5	1.699	1.574
MoS _{0.75} Se _{1.25}	0.625	1.618	1.521
MoS _{0.5} Se _{1.5}	0.75	1.609	1.509
MoS _{0.25} Se _{1.75}	0.875	1.566	1.412
MoSe ₂	1	1.567	1.413

6.2.4 $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy electron and hole effective masses

In solids, owing to the many-particle interactions, the electron is a quasiparticle and thus the electron mass, determined from a number of experiments, differs from the mass of a free electron (m_0) [158]. The effective electron mass (m^*) in solids is usually provided relatively to free electron mass as ratio m^*/m_0 and the deviation of the ratio from 1 ($m^* > m_0$ or $m^* < m_0$) is observed experimentally. In the band theory for the isotropic case the effective mass m^* can be calculated according to the following equation:

$$m^* = \hbar^2 \left(\frac{d^2 E}{dk^2} \right)^{-1}. \quad (6.8)$$

where $\hbar$ is the Planck constant; E is the energy of electron as a function of the wave vector k. Similarly, we can introduce an effective mass of holes. In our case, strictly speaking, we can calculate the effective mass of electrons and holes from the Kohn-Sham band structures. The second derivative of the total energy

should be calculated around c-band minimum (v-band maximum, K point in our case) and could be obtained from the calculated band diagrams for $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy.

Figure 6.27. Effective mass of electron and hole and its derivative as function of substitution rate. Effective mass is given in masses of free electron (m_0).

Figure 6.27 illustrates the variation of the electron and hole effective mass (m^*/m_0) with change of the substitution rate x in the alloy. The maximum of the electron effective mass is observed for $x \approx 0.75$. Practically for the whole region of substitution rate x the electron effective mass is smaller than the free electron mass ($m_e^* < m_0$). It should be also noted that for the substitution rate in the range $0.6 < x_S < 0.9$ ($0.1 < x_{Se} < 0.4$) some peculiarity is observed (electrons become heavier than holes), but more detailed calculations are needed. Comparison of the effective masses of electrons (holes) in the alloy with the effective masses of electrons in MoS_2 and MoSe_2 monolayers reveals that electrons (holes) become slightly heavier in the alloy (see **Figure 6.27**).

Table 6.10. Effective masses of electrons, holes and excitons in MoS₂ and MoSe₂ monolayers. Values are derived from Kohn-Sham band structures obtained from PZ LDA and PBE GGA calculations. Effective masses obtained with G₀W₀, FLAPW + GGA, and HSE are referenced from the literature. All effective masses are in m₀ units (free electron mass).

1L	PZ LDA	PBE GGA	G ₀ W ₀ ^{a)}	FLAPW +GGA ^{b)}	HSE ^{c)}
MoS ₂	m _e * = 0.32 m _h * = 0.41 $\mu_{exc}^{direct} =$ 0.18	m _e * = 0.33 m _h * = 0.40 $\mu_{exc}^{direct} =$ 0.18	m _e * = 0.55 m _h * = 0.56 $\mu_{exc}^{direct} =$ 0.28	m _e * = 0.48 m _h * = 0.64 ($\mu_{exc} =$ 0.27)	m _e * = 0.37 m _h * = 0.44 ($\mu_{exc} =$ 0.20)
MoSe ₂	m _e * = 0.40 m _h * = 0.50 $\mu_{exc}^{direct} =$ 0.22	m _e * = 0.42 m _h * = 0.49 $\mu_{exc}^{direct} =$ 0.23	m _e * = 0.49 m _h * = 0.61 $\mu_{exc}^{direct} =$ 0.27		

^{a)} Ref. [148]; ^{b)} Ref. [186]; ^{c)} Ref. [187].

We have obtained the following effective masses in MoS₂ monolayer: m_e*=0.33m₀ and m_h*=0.40m₀ (μ_{exc}^{direct} =0.18m₀) and in MoSe₂ are m_e*=0.42m₀ and m_h*=0.49m₀ (μ_{exc}^{direct} =0.23m₀) from Kohn-Sham band structure calculated using PBE GGA (see **Table 6.10**). The exciton effective mass was calculated from the effective masses of electron and hole according to $\mu_{exc}^{-1} = (m_e^*)^{-1} + (m_h^*)^{-1}$ equation. The comparison with literature demonstrates that our values of the effective masses of electrons, holes, and excitons agree with the results obtained from HSE calculation [187]. The comparison with G₀W₀ results shows that KS PBE GGA gives smaller values of the effective masses of electrons and holes [148]. Nevertheless, similarly to G₀W₀ and HSE calculations in MoS₂ and MoSe₂ monolayers electrons are lighter than holes. Such relationship (m_e* < m_h*) remains also in MoS_{2(1-x)}Se_{2x} alloy. Also in our calculations for MoS₂ and MoSe₂

monolayers (KS with PBE GGA and PZ LDA) both electrons and holes have effective masses smaller than a free electron mass, which agrees well with results obtained with G_0W_0 and HSE [148], [187].

The values of the effective masses in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ are in the range between effective masses of electrons (holes) in pure MoS_2 and MoSe_2 monolayers.

6.3 Conclusions

In this chapter, we performed a complete analysis of the structure, energy of formation and electronic properties of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy for substitution rate from 0% to 100% (namely 12.5%, 25%, 37.5%, 50%, 62.5%, 75%, 87.5%, 100%). Based on the analysis performed, the following main conclusions can be drawn.

Structure

Different distributions of the substitution atoms (Se in MoS_2 matrix) in the supercell of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy for the substitution rates ($0 \leq x \leq 1$) have been studied. The analysis revealed that the probability of formation of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with the asymmetry parameter $s \approx 0$ is about 0.9 for the entire region of variation of the substitution rate (x). Thus, the most likely structural arrangement of atoms (Se, S) in alloy during the synthesis is a structure with a symmetric filling of the top and bottom chalcogen planes.

Energy of formation, bond length and lattice constant

A detailed analysis of the formation energy of the alloy demonstrated that the range of substitution rate x splits on the region with a negative ($x < 0.65$) and positive ($x > 0.65$) formation energy of the alloy. The energy of formation of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy reaches its minimum at the substitution rate $x \sim 0.5$.

The free energy of the alloy for the whole substitution rate x range has been calculated. It is shown that an inhomogeneous structure of the alloy can be

formed during the synthesis for substitution rates of Se atoms $x < 0.5$, which is confirmed by the analysis of experimental PL spectra of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy.

We also analyzed the substitution rate dependence of the lattice constant of the alloy. For the entire range of substitution rates, a deviation from a linear substitution rate dependence is observed, due to the negative energy of formation of the alloy.

Electronic properties

The analysis of electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy included calculations of fundamental and optical band gap, projected density of states, band structures and effective masses.

The calculated Kohn-Sham band structures suggest that $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy is a direct gap semiconductor, similarly to the MoS_2 and MoSe_2 monolayers. With the variation of substitution rate of Se atoms (x) from 0 to 1 in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy c-band minimum and v-band maximum gradually shift from respective positions in MoS_2 to MoSe_2 . It is also demonstrated that PBE GGA Kohn-Sham band gaps significantly underestimate optical band gap of the alloy (for about 0.25 eV), while PZ LDA Kohn-Sham band gaps deviate for about 0.10 eV from experimental values.

The analysis of the projected density of states shows that around c-band minimum more metal states present, while around v-band maximum the number of metal (Mo) and chalcogen (S and Se) states are comparable. The gradual increase in substitution rate of S with Se in the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy leads

respectively to the gradual increase in the number of Se states comparing to the number of S states.

The fundamental and optical band gap of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy were calculated using recently proposed GVJ-2e method. The GVJ-2e fundamental band gaps of the alloy are in the range of 2.39 eV – 2.12 eV (GVJ-2e fundamental band gaps of MoS_2 and MoSe_2 monolayers).

The optical band gaps of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer were calculated from GVJ-2e fundamental band gaps with account of interpolated exciton binding energies. For the substitution rate x in the range from 0 to 1, the calculated optical band gap of the alloy agrees well with the experimental ones obtained from the analysis of the PL spectra. The dependency of the band gap on the substitution rate deviates from linear.

The electron states and effective masses of the electrons and holes of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($0 < x < 1$) alloy have been calculated from Kohn-Sham band structures. For effective masses of holes and electrons, the ratio $m_{e,h}^*(\text{MoS}_2) < m_{e,h}^*(\text{alloy}) < m_{e,h}^*(\text{MoSe}_2)$ is satisfied practically for the entire substitution rate range x . And also for most of the Se substitution rates the following relationship is observed $m_e^* < m_h^* < m_0$ (where m_0 is free electron mass).

Percolation theory

It is shown that the physics of the formation of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy is well described within the framework of the percolation theory. The characteristic values of the percolation thresholds for the formation of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy are determined. It is shown that the behavior of the formation energy of the alloy

is described by the percolation theory for the *sites* problem of flow through lattice. The calculated value of the percolation threshold $X_c \approx 0.4$ lies in the interval of theoretical values of the percolation thresholds for the square ($X_c \approx 0.57$) and cubic ($X_c \approx 0.3$) lattices. This fact is due to the quasi-two-dimensionality of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy.

The nonlinear behavior of the lattice constant of the alloy and the width of the band gap is described by the percolation theory for the lattice *bond* problem. The following values of the percolation thresholds $X_c(\text{Se}) \approx 0.25$ and $X_c(\text{S}) \approx 0.2$ were obtained. Calculated percolation threshold values correlate well with theoretical value $X_c(\text{theory}) = 0.25$.

The calculated behavior of the band gap of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy on the substitution rate x is in good agreement with the experimental dependence obtained on the basis of the analysis of the PL spectra.

Based on the analysis of the substitution rate dependence of the physical properties of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy, it was shown that for the $x < 0.25$ substitution rates, the alloy is a heavily doped semiconductor and only for substitution rates exceeding $x \sim 0.25$ is the formation of the proper $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy.

Chapter 7. Conclusions and Future Plans

7.1 Conclusions

Transition metal dichalcogenides monolayers are promising materials for many applications in electronics and optoelectronics. And exploration of their properties is performed both theoretically and experimentally. Although structural properties are quite often in a good agreement with experimental results, the same is not always true for electronic properties. Among widely used approximations LDA and PBE tend to produce optical band gaps deviating significantly from experimentally measured with PL. The same is true when hybrid functionals (ex. HSE) are used. In TMD monolayers the excitons have large binding energies (~ 0.5 eV), thus fundamental band gap differs significantly from an optical band gap. The calculation of the fundamental band gap is usually performed with GW, and calculated band gaps could differ sometimes for more than 30 % from experimentally measured. Usually STS measurement is used to obtain the fundamental band gap in monolayer TMDs experimentally, and results of such measurements are available only for selected monolayers. Moreover it is well known that GW calculations are computationally very expensive. Another important drawback of the available methods for band gap calculation is the lack of correlation in accuracy for traditional materials and for 2D structures. Quite often methods which accurately predict band gaps for bulks, can underestimate band gaps for 2D materials. Thus accurate theoretical exploration of electronic properties (and especially of the band gap) of emerging materials is a very challenging task.

The thesis focused (1) on implementing the general method for accurate band gap calculations, and (2) on theoretical exploration of structural and electronic properties of transition metal dichalcogenides in their bulk and monolayer forms and (3) $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy.

1. *GVJ-2e method for band gap calculation*

The proposed *GVJ-2e method* for the band gap calculation is developed within DFT framework and is based solely on the total energy calculations. The GVJ-2e method is adjustable parameters free. The method suggests that a non-local part of the exchange-correlation energy plays a significant role in the band gap calculation.

The application of the method on traditional bulk semiconductors (ex. Si, Ge, C, etc.) and wide gap insulators (ex. Xe, Kr) demonstrated a good agreement of the theoretical band gap with experimental one. For proposed GVJ-2e method mean absolute error (MAE) is 0.08 eV which is the smallest among mean absolute errors given by other methods: 0.51 eV (GW), 0.14 eV (HSE), 0.52 eV (MBJLDA), and 2.26 eV (LDA). Mean absolute percentage deviation (MAPD) for GVJ-2e method is even more impressive and is 3 %, while other methods have 19 % (GW), 10 % (HSE), 9 % (MBJLDA), and 50 % (LDA).

2. *Bulk and monolayer MoS_2 , MoSe_2 , WS_2 , WSe_2*

The structural and electronic properties of bulk and monolayer TMDs (MoS_2 , MoSe_2 , WS_2 , WSe_2) were studied. The calculated relaxed lattice constants of bulk TMDs deviated from experimentally obtained for less than 2 %.

The analysis of the calculated *Kohn-Sham band structures* of bulk and monolayer MoS₂, MoSe₂, WS₂, WSe₂ confirms the transition from the indirect band gap in bulk to direct band gap in monolayer. The investigation of the projected density of states (*pDOS*) suggests that more metal states present around c-band minimum, while around v-band maximum the numbers of metal and chalcogen states are comparable (for both monolayer and bulk).

The calculated *fundamental band gaps* with GJV-2e method for considered TMDs are in good agreement with available STS measurements. The *optical band gaps* were calculated from the fundamental band gaps with consideration of exciton binding energies. The obtained optical band gaps of MoS₂, MoSe₂, WS₂, WSe₂ are in good agreement with PL measurements.

The mean absolute error (MAE) of GJV-2e *fundamental band gaps* of bulk and monolayer TMDs is 0.06 eV, which overcomes MAE of GW (0.23 eV) and G₀W₀ (0.09 eV) methods. For the GJV-2e *optical band gaps* (calculated from GJV-2e fundamental band gaps) MAE is 0.04 eV, which is lower than MAE of other widely used methods such as HSE 0.17 eV, TB-mBJ 0.14 eV, and sX 0.11 eV.

3. **Monolayer alloy MoS_{2(1-x)}Se_{2x}**

For the MoS_{2(1-x)}Se_{2x} monolayer alloy the entire range of substitution rates from 0% to 100% of Se substitution atoms was considered. The study of the *structural properties* of MoS_{2(1-x)}Se_{2x} alloy revealed that almost symmetric distribution of Se atoms between top and bottom chalcogen planes in MoS₂ matrix is energetically more favorable. Thus the

configurations of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy with most of Se atoms concentrated on a single plane are less likely to occur during the growth. The analysis of the lattice constant in the framework of the percolation theory (bond problem) revealed two percolation thresholds for Se and S sublattices: $X_c(\text{Se}) \approx 0.25$ and $X_c(\text{S}) \approx 0.2$.

The analysis of the *energy of formation* revealed the presence of the two regions of substitution rates: with *negative* energy of formation ($x < 0.65$) and *positive* ($x > 0.65$, corresponds to 65% of S atoms substituted by Se). The energy of formation reaches its *minimum* at the substitution rate $x \sim 0.5$ (50% of S atoms are substituted by Se). From the analysis using the percolation theory for the sites problem, percolation threshold $X_c \approx 0.4$ is obtained. Such value lies in the interval of the theoretical values of the percolation thresholds for the square ($X_c \approx 0.57$) and cubic ($X_c \approx 0.3$) lattices. This fact is due to the quasi-two-dimensionality of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy. For the substitution rates of Se atoms smaller than 0.5 ($x < 0.5$), $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy has *inhomogeneous structure*, which is confirmed from analysis of the PL peak width.

The investigation of the *electronic properties* of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy confirms the presence of the direct band gap. The calculated fundamental band gap of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ is in the range of the fundamental band gaps of MoS_2 and MoSe_2 monolayers. The calculated optical band gaps of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ agree with experimentally measured PL peaks. Also a non-linear dependency of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloy band gap of substitution rate x is revealed.

The study of the *holes* and *electrons effective masses* (m_e^* , m_h^*) from the calculated Kohn-Sham band structures of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ suggests that for most of the substitution rates (x) $m_e^* < m_h^* < m_0$ (where m_0 is free electron mass). Such results agree with HSE and G_0W_0 calculations.

Finally, the proposed GVJ-2e method could be effectively used for the band gap prediction of both 3D and 2D materials (without inner limitations on the chemical composition). Accuracy and computational efficiency of GVJ-2e method enables using it for search and exploration of new materials (both 3D and 2D) with desired electronic properties. The careful theoretical study of structural and electronic properties of bulk and monolayer TMDs, and $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy provides accurate description of their structural and electronic properties. And also our study demonstrates the possibility of band gap engineering within monolayer by variation of its chemical composition.

7.2 Future Plans

Future work could consider further application of the developed method for the band gap calculation (GVJ-2e) for another TMD alloys (for ex. MoWS_2 , where metal atoms of Mo are substituted with W) and new 2D materials. And also electronic properties of recently emerging mixed-dimensional (2D + nD, where n is 0, 1 or 3) heterostructures could be studied. GVJ-2e method not only allows to obtain the band gap of material under investigation, but is also capable to correctly predict electronic properties of materials with defects. Thus another

area of research could be defects in 2D materials (ex. chalcogen vacancy in pure monolayer TMDs and their alloys).

The GVJ-2e method was verified on semiconductors (Si, Ge, C etc.) and wide gap insulators (Xe, Ne, Ar, Kr). Nevertheless GVJ-2e method, as a new method, will be verified also on nonmagnetic metal oxides, strong correlated materials, and (anti) ferromagnetic insulators. Also the theoretical study of structural and electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy could be continued for more substitution rates. Particularly substitution rates $x=0.7$ and $x=0.8$ could be considered to study in more details effective masses of electrons and holes in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer alloy.

7.3 Publications and conferences

Journal articles

1. **J. Gusakova**, V. Gusakov, B. K. Tay, “General approach for band gap calculation of semiconductors and insulators”, *Phys. Status Solidi A* 213, 2834–2837 (2016).
2. **J. Gusakova**, X. Wang, L. L. Shiau, A. Krivosheeva, V. Shaposhnikov, V. Borisenko, V. Gusakov, B. K. Tay , “Electronic Properties of Bulk and Monolayer TMDs: Theoretical Study Within DFT Framework (GVJ-2e Method)”, *Phys. Status Solidi A* 214, 1700218 (2017).
3. **J. Gusakova**, V. Gusakov, B. K. Tay, “DFT study of structural and electronic properties of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($x=0.25$)”, *J. Appl. Phys.*, 123, 161594, (2018).

Conferences

1. **J. Gusakova**, B. K. Tay, V. Gusakov, “Efficient DFT method for calculating band gap and deep levels in semiconductors”, 28th International Conference on Defects in Semiconductors (ICDS), July 27-31, 2015, Helsinki, Finland.
2. **J. Gusakova**, B. K. Tay, V. Gusakov, “General approach for band gap calculation for semiconductors and insulators”, European Materials Research Society (E-MRS), Spring Meeting, May 2-6, 2016, Lille, France (Best Poster in Section Award).
3. **J. Gusakova**, B. K. Tay, X. Wang, L. L. Shiau, V. E. Gusakov , V. E. Borisenko, “Band gap calculation of bulk and monolayer TMDs with new

GVJ-2e approach within DFT framework”, Nanomeeting, 30 May -2 June,
2017, Minsk, Belarus

Appendix A

Convergence with respect to kinetic energy cutoff

The kinetic energy cutoff is a mandatory parameter of DFT computation in Quantum Espresso package. Essentially cutoff energy is a property of used pseudopotential for a corresponding atom. We have considered convergence of the total energy per atom with respect to the kinetic energy cutoff for PZ LDA and PBE GGA pseudopotentials. **Figure A1** demonstrates that the total energy per atom converges with respect to the kinetic energy cutoff for PBE and LDA pseudopotentials.

Figure A1. Total energy per atom versus cutoff energy for bulk MoS_2 in PZ LDA and PBE GGA (paw pseudopotentials).

The same value of the kinetic energy cutoff should be used if one needs to compare the results obtained using different exchange-correlation energy approximations and pseudopotentials. We used the kinetic energy cutoff of 40 Ry (MoS_2 and MoSe_2) and 50 Ry (WS_2 and WSe_2) in the following calculations of structural and electronic properties of both bulk and monolayer structures.

Convergence with respect to k-points

We consider different k meshes in order to investigate the convergence with respect to number of k points. Brillouin zone was sampled using Monkhorst-Pack approach [67]. The meshes have different number of irreducible k points. It should be mentioned that computation time increases with increase in number of k points used. The bigger dimensions in real space correspond to smaller dimensions in the reciprocal space. To find the mesh $k_x \times k_y \times k_z$ with optimal total number of k points we analyzed the total energy per atom versus number k points. When the change in the total energy per atom is less than 0.01 eV, the smallest corresponding number of k points was selected.

Figure A2. Total energy per atom versus number of k points for bulk WS_2 (PZ LDA and PBE GGA).

For bulk TMDs we consider meshes with 7, 42, 86, 219, 333, 628 k points. **Figure A2** plots the dependency of the total energy per atom versus number of k points for bulk WS_2 for LDA and PBE exchange-correlation energy approximations. For bulk TMDs the variation of total energy per atom is much less than 0.01 eV for 42 and more k points for both PZ LDA and PBE GGA

approximations. We will further use the mesh with 86 irreducible k points (12x12x3) for both PZ LDA and PBE GGA calculations.

There is a difference between meshes used in k space for bulk materials and for monolayers. For monolayers along the z direction (perpendicular to the layer) should be used $k_z = 1$, so the mesh $k_x \times k_y \times k_z$ will take the form $k_x \times k_y \times 1$, where $k_x = k_y = N$. In order to study the convergence we will vary N from 4 till 16, and corresponding number of irreducible k points will range from 7 to 73.

Figure A3. Total energy per atom versus number of k points for monolayer WS₂ (PZ LDA and PBE GGA).

Figure A3 demonstrates convergence of the total energy per atom versus number of k points for WS₂ monolayer. For TMD monolayer the variation of the total energy per atom is much less than 0.01 eV for 13 and more k points for both PZ LDA and PBE GGA approximations. The similar dependencies are observed also for MoS₂, MoSe₂, WSe₂. We will further use the mesh with 31 irreducible k points (10×10×1) for calculations using PZ LDA and PBE GGA pseudopotentials and approximations. Thus the resulting k points meshes of 12×12×3 (bulk TMDs) and 10×10×1 (monolayer TMDs) will be used in further calculations.

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