

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**THEORY OF SPINTRONICS IN LATERAL AND VERTICAL
HETEROSTRUCTURES OF MONOLAYER
TRANSITION–METAL DICHALCOGENIDES**

MEHMET ARAS
A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF PHYSICS

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

TEK KATMANLI GEÇİŞ–METALİ
DİKALKOJENLERİNİN YANAL VE
DİKEY HETEROYAPILARINDA
SPİNTRONİK TEORİSİ

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GEBZE
2022



DOKTORA JÜRİ ONAY FORMU

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 07/02/2022 tarih ve 2022/08 sayılı kararıyla oluşturulan jüri tarafından 25/02/2022 tarihinde tez savunma sınavı yapılan Mehmet ARAS'ın tez çalışması Fizik Anabilim Dalında DOKTORA tezi olarak kabul edilmiştir.

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...../...../..... tarih ve/..... sayılı kararı.

SUMMARY

Electronic and magnetic properties of various forms of lateral (in-plane) and vertical (van der Waals) heterostructures constructed from transition-metal dichalcogenide monolayers viz.; semiconducting MoTe_2 , metallic NiTe_2 , and half-metallic FeTe_2 have been investigated using the ab-initio calculations. The objectives are to reveal the effects of size and dimensionality of constituents on the electronic and magnetic structures of the heterostructures and composite materials. The heterostructures composed of semiconducting MoTe_2 and metallic NiTe_2 display a number of electronic properties ranging from composite metals to metal-semiconductor junctions with a tunable Schottky barrier. Besides, true magnetic ground states of FeTe_2 , VS_2 , and NiTe_2 monolayers, which comprise inhomogeneous magnetic moment configurations are revealed. In contrast to earlier studies considering only the magnetic moments of transition-metal atoms, the chalcogen atoms by themselves have significant, antiparallel magnetic moments, which is reminiscent of ferrimagnetic order, owing to the spin polarization through p - d hybridization. The lateral heterostructures formed from the stripes of magnetic FeTe_2 and NiTe_2 constituents are found to be half-metallic within both constituent stripes. Half-metallicity spreads from the FeTe_2 side of the junction to the adjacent NiTe_2 side, which is metallic when stand-alone, through strong Fe-Te-Ni bonds at the boundary. In contrast, in the thin, vertical heterostructures, where the interlayer coupling is rather weak, the half-metallic character is retained only in the FeTe_2 side; the NiTe_2 side remains a spin-polarized metal. Hence, these vertical heterostructures form a semiconductor-metal junction with a Schottky barrier for one spin direction to function as a diode or spin valve, but a metal-metal junction for the opposite spin direction to function as a conductor.

Key Words: Transition-Metal Dichalcogenides, Lateral and Vertical Heterostructure, Schottky Barrier, Half-Metallicity, Ferrimagnetic, Spintronic.

ÖZET

Tek katmanlı geiş–metali dikalkojenleri; yarıiletken MoTe_2 , metalik NiTe_2 ve yarı–metalik FeTe_2 , ile oluşturulan çeşitli biçimlerde yanal (düzlem–ii) ve dikey (van der Waals) heteroyapıların elektronik ve manyetik özellikleri ab–initio hesaplamaları kullanılarak incelenmiştir. Hedefimiz, bileşenlerin büyüklük ve boyutsallığının heteroyapıların ve kompozit malzemelerin elektronik ve manyetik yapıları üzerindeki etkilerini ortaya çıkarmaktır. Yarıiletken MoTe_2 ve metalik NiTe_2 ’den oluşan heteroyapılar, kompozit metallere ayarlanabilir Schottky bariyerli metal–yarıiletken eklemlerine kadar bir dizi elektronik özellik göstermektedir. Bunun yanında, tek katmanlı FeTe_2 , VS_2 ve NiTe_2 geiş metali dikalkojenlerinin gerçek manyetik temel durumları olarak, homojen olmayan manyetik moment konfigürasyonlarına sahip olduğu ortaya çıkarılmıştır. Yalnızca geiş–metali atomlarının manyetik momentlerini dikkate alan daha önceki çalışmaların aksine, kalkojen atomları, p – d hibridizasyonu yoluyla spin polarizasyonu sonucu, ferrimanyetik düzeni andıran, kendi başlarına önemli, antiparalel manyetik momentlere sahiptir. Manyetik FeTe_2 ve NiTe_2 şeritlerinden oluşturulan yanal heteroyapılar, her iki bileşen şerit için de yarı–metalik olduğu bulunmuştur. Yarı–metaliklik, eklemin FeTe_2 tarafından sınırdaki güçlü Fe–Te–Ni bağları yoluyla, tek başına metalik olan bitişik NiTe_2 tarafına yayılır. Buna karşılık, ara katman etkileşimlerinin oldukça zayıf olduğu, ince dikey heteroyapılarda, yarı–metalik karakter sadece FeTe_2 tarafında korunurken; NiTe_2 tarafı ise spin–polarize metal olarak kalır. Bu nedenle, bu dikey heteroyapılar, bir spin yönü için diyot veya spin vanası olarak işlev gören Schottky bariyeri ile yarıiletken–metal eklemi oluştururken, zıt spin yönü için ise iletken olarak işlev gören bir metal–metal bağlantısı oluşturmaktadır.

Anahtar Kelimeler: Geiş–Metali Dikalkojenleri, Yanal ve Dikey Heteroyapılar, Schottky Bariyeri, Yarı–Metaliklik, Ferrimanyetik, Spintronik.

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude and respect to my supervisor Prof. Çetin KILIÇ for his extensive patience, guidance, motivation, encouragement, and continuous support throughout my PhD study and research.

I should also express my sincere appreciation to Prof. Salim ÇIRACI for giving me the opportunity to work under his supervision with his great inspiration, motivation and immense knowledge.

I would like to thank my thesis committee members Prof. F. Necati Ecevit, Prof. Savaş Berber, Assoc. Prof. H. Hakan Gürel, and Assoc. Prof. Doğan Erbahar for their support and understanding.

I am thankful to my groupmates Dr. Sümeyra Güler-Kılıç and Yunus Emre Okyaylı for their continuous support, and invaluable discussions in our group meetings.

I would like to extend my special thanks to my colleagues Dr. Yasin Şale, and Serdar Gören. I will always remember the good times we shared and I hope our friendship will last a lifetime.

Last but not the least, I am grateful to my parents, sister, nephew and nieces for their presence, endless love and trust. Dad and Mom, I would like to thank you once again for everything you did for me.

The numerical calculations reported in this thesis were performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources) and the National Center for High Performance Computing of Turkey (UHeM) under grant number 4005032018.

TABLE of CONTENTS

	<u>Page</u>
SUMMARY	v
ÖZET	vi
ACKNOWLEDGEMENT	vii
TABLE of CONTENTS	viii
LIST of ACRONYMS and ABBREVIATIONS	x
LIST of FIGURES	xvii
LIST of TABLES	xx
 1. INTRODUCTION	 1
1.1. The Scope and Content of the Thesis	5
2. METHOD	11
2.1. Density Functional Theory (DFT)	11
2.1.1. Local Density Approximation (LDA)	13
2.1.2. Generalized Gradient Approximations (GGA)	18
2.1.3. Strong Correlation Effect and LDA+ <i>U</i> Method	19
2.1.4. Heyd–Scuseria–Ernzerhof (HSE) Hybrid Functional	20
2.2. Computational Details	21
3. RESULTS AND DISCUSSIONS	23
3.1. Planar Heterostructures of Transition–Metal Dichalcogenides:	
MoTe ₂ /NiTe ₂	23
3.1.1. 2D Single Layer Transition–Metal Dichalcogenides:	
MoTe ₂ and NiTe ₂	23
3.1.2. Atomistic Model and Stability	25
3.1.3. MoTe ₂ /NiTe ₂ Composite Structures: δ –Doping	29
3.1.4. MoTe ₂ /NiTe ₂ Heterostructure: Schottky Barrier	31
3.1.5. Single Metal–Semiconductor Junction and Tunneling Barrier	37
3.2. Lateral and Vertical Heterostructures of Transition–Metal	
Dichalcogenides of MoTe ₂ /NiTe ₂	40
3.2.1. Atomistic Models and Energetic Stability	40
3.2.2. Lateral Heterostructures of MoTe ₂ /NiTe ₂	43

3.2.3. Vertical Heterostructures of $\text{MoTe}_2/\text{NiTe}_2$	48
3.3. Magnetic Ground State in FeTe_2 , VS_2 , and NiTe_2 Monolayers	55
3.3.1. Inhomogeneous Spin Arrangement:	
Antiparallel Magnetic Moments at Chalcogen Atoms	55
3.3.2. Electronic Structures of FeTe_2 , VS_2 , and NiTe_2 Monolayers	66
3.4. Magnetic Heterostructures of Transition–Metal Dichalcogenides:	
$\text{FeTe}_2/\text{NiTe}_2$	74
3.4.1. FeTe_2 and NiTe_2 Monolayers	74
3.4.2. Armchair Lateral Heterostructures of $\text{FeTe}_2/\text{NiTe}_2$	76
3.4.3. Vertical Heterostructures of $\text{FeTe}_2/\text{NiTe}_2$	83
4. CONCLUSIONS	85
REFERENCES	92
BIOGRAPHY	107
APPENDICES	108

LIST of ACRONYMS and ABBREVIATIONS

<u>Acronyms and Abbreviations</u>	<u>Descriptions</u>
$\text{\AA}$	: Angstrom
$\bar{\rho}$	: Averaged charge
$\Delta\bar{\rho}$	: Averaged charge transfer
σ	: Conductivity
ΔN	: Electronic Charge
δ	: Delta
ϵ	: Strain
Φ_B	: Tunneling Barrier
ϕ	: Work Function
eV	: Electron Volt
E_C	: Cohesive Energy
E_f	: Formation Energy
E_{jf}	: Junction Formation Energy
E_T	: Total Energy
E_S	: Schottky Barrier
E_g	: Band Gap
E_{CB}	: Conduction Band Edge
E_{VB}	: Valence Band Edge
E_F	: Fermi Level
K	: Kelvin
μ	: Magnetic Moment
μ_B	: Bohr Magneton
M_{SC}	: Supercell Magnetic Moment
T	: Temperature
T_C	: Curie Temperature
V_{macro}	: Macroscopic Potential
$\bar{V}$	: Plane averaged potential
A	: Lateral Heterostructure with Armchair Interface
BL	: Bilayer

CBM	: Conduction Band Maximum
DDEC	: Density Derived Electrostatic and Chemical Approach
DFT	: Density Functional Theory
DOS	: Density of States
D3	: Grimme Dispersion Correction
G	: Conductance
HK	: Hohenberg–Kohn
HSE	: Heyd–Scuseria–Ernzerhof Hybrid Functional
KS	: Kohn–Sham
LDA	: Local Density Approximation
LDOS	: Local Density of States
LSDA	: Local Spin Density Approximation
MAE	: Magnetic Anisotropy Energy
MD	: Molecular Dynamics
ML	: Multilayer
PBE	: Perdew–Burke–Ernzerhof
PDOS	: Projected Density of States
SL	: Single Layer
SOC	: Spin Orbit Coupling
TL	: Trilayer
TMDC	: Transition Metal Dichalcogenides
TF	: Thomas–Fermi
U	: Effective Hubbard Parameter
V	: Vertical Heterostructure
VASP	: Vienna Ab initio Simulation Package
VBM	: Valence Band Maximum
vdW	: van der Waals
Z	: Lateral Heterostructure with Zigzag Interface

LIST of FIGURES

<u>Figure No:</u>	<u>Page</u>
1.1: Top and side views of the atomic structure of (a) H - and (b) T -phase 2D monolayer transition-metal dichalcogenides (TMDCs). The primitive unit cells are delineated and have Bravais lattice vectors $\vec{a}$ and $\vec{b}$ ($ \vec{a} = \vec{b} $).	2
2.1: Schematic representation of the self-consistent solution of the Kohn-Sham equations.	16
3.1: (a) Top and side views of the optimized atomic structure of 2D SL transition-metal dichalcogenides, MoTe_2 and NiTe_2 . The layer thickness is denoted by Δ . The rectangular unit cell is delineated and has lattice constants a and b . (b) The electronic energy bands are calculated within the LSDA using the optimized atomic structures. The zero of energy of the semiconducting MoTe_2 is set at its intrinsic Fermi level.	24
3.2: (a) Top and side views of atomistic model of SL, inplane composite structures $Z:S_p/M_q$ with $p = 20$, $q = 10$. The 2D rectangular unit cell with Bravais lattice vectors $\vec{a}$ and $\vec{b}$ is delineated by thin lines. Two types of boundaries having zigzag edge geometry between NiTe_2 and MoTe_2 stripes are indicated by I_I and I_{II} . The xz -plane averaged self-consistent charge density $\bar{\rho}(y)$ corresponds to the optimized structure. (b) Trajectories of atoms $Z:S_p/M_q$ in the xy - and yz -planes attained from the average position of atoms in each 100 steps in the course of ab initio MD iterations at $T = 500$ K. (c) Variation of the temperature T and average temperature T versus MD steps running at $T = 500$ K. (d)–(f) Same for $A:S_p/M_q$.	26
3.3: Energy bands of specific composite structures. (a) $Z:S_2/M_2$, a line compound of MoTe_2 and NiTe_2 , showing a metallic state. (b) $Z:S_{20}/M_2$, stripes of semiconducting $(\text{MoTe}_2)_{20}$ which are δ -doped by narrow metallic $(\text{NiTe}_2)_2$ stripes along their zigzag edges. Metallic bands are localized in the M stripe. (c) $A:S_{20}/M_2$, in which stripes of	

semiconducting $(\text{MoTe}_2)_{20}$ are δ -doped by narrow metallic $(\text{NiTe}_2)_2$ stripes along their armchair edges is a narrow band gap semiconductor. 30

3.4: The xz -plane averaged charge density $\bar{\rho}(y)$ and charge transfer $\Delta\bar{\rho}(y)$ in $\text{Z:S}_{20}/\text{M}_{10}$ (a) and in $\text{A:S}_{20}/\text{M}_{10}$ (b). $\Delta\bar{\rho}(y)$ is computed by subtracting the sum of charge densities of 2D SL MoTe_2 and 2D SL NiTe_2 from the charge density of the heterostructure. The upper panels show optimized atomic configurations of each composite structure with two boundaries I_I and I_II . The blue (green) and red balls represent Mo (Ni) and Te atoms, respectively. The total charge transfer at the boundaries is $-0.8e$ and $-1.1e$ in $\text{Z:S}_{20}/\text{M}_{10}$ and $\text{A:S}_{20}/\text{M}_{10}$, respectively. 32

3.5: $\text{Z:}(\text{MoTe}_2)_{20}/(\text{NiTe}_2)_{10}$ (or $\text{Z:S}_{20}/\text{M}_{10}$) heterostructure. (a) The xz -plane averaged potential $\bar{V}(y)$ (in turquoise) and the macroscopic average potential $V_{\text{macro}}(y)$ (in red). The alignment and bending of VB and CB edge energies with respect to the Fermi level E_F (marked by the dash-dotted line) is shown. The Schottky barrier height E_S relative to E_F is depicted. The local densities of states (LDOS) in the vicinity of E_F are shown at *metallic M*, *semiconducting S*, and boundary regions by insets. (b) Optimized atomic configuration of $\text{Z:S}_{20}/\text{M}_{10}$ is described by blue (green) and red balls representing Mo (Ni) and Te atoms, respectively. $\vec{a}$ and $\vec{b}$ are the lattice translation vectors of the 2D rectangular cell of the heterostructure. (c) Energy bands weighted by the contribution of particular bonds designated in (b) by A, B, and C. Thicker bands denote higher contribution. 34

3.6: $\text{A:}(\text{MoTe}_2)_{20}/(\text{NiTe}_2)_{10}$ (or $\text{A:S}_{20}/\text{M}_{10}$) heterostructure. (a) The xz -plane averaged potential $\bar{V}(y)$ (in turquoise) and the macroscopic average potential $V_{\text{macro}}(y)$ (in red). The alignment and bending of VB and CB edge energies with respect to the Fermi level E_F (marked by the dash-dotted line) is shown. The Schottky barrier height E_S relative to E_F is depicted. The local density of states (LDOS) in the vicinity of E_F is shown at *metallic M*, *semiconducting S*, and boundary regions in the insets. (b) Optimized atomic configurations of $\text{A:S}_{20}/\text{M}_{10}$ is described by blue (green) and red balls representing Mo (Ni) and Te atoms, respectively. $\vec{a}$ and $\vec{b}$ are the lattice translation vectors of the 2D

- rectangular cell of the heterostructure. (c) Energy bands weighted by the contribution of particular atoms indicated in (b) by A, B, and C. 35
- 3.7: (a) (Left) Energy band structure of $Z:S_{20}/M_{10}$ in momentum space. (Right) Isosurfaces of charge densities of the selected band states A, B, C, D, and E. The isosurface charge density is $0.5 \times 10^{-3} e/\text{\AA}^3$. (b) Same for $A:S_{20}/M_{10}$. 36
- 3.8: A finite-size metal-semiconductor junction $Z:(\text{NiTe}_2)_{10}-(\text{MoTe}_2)_{10}$. (a) The atomic configuration and vacuum space at both sides. Numerals indicate specific regions and Mo-Te or Ni-Te bonds in the junction. (b) Contributions of specific regions are indicated by numerals in (a) to the energy bands. Thicker bands denote higher contribution. Bands are metallic at the NiTe_2 side, but a gap is opened in the MoTe_2 side. In panels ⑤ and ⑥ no states exist between E_{CB} and E_{VB} . (c) xz -plane averaged electronic potential and its average $V_{\text{macro}}(y)$. 38
- 3.9: $(\text{NiTe}_2)_{10}-(\text{MoTe}_2)_{10}-(\text{NiTe}_2)_{10}$ (or $M_q-S_p-M_q$) junction functioning as a tunneling barrier between two metal electrodes also as a nanocapacitor. (a) The optimized atomic configuration with boundaries I_I and I_{II} . Numerals indicate specific regions and Mo-Te or Ni-Te bonds. (b) Contributions of specific regions indicated by numerals in (a) to the energy bands. Thicker bands denote higher contribution. Bands are metallic at the NiTe_2 side, but a gap is opened in the MoTe_2 side. (c) xz -plane averaged electronic potential $\bar{V}(y)$, and its average $V_{\text{macro}}(y)$. (d) Schematic description of the tunneling barrier with barrier energy Φ_B between two metals at both sides. (e) Formation of RTDB structure with $M_q-S_p-S_t-S_p-M_q$, where S_t denotes hexagonal or trigonal SL transition-metal dichalcogenides stripe with narrow band gap. 39
- 3.10: (a) Top and (b) side views of atomistic model of SL, lateral heterostructure $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ with $p = 10$ and $q = 10$. Blue, magenta, and gold balls indicate Mo, Ni, and Te atoms, respectively. Two-dimensional rectangular unit cell with Bravais lattice vectors $\vec{a}$ and $\vec{b}$ is also shown. I_1 and I_2 are interfaces (or boundaries) between different constituent TMDC stripes along the armchair edges. (c) Side view of the vertical heterostructure $V:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ with $p = 3$ and

- $q = 3$. (d) Top view. Three-dimensional hexagonal unit cell is delineated in side and top views. 41
- 3.11: Transition from metal to metal–semiconductor junction with increasing $p = q$ in $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ heterostructure. The band gap between the conduction E_{CB} and valence band E_{VB} edges at the center of MoTe_2 is shaded. The zero of energy is set at the Fermi level E_{F} . 44
- 3.12: $A:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$ lateral heterostructure. (a) Unit cell with 2D rectangular lattice and corresponding Brillouin zone, BZ. (b) Bands projected to the Te–Mo–Te unit in the unit cell and corresponding asymmetric spin–polarized projected densities of states. (c) Bands projected to the Te–Ni–Te unit in the unit cell with spin–polarized *projected* densities of states. (d–f) Same for $A:(\text{MoTe}_2)_5/(\text{NiTe}_2)_5$. Bands are projected to the Te–Mo–Te and Te–Ni–Te units in the labeled unit cells. Zero of energy is set to the common Fermi level. 45
- 3.13: Heterostructure $A:(\text{MoTe}_2)_{10}/(\text{NiTe}_2)_{10}$. (a) Unit cell with lattice vectors. (b) Plane averaged electronic potential energy and its average along y –direction, $\bar{V}(y)$. (c) Spin–polarized densities of states projected to Te–Mo–Te and Te–Ni–Te units in the labeled unit cells. (d) Formation of metal (NiTe_2 stripe)–semiconductor (MoTe_2 stripe) *junction* with band lineup and Schottky barrier. (e) Bands projected to the Te–Mo–Te and Te–Ni–Te units in the unit cells specified in (c). 47
- 3.14: Electronic energy band structure of monolayer, bilayer, trilayer, and periodic bulk MoTe_2 . The zero of energy is set at the top of the valence band. 49
- 3.15: (a) $V:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$ heterostructure. Unit cell, energy bands, and corresponding state densities projected to adjacent Mo–Te₂ and Ni–Te₂ pairs. (b) $V:(\text{MoTe}_2)_3/(\text{NiTe}_2)_3$ heterostructure with a well–defined metal–insulator junction. (c) $V:(\text{MoTe}_2)_1/(\text{NiTe}_2)_5$. δ –doping of NiTe_2 slab by a single sheet of MoTe_2 . (d) $V:(\text{MoTe}_2)_5/(\text{NiTe}_2)_1$. δ –doping of semiconducting MoTe_2 slab by a single sheet of metallic NiTe_2 . 51
- 3.16: $V:(\text{MoTe}_2)_4/(\text{NiTe}_2)_4$ heterostructure. (a) The unit cell and chalcogen–cation–chalcogen units are specified by numerals. (b) Plane averaged electronic potential $\bar{V}(z)$. (c) Densities of states projected to chalcogen–cation–chalcogen units. The fundamental band gap at

- MoTe₂ side is shaded. (d) Bands projected to chalcogen–cation–chalcogen units. 53
- 3.17: Magnetic ground state of FeTe₂ monolayer in *H* structure predicted by hybrid, semilocal DFT, and DFT+*U* calculations. (a) The total energies as a function of the magnetic moment per formula unit μ_{tot} , obtained from the LDA ($U = 0$), PBE ($U = 0$), and HSE calculations. (b)–(f) The densities of states (DOS) of the minority (spin–down, $\downarrow$) and majority (spin–up, $\uparrow$) states of FeTe₂ within various approximations for the electron–electron interaction. 57
- 3.18: (a) Top and side views of the isosurfaces of the HSE–calculated spin density $\rho_s(r)$ for FeTe₂, VS₂, and NiTe₂ monolayers in their lowest–energy structures, corresponding to the isovalues of +0.01, +0.0075, and +0.005 (yellow) and –0.01, –0.0075, and –0.005 (cyan) $\mu_B/\text{\AA}^3$, respectively. (b) Local magnetic moments μ_M and μ_X calculated at the transition–metal (*M*) and chalcogen (*X*) atoms, respectively. The blue and red arrows (located at the *M* and *X* atom sites, respectively) are drawn, not to scale, to indicate opposing spin polarization of the transition–metal and chalcogen atoms. 58
- 3.19: (a) The bar plots of μ_{tot} and its components μ_M and $2\mu_X$, obtained at five levels of approximation, i.e., LDA, PBE, LDA+*U*, PBE+*U*, and HSE. (b) The plot of $2\mu_M/\mu_{\text{tot}}$ with respect to μ_M/μ_{tot} . 59
- 3.20: The variation of the supercell total energy E_{SC} with the supercell magnetic moment M_{SC} . The solid and open symbols represent the HSE–calculated and fitted points, respectively. The solid lines connecting the calculated as well as fitted points are drawn to guide the eye. The isosurfaces of the spin density for the $M_{\text{SC}} = 0\mu_B$, $4\mu_B$, and $8\mu_B$ configurations are shown as insets. 61
- 3.21: A comparison of two parametrizations of E_{SC} as a function of M_{Fe} and M_{Te} using $E_{\text{SC}} = E_0 + E_2 + E_4$ and $E_{\text{SC}} = E_0 + E_2$ with the E_2 and E_4 terms given in Equation 3.3. As in Figure 3.20, the filled and empty symbols represent the HSE–calculated and fitted points, respectively, and the solid lines connecting the calculated and fitted points are drawn to guide eye. The filled symbols, the empty symbols in magenta, and the black and magenta curves are the same as those in Figure 3.20. 64

- 3.22: Orbital projected bands and state densities of majority ($\uparrow$) and minority ($\downarrow$) spin states, calculated using HSE, for H -FeTe₂ (upper panels), H -VS₂ (middle panels), and T -NiTe₂ (lower panels) monolayers. The open circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition-metal (Fe, Ni, and V) and chalcogen (Te and S) atoms, which are also colored as indicated at the top. The zero of energy is set to the Fermi level for metals and to the energy of the highest occupied spin state for semiconductors. 66
- 3.23: Orbital projected bands and state densities majority ($\uparrow$) and minority ($\downarrow$) spin states, calculated using HSE, for T -FeTe₂ (upper panels), T -VS₂ (middle panels) and H -NiTe₂ (lower panels) monolayers. The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal (Fe, Ni and V) and chalcogen (Te and S) atoms, which are also colored as indicated at the top. Zero of energy is set to the Fermi level for metals and to the energy of the highest occupied spin-state for semiconductors. 68
- 3.24: The energy versus strain curves for H -FeTe₂ and T -FeTe₂ monolayers. As long as H - and T -phases remain the lower- and higher-energy phases, respectively, *no* phase transition takes place under applied biaxial strain for ($-0.10 < \epsilon < 0.10$). 69
- 3.25: The variation of (a) the spin-down band gap $E_g^{\downarrow}$, (b) the magnetic moment per formula unit μ_{tot} , and (c) the magnetic moments at Fe and Te atoms, μ_{Fe} and μ_{Te} , respectively, with the biaxial strain for H -FeTe₂ (in red) and T -FeTe₂ (in blue) monolayers. (d)–(f) The same with the inverse number of layers $1/n$ for FeTe₂ multilayers. 70
- 3.26: Orbital projected majority ($\uparrow$) and minority ($\downarrow$) spin bands, calculated using HSE, for H -FeTe₂ monolayer under biaxial *compressive* strain. The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal Fe, and chalcogen Te atoms, which are also colored as indicated at the top. 71

- 3.27: Orbital projected majority ($\uparrow$) and minority ($\downarrow$) spin bands, calculated using HSE, for $H\text{-FeTe}_2$ monolayer under biaxial *tensile* strain. The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal Fe and chalcogen Te atoms, which are also colored as indicated at the top. 72
- 3.28: Orbital projected majority ($\uparrow$) and minority ($\downarrow$) spin bands, calculated using HSE, for FeTe_2 monolayer, multilayers (bilayer, trilayer, fourlayer) and 3D layered FeTe_2 crystal (bulk). The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal Fe and chalcogen Te atoms, which are also colored as indicated at the top. 73
- 3.29: (a) Top and side views of the optimized atomic structure of lateral heterostructure $A:(\text{FeTe}_2)_5/(\text{NiTe}_2)_5$. The blue, green and red balls represent the Fe, Ni and Te atoms, respectively. The sticks representing the Fe–Te and Ni–Te bonds are colored to indicate the bond–length strain ε distribution, computed with respect to the bond lengths in the bare FeTe_2 and NiTe_2 monolayers. The subcells containing one formula unit are specified by encircled numerals. (b) Isosurfaces of spin density $\rho_s(r)$ and atomic magnetic moments (in units of Bohr magneton). The algebraic sum of atomic magnetic moments in the FeTe_2 and NiTe_2 stripes are $+11.8 \mu_B$ and $-1.8 \mu_B$, respectively. (c) The spin–polarized local density of states (LDOS) for subcells ③ and ⑧ and total density of states (DOS). (d) Energy diagram showing the spatial variation of the spin–down conduction and valence band edge energies. The Fermi level is indicated by the dotted–dashed line. (e) The change in the electronic charge ΔN at each subcell with respect to the free–standing FeTe_2 and NiTe_2 monolayers. 78
- 3.30: Atomic and electronic structures of (a) $A:(\text{FeTe}_2)_3/(\text{NiTe}_2)_1$, and (b) $A:(\text{FeTe}_2)_1/(\text{NiTe}_2)_3$ heterostructures (compounds). The spin–polarized total density of states (DOS) and local density of states (LDOS) for subcells ① and ③ are plotted. The blue, green and red balls represent the Fe, Ni and Te atoms, respectively, next to which the atomic magnetic moments (in units of Bohr magneton) are given as italic

numbers. Note that $\mu_{\text{tot}} = p\mu_{\text{Fe}} + q\mu_{\text{Ni}} + 2(p+q)\mu_{\text{Te}}$ for $\text{A}:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$. The sticks representing the Fe–Te and Ni–Te bonds are colored to indicate the bond-length strain ε distribution, computed with respect to the bond lengths in the bare FeTe₂ and NiTe₂ monolayers. Since these heterostructures display a uniform band gap throughout the unit cell, they are specified also as compounds.

79

3.31: Variation of the (a) total magnetic moment μ_{tot} in units of Bohr magneton μ_B percell, and (b) average magnetic moment $\mu = \mu_{\text{tot}}/p$ of the lateral $\text{A}:(\text{FeTe}_2)_p/(\text{NiTe}_2)_p$ structures, obtained from the LDA, PBE+D3, and HSE calculations.

80

3.32: The band edge energies for spin-down electrons in the FeTe₂ monolayer and in a variety of $\text{A}:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$ heterostructures. The Fermi level is indicated by the dashed line, which is taken as the zero of band energy. The spin-down band gap ($E_g^\downarrow$) values in the FeTe₂ (blue) and NiTe₂ (green) are given by blue and green arrows, respectively. Periodic heterostructures having the same $E_g^\downarrow$ value in both sides of the junction are designated as compounds. The band offsets for $p = q = 4$ and 5 are marked by the red double-sided arrows.

82

3.33: Atomic and electronic structures of vertical heterostructures (a) $\text{V}:(\text{FeTe}_2)_1/(\text{NiTe}_2)_1$, and (b) $\text{V}:(\text{FeTe}_2)_1/(\text{NiTe}_2)_1$. Left: Side views of atomic structures. The blue, green and red balls represent the Fe, Ni and Te atoms, respectively. The sticks representing the Fe–Te and Ni–Te bonds are colored to indicate the bond-length strain ε distribution, computed with respect to the bond lengths in the bare FeTe₂ and NiTe₂ monolayers. Numerals in circles identify the layers. Middle: The atomic (μ_{Fe} , μ_{Ni} , μ_{Te}) magnetic moments in units of Bohr magneton. The magnetic moments at transition-metal and chalcogen atoms are aligned antiparallel as long as $\mu_{\text{Fe}}, \mu_{\text{Ni}} > 0$ and $\mu_{\text{Te}} < 0$. Right: Density of states projected to the specific layers indicated by numerals (LDOS) and total density of states (TDOS).

84

LIST of TABLES

<u>Table No:</u>	<u>Page</u>
3.1: Calculated values of the local strain ϵ (in %) at different regions (as indicated in the first row) of two composite structures A: and Z: S_{20}/M_{10} with S (MoTe ₂) and M (NiTe ₂). Strain values are deduced from changes of bond lengths d_{X-Te} ($X = \text{Mo, Ni or Te}$) relative to those of parent 2D SL constituents.	27
3.2: The calculated values of the average cohesive energy E_C (eV per pair), the formation energy E_f per cell at $T = 0$ K relative to 2D SL constituents (eV per cell), and the junction formation energy E_{jf} at $T = 0$ K relative to the corresponding nanoribbons (eV per cell).	28
3.3: Optimized values of lateral heterostructure A:(MoTe ₂) _p /(NiTe ₂) _q for $1 \leq p = q \leq 10$, values of average cohesive energy $\bar{E}_C$, average formation energy $\bar{E}_f$, two-dimensional rectangular lattice constants a and b , and fundamental bandgap E_g .	43
3.4: Optimized values of vertical heterostructure V:(MoTe ₂) _p /(NiTe ₂) _q , values of average cohesive energy $\bar{E}_C$, average formation energy $\bar{E}_f$, superlattice constants $a = b$ and c , interface spacing d_{int} , and fundamental indirect bandgap E_g .	43
3.5: The difference between the optimized total energies, ($E_H - E_T$, in meV per formula unit) of H - and T -phases for FeTe ₂ , VS ₂ , and NiTe ₂ monolayers.	56
3.6: The HSE-calculated values of the local magnetic moments μ_M and μ_X in antiferromagnetic ($M_{\text{SC}} = 0$) and magnetic ground ($M_{\text{SC}} \neq 0$) states.	63
3.7: The values of the supercell magnetic moment M_{SC} and the local magnetic moments μ_{Fe} and μ_{Te} for the H -FeTe ₂ monolayer, obtained from the collinear and noncollinear PBE+ U calculations with and without spin-orbit coupling (SOC), respectively. Noncollinear configurations are indicated by "In plane" ("Out of plane") in the second column, which means that the magnetization vectors are aligned in (perpendicular to) the monolayer plane.	65

1. INTRODUCTION

Since the successful isolation of graphene layers from graphite in 2004 [1], two-dimensional (2D) materials [2] and their technological applications have become the focus of materials physics research. 2D materials are layered materials with strong in-plane and weak van der Waals-like bonding between layers. This bonding structure allows for atomically precise division by various intercalation methods or layer-by-layer growth by various crystal growth techniques.

There are many layered crystals similar to graphite in nature. Recently, a large number of stable layered 2D materials, such as graphene, hexagonal boron nitrides (hBN), black phosphorus (BP), transition-metal dichalcogenides (TMDCs), metal carbides and nitrides (MXenes), metal- and covalent-organic frameworks (MOFs and COFs), etc., have been discovered and produced in the laboratory environment with the development of exfoliation, intercalation and growth techniques.

On the other hand, although graphene has exceptional electronic and mechanical properties due to its zero electronic bandgap, it possesses a limitation for applications in some electronic and optoelectronic devices. Therefore, researchers have paid significant attention to other 2D materials that have finite bandgap energies like TMDCs.

The generic formula for TMDC structures is MX_2 , where M (Cr, Fe, Mn, Mo, Ni, V, W, Ti, etc.) and X (S, Se or Te) represents transition-metal and chalcogen atoms, respectively. TMDCs are composed of three atomic planes, where transition-metal atom is sandwiched between two layers of chalcogen atoms. TMDCs are generally found in two types of crystal structures. These are trigonal prismatic (H) and octahedral (T) structures with hexagonal (D_{6h}) and tetragonal (D_{3d}) symmetries, respectively. In Figure 1.1, the top and side views of the atomic structures of H - and T -phases 2D SL transition-metal dichalcogenides are shown.

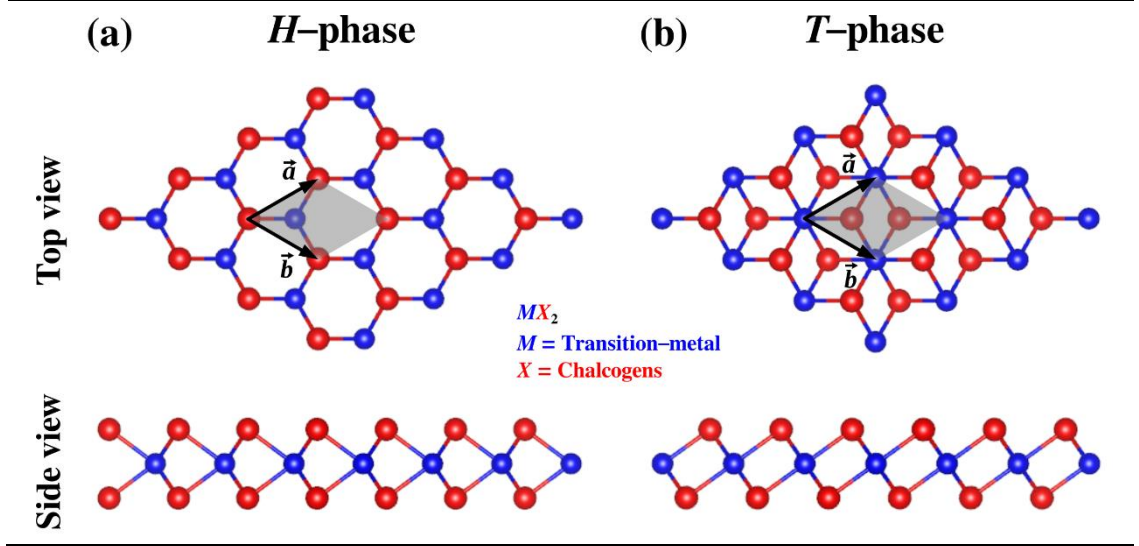


Figure 1.1: Top and side views of the atomic structure of (a) *H*- and (b) *T*-phase 2D monolayer transition-metal dichalcogenides (TMDCs). The primitive unit cells are, delineated and have Bravais lattice vectors $\vec{a}$ and $\vec{b}$ ($|\vec{a}| = |\vec{b}|$).

Already, numerous stable mono- and multi-layer TMDCs have been synthesized in laboratory conditions, and the structures and properties of dozens more have been theoretically predicted. TMDCs show high stability and critical physical and chemical properties [3–8] are now widely accepted to be a class of two-dimensional (2D) materials which are in various aspects superior to 2D graphene, group-IV elements and group-III-V compounds and offer a variety of potential applications. Since TMDC structures show metal, semiconductor, half-metal, semimetal and even superconducting properties, experimental and theoretical researches of the basic properties of these structures and investigating their use in technology is very important for the production of new generation devices.

2D TMDCs present unprecedented and tunable properties because of the large surface-to-volume ratios and sensitive to external interactions, thus, modulation of the electronic structure of materials has become easier, thus, another objective of scientific researches. A modification method is to change the dimension of materials. Electronic properties of 2D TMDC materials are often very different from their 3D counterparts. For instance, indirect to direct band gap and metallic to half-metallic transitions occur when the number of layers is reduced. [9, 10] Another way to change the properties of the materials is to create lateral (in-plane) and/or vertical (van der Waals) heterostructures. The layered nature of 2D TMDCs with their diverse

electronic, optical, and magnetic properties offers an opportunity and freedom in fabricating the heterostructures based on monolayer TMDCs. These structures can be laterally stitched or vertically stacked, like atomic-sized thin Lego pieces, to construct nano-engineered heterostructures and to use them as building blocks for the realization of devices with complex functionalities.

Unusual electronic properties and important device capacities thereof have been heralded by early theoretical studies on planar or in-plane heterostructures of nanoribbons. [11, 12] Much recently, the realization of vertical van der Waals solids [13, 14], as well as lateral, in-plane heterostructures of single-layer (SL) transition metal dichalcogenides [15–19], have opened an active field of experimental and theoretical research. A variety of lateral and vertical heterostructures have been fabricated with combinations of single-layer (SL) or multi-layer (ML) transition-metal dichalcogenides with other TMDCs, as well as with two-dimensional (2D) materials.

Exploiting electronic structures of junctions or heterostructures and realizing diverse operation properties in crystals or slabs have been one of the prime activities in device physics and materials science since 1980s. Initially, quantization of electrons unveiled in 2D electrons confined in these junctions have led to the discovery of integer and fractional quantum Hall effects. [20] Later, semiconductor/semiconductor junctions brought about a number of interesting phenomena, such as normal, eclipsed and staggered band line ups and single or multiple quantum well structure generated thereof, quantum size effects, and etc. [21, 22]. The formation of Schottky barrier and realization of diode function have been intensively explored in semiconductor/metal junctions. [23, 24] Recently, realization of similar effects in the strictly 2D monolayers through in-plane lateral and vertical heterostructures, as well as width modulated nanoribbons have been the subject of several recent theoretical and experimental studies. [25–27] It has been shown that lateral heterostructures with large alternation of constituents realized from the stripes of strictly 2D monolayers give rise to wide range of features and functionalities. These are 2D metallic or narrow band gap semiconducting compounds, narrow 1D metallic interconnects or nanowires in a wide 2D semiconductor sheet, tunneling barriers and resonant tunneling double barrier structures, nanocapacitor, single and periodic metal–semiconductor junctions forming Schottky barrier, etc.; see references [9] and [10] and references therein.

While experimental and theoretical research on the monolayer and multilayer transition–metal dichalcogenides are continuously growing, the realization of vertical van der Waals solids [28, 29] as well as lateral, in–plane heterostructures [15, 17, 18, 30] of TMDC monolayers brought about new ideas for novel devices. [14, 31–37] Vertical and lateral semiconductor/semiconductor junctions were considered as p – n diodes, [38–51] photodiodes, [46, 47] photodetectors, [43, 44, 52], solar cells [53], and field effect transistors (FETs) [25, 26, 31], and electron–driven nanomanipulation, [54] which were also the main subject of numerous theoretical studies. [32–39] In contrast, TMDC–based heterostructures comprising metal/semiconductor junctions have been studied to a much lesser extent, albeit their unusual electronic properties and important device capacities thereof have been heralded by early experimental [39, 42] and theoretical [41, 43, 44] studies. It should also be pointed out that using metallic SL TMDCs stacked with semiconducting SL TMDCs (as in vertical heterostructures) has been explored [45, 46] as a viable strategy for achieving an efficient and stable electrical contact between 2D semiconductors and metal electrodes.

Furthermore, two–dimensional magnetism has long been the focus of fundamental questions in condensed matter physics. Much earlier, theoretical models, such as 2D Ising, XY, and Heisenberg models, indicated that the magnetic order in 2D monolayers is rather complex and depends on a spin dimensionality of 1 to 3, even if the long–range order of magnetic moments in 3D crystals can occur for $T > 0$ K, and that of 1D systems at $T = 0$ K. In particular, the magnetic order may deviate strongly by going from three to two dimensions. However, recent observations of magnetic order in 2D monolayers like CrGeTe₃ [62] and CrI₃ [63] have reactivated interest in magnetic MX_2 monolayers by bringing the second and third–nearest–neighbor exchange interactions [64] and magnetic anisotropy [65] into focus. Furthermore, owing to the weak van der Waals interlayer interaction, multilayers of MX_2 and their heterostructures [9, 10, 15–17, 41] have been considered as novel materials [3, 13, 66] with intriguing electronic and magnetic properties. It is anticipated that confinements of electrons into 2D monolayers or very thin films can lead to interesting dimensionality effects in magnetic states.

Very recently, the first example of magnetic order in a 2D material was reported experimentally. [103] As the realization of 2D magnetic crystals was a great challenge [55], spin–polarized calculations [56] revealed that the magnetic ground

state can be indigenous to some MX_2 monolayers, since one of their constituents can be a magnetic transition-metal atom (e.g., $M = \text{Sc, Ti, V, Cr, Mn, Fe, Ni}$). It has been contemplated that the magnetic long-range order of specific layered three-dimensional (3D) MX_2 crystals would persist even after the exfoliation of MX_2 monolayers. With an intrinsic magnetic moment, MX_2 monolayer can be a ferromagnetic metal, ferromagnetic semiconductor, and even a half-metal. [57] The super-exchange interaction [58, 59] between nearest metal M atoms through the adjacent chalcogen X atom has been considered as a mechanism leading to ferromagnetic ground state. In some monolayers, spin-orbit interactions resulting in spin-valley coupling can lead to critical spintronic properties. [60, 61]

Owing to the most recent studies unveiling various magnetic features, the range of interest in these magnetic 2D MX_2 -based materials has expanded tremendously. [57] On the theoretical side, the ground-state magnetic order of some TMDC monolayers and modifying their magnetic properties by external agents have been studied intensely with the aid of density functional theory (DFT) calculations performed at various levels of approximations. Now the prime issue is whether these studies can conclude with similar predictions on the magnetic properties despite the different approximations used for the electron-electron interaction. In fact, earlier DFT calculations using local and semi-local functionals yielded unrealistic magnetic ground states for magnetic TMDC monolayers. This issue is crucial for an understanding of magnetic 2D MX_2 crystals, but remains unresolved so far.

1.1. The Scope and Content of the Thesis

Within the scope of the thesis; structural, energetic, electronic, magnetic and spintronic properties of monolayer TMDCs and their lateral and vertical heterostructures are investigated and predicted via computational methods within the framework of DFT. Accordingly, heterostructures of layered TMDCs are studied in order to reveal possible properties and their alternative applications. For this purpose, periodically repeating and finite-size commensurate composite structures of in-plane junctions of monolayer stripes and vertical stacking van der Waals heterostructures of TMDCs have been designed. Electronic and magnetic properties and functionalities of heterostructures have been examined, hence possible application areas and device capacities will be suggested.

In Section 3.1, we show that periodically repeating, commensurate junctions of nanoribbons (stripes) forming SL in-plane composite structures, $(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ (specified in the text as S_p/M_q with p and q being the numbers of formula units) constitute a class of materials offering crucial fundamental features and diverse device applications. Since both 2D constituents have been synthesized already [67], earlier growth studies [17, 18, 68] and present theoretical analysis of energetics and stability let us expect that these SL composite structures with sharp boundaries can readily be produced [69–73] and remain stable in diverse applications.

Various combinations of p and q starting from $p = 2$ and $q = 2$ results in composite materials with tunable properties such as metal, narrow band gap semiconductor and metal/semiconductor as well as metal/magnetic metal junctions. The δ -doping corresponding to $q = 2$ but $p \gg 2$ forms strictly one-dimensional (1D) metals (or nanowires) in a 2D semiconductor. For large S (semiconducting) and M (metallic) stripes corresponding to $p \gg 1$ and $q \gg 1$, electronic states become confined so that they attain the properties of their parent 2D constituents, but the charge is transferred across the 1D boundaries between them. Eventually, an asymmetric Schottky barrier of significant height is constructed together with strictly 1D metallic states propagating at the boundaries in a 2D single-layer structure. Since impurities are absent at the boundaries, linear bending of the band edges near the boundaries is attained.

Moreover, a composite with finite width made by commensurately joined $M_q-S_p-M_q$ stripes and capped by vacuum from both sides can form a nanocapacitor or a tunneling barrier (or a resonant tunneling double barrier (RTDB) through a combination $M_q-S_p-S_t-S_p-M_q$). Notably, most of the fundamental features revealed in these composite structures are not sensitive to the specific values of structural parameters p , q , and t ; they require only wide enough stripes allowing localization.

In Section 3.2, lateral (in-plane) and vertical (van der Waals) heterostructures made of nearly lattice matched metallic (SL NiTe_2) and semiconducting (SL MoTe_2) TMDCs were presented. The objectives are to reveal the effects of size and dimensionality of constituents on the electronic structure of these heterostructures and composite materials. The periodically repeating, lateral, and commensurate junctions of semiconducting MoTe_2 and metallic NiTe_2 stripes along their armchair edge make a class of new materials. These armchair edged lateral heterostructures we treat in this section are specified as $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ with $1 \leq p$ and $q \leq 10$,

where p and q are the numbers of formula units in the lateral primitive unit cell. Depending on the values of p and q , these lateral structures display a number of properties ranging from composite metals to metal–semiconductor junction having a Schottky barrier, which can be tuned by varying p .

The situation in vertical heterostructures, which are constructed from the stacking of SL MoTe₂ and NiTe₂ layers and are specified as V:(MoTe₂) _{p} /(NiTe₂) _{q} with $1 \leq p$ and $q \leq 5$, is, however, different. Because of weak van der Waals (vdW) interlayer interaction, the coupling between adjacent TMDCs stacked vertically is rather weak, and it has small but crucial effects on the electronic structure. This enhances confinements of electrons in different constituents. Despite the weak interlayer interaction, the resulting electronic structures in composite vertical structures with very thin as well as wide alternation of constituents are of current interest.

SL TMDC constituents investigated in this thesis have been synthesized long ago. [67] Dynamical and thermal stability analysis has demonstrated that many freestanding SL TMDCs (including MoTe₂ and NiTe₂) with hexagonal and trigonal structures are stable. [56] Vertical stacks of TMDCs and their heterostructures were also found to be stable. [16] The stability of freestanding layers is clearly enhanced if they were grown on specific substrates. In this respect, the stability of bilayers and multilayer stacks is also enhanced. Recent theoretical stability analysis [10, 56] and extensive structure optimization calculations carried out here as well as recent experimental studies [16, 17, 68, 70, 74–76] indicate that the vertical and lateral heterostructures treated in the present study are stable and can be fabricated. It should also be pointed out that lateral homojunctions combining hexagonal (*semiconducting*) and monoclinic (*metallic*) phases of MoTe₂ have already been fabricated via laser–induced phase patterning. [74] Furthermore, bilayer (*vertical*) heterostructures composed of MoS₂ and MoTe₂ monolayers were successfully prepared by a (mechanical) dry transfer process. [76]

In Section 3.3, the magnetic properties of three selected TMDC monolayers, viz., FeTe₂, VS₂, and NiTe₂ are investigated. Because of their potential applications, binary nickel tellurides including their mono– and multi–layers have been an active subject of experimental and theoretical studies. [77, 78] Recent studies have conveyed that FeTe₂ holds great promise in spintronics. [9, 10, 79] Our objective is to present an extensive analysis in order to examine how the magnetic ground states

and resulting electronic properties of three selected TMDC monolayers depend on the method of calculation and the level of approximation.

We find that while the VS₂ monolayer is a magnetic semiconductor with a net magnetic moment $\mu = 1\mu_B$ per formula unit, the FeTe₂ monolayer is a half-metal with an integer magnetic moment of $\mu = 2\mu_B$. While the DFT+*U* calculations predict no spin polarization for the NiTe₂ monolayer in agreement with the semilocal DFT calculations [10], the HSE results indicate that the NiTe₂ monolayer is a magnetic metal with a relatively small magnetic moment $\mu < 1\mu_B$. This disagreement is addressed by comparison with very recent experimental findings. [80, 81] It is noteworthy that owing to the spin polarization of chalcogen atoms through *p-d* hybridization the studied TMDC monolayers have magnetic ground states with local magnetic moments at chalcogen atoms antiparallel to those at transition-metal atoms. This situation is reminiscent of ferrimagnetic order.

The spin polarization of oxygen atoms via *p-d* hybridization was recently reported for 3D transition-metal oxides [82, 83] and iron oxide clusters [84], and causes substantial changes in the exchange interactions. In addition, the chalcogen atoms in 1*T*-CrX₂ (X = Se, Te) monolayers are also found to be spin polarized. [85] In line with these findings, our results show that the *p-d* hybridization renders the chalcogen *p* band spin-polarized in FeTe₂, VS₂, and NiTe₂ monolayers. Antiparallel local magnetic moments in different atoms of diverse 3D Heusler compounds (e.g., MnCrSb, Mn₃Ga, and NiMnSb) with compensating magnetic moments fulfilling the Slater-Pauling rule [86–88], zinc blende Mn-doped transition-metal dichalcogenides [89], and half-metallic Mn₂VAl [90] and LuCu₃Mn₄O₁₂ [91] showing ferrimagnetic order were reported earlier. Furthermore, the 2D MXene Mo₃N₂F₂ was recently predicted to be a ferrimagnetic half-metal. [92] This study, however, expounds on the magnetic ground states with antiparallel alignment of local magnetic moments at transition-metal and chalcogen atoms in three representative 2D single-layer transition-metal dichalcogenides with half-metallic, semiconducting, and metallic behaviors.

It is sensible to distinguish if a material has a parallel, antiparallel, or inhomogeneous spin arrangement, especially from an application point of view. For example, an advantage of using an antiferromagnet or ferrimagnet in lieu of a ferromagnet is to reduce the stray fields in spintronic devices such as magnetic tunnel junctions (MTJs). [93–96] The use of magnets with negative exchange coupling

brings also advantages in spin transfer applications, owing to a much shorter time scale of magnetization dynamics and reversal compared to that of a ferromagnet with positive exchange coupling. [97–100] In view of the present results, MX_2 monolayers with inhomogeneous magnetic moment distribution can find use in 2D MTJs [101] and spin transfer applications. This may extend the domain of interest in magnetic 2D MX_2 -based materials to spintronic devices.

Finally, in Section 3.4, owing to recent observations of magnetic order in two-dimensional (2D) materials much attention has been drawn to magnetic TMDC monolayers. [36, 55, 101–105] In order to discover novel spintronic devices, the magnetic, lateral and vertical heterostructures of TMDCs have been intensively explored recently. Lateral heterostructures constructed by the alternating single-layer (SL) stripes of TMDCs joined commensurately along their armchair (A) or zigzag (Z) edges, $A(Z):(MoTe_2)_p/(NiTe_2)_q$, has revealed crucial physical effects, such as electron localization in wide stripes leading to the confinement phenomena and metal–insulator transition. [9] Even more critical properties have been predicted in heterostructures made of magnetic TMDC nanoribbons (stripes). [10] For example, when the semiconducting ($MoTe_2$) stripe was replaced by a magnetic ($FeTe_2$) stripe, the resulting composite structure was found to exhibit the spin valve effect. In fact, spintronic applications with 2D TMDCs have been discussed in a number of recent studies. [106, 107] Furthermore, the formation of tunable and linear Schottky barrier or construction of strictly 1D nanowires in a 2D semiconducting sheet through a δ -doping were deduced. Meanwhile, a most recent theoretical study [108] based on DFT using various approximations for the electron–electron interaction has revealed an inhomogeneous magnetic ground state in a number of TMDC monolayers. In particular, it was found that the chalcogen atoms in the $FeTe_2$ and $NiTe_2$ monolayers have magnetic moments antiparallel to that of the transition metal atoms, which is reminiscent of ferrimagnetic order.

In view of these findings, we investigate the electronic and magnetic properties of the periodic, lateral, i.e., $A:(FeTe_2)_p/(NiTe_2)_q$ and vertical, i.e., $V:(FeTe_2)_p/(NiTe_2)_q$, heterostructures (where p and q are denoting the number of formula units of $FeTe_2$ and $NiTe_2$ in the unit cell, respectively) by performing hybrid–functional (HSE) calculations, using the correct magnetic ground state of constituent TMDC monolayers. Our study unveils the following important features of the foregoing heterostructures:

- (i) The lateral heterostructures combine both semiconductor/semiconductor and metal/metal junctions for different spin directions, where the half-metallic character can be retained throughout the heterostructure. When the constituent stripes are narrow, the indirect band gap of spin down electrons varies strongly with their widths of stripes, but it becomes uniform throughout the structure and hence attains the same value at either sides of junction. Electronically, these structures are considered to be single compounds materials, even if they are made by alternatingly different constituent TMDC monolayers and are unanimously specified as heterostructure. However, when the constituent stripes become wider, the band gap differs at either sides of the junction and their normal band-lineup and resulting band-offsets vary with the widths of constituent stripes. Accordingly, these predictions report a half-metallic heterostructure; the band offsets of its spin down electrons are tunable with the widths of constituents.
- (ii) In the vertical heterostructures, one side of the junction is half-metallic, while the other side is spin-polarized metal, which leads to a semiconductor/metal junction with a Schottky barrier for one spin direction, but a metal/metal junction for the opposite spin direction. Similar to the situation in bare monolayers, the magnetic moments at the transition metal atoms are antiparallel to those at the chalcogen atoms in the unit cell.
- (iii) The antiparallel alignment of local magnetic moments at constituent elements constructed through the spin polarization at chalcogen atoms as a result of p - d hybridization and hence the negative exchange coupling between transition-metal and chalcogen atoms may lead to efficient spin transfer in spintronic applications.

2. METHOD

Quantum mechanical wavefunction contains all information to predict and characterize a physical system. However, analytical solution of the many-body Schrödinger equation is practically impossible. At this point, density functional theory (DFT), which makes a great simplification within an acceptable approximation in the framework of quantum mechanical principles, stands out as a practical tool for the solution of the Schrödinger wave equation of a many-body system. DFT is a versatile theory used in modeling and simulating an unlimited number of materials in physics, chemistry, and materials science. It, also, enables investigation and description of ground state electronic, magnetic and structural properties of atoms, molecules, crystals, defects and complex structures that are difficult to characterize experimentally.

2.1. Density Functional Theory (DFT)

DFT is a widely used theory in the quantum mechanical study of interacting many-electron systems. The main idea of DFT is based on the principle that all the properties of the studied many-electron system can be written as a functional of ground state electron density and is written as a scalar function of position, thus entire many-body system becomes dependent only on three spatial coordinates. The fundamental ideas in DFT development date back to the advent of quantum mechanics. In 1926, Schrödinger published his revolutionary paper which included the equation that paves the way for wave mechanics. [109]

$$\hat{H} \Psi = E \Psi \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is a set of solutions (eigenstates i.e. wavefunction) of the Hamiltonian and E is the associated eigenvalue (ground state energy) that satisfies the equation. However, for an interacting many-body system, it is practically impossible to determine the wavefunctions of each particle and to solve the time-independent, non-relativistic Schrödinger equation.

Shortly after Schrödinger published the paper, Thomas-Fermi (TF) model, which is the predecessor of DFT, is developed by Thomas in 1927 [110] and by

Fermi in 1928 [111], independently. According to the TF model, many-body system was described with electronic density instead of wavefunctions. Depicting the system with charge density makes the solution of the problem quite easy. The TF model is based on the assumption that the charge density is homogeneously distributed in the phase space, and the kinetic, exchange and correlation energies are defined for the homogeneous electron gas. Although this was an important step, the model can only give meaningful results for simple systems due to the lack of exchange and correlation interactions.

Although density functional theory has its roots in the TF model, DFT is based on two fundamental mathematical theorems proved by Hohenberg and Kohn [112] and derivation of a set of equations by Kohn and Sham [113] in mid-1960s. The Hohenberg–Kohn (HK) theorems are related to any system consisting of electrons moving under the influence of an external potential $V_{ext}(r)$. The first HK theorem proves that the external potential $V_{ext}(r)$ of the system can be determined as a unique functional of electron density $\rho(r)$ and the corresponding minimum value of total energy is the ground state energy. Another way to rephrase the first HK theorem is that the ground state charge density uniquely determines the potential and thus all properties, including the ground state energy and wavefunctions.

The external potential $V_{ext}(r)$ acting on an electron gas is determined by the ground state electron density $\rho(r)$, and the potential is specific to the ground state density of the electronic system, in other words, the ground states of systems with two different external potentials, $V_{ext}(r)$ and $V'_{ext}(r)$, cannot be equal. If we assume that two non-degenerate systems with external potentials $V_{ext}(r)$ and $V'_{ext}(r)$ give rise to the same ground state charge density $\rho(r)$, there is no wavefunction that can give energy less than the energy of Ψ for H because of the variational principle.

$$E = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle \quad (2.2)$$

Since there is two identical ground state densities $\rho(r)$ for two hamiltonians $\hat{H}$ and $\hat{H}'$, we can write the expectation value as in Equation 2.3.

$$E < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle + \int [V_{ext}(r) - V'_{ext}(r)] \rho(r) dr \quad (2.3)$$

Exchanging the labels in Equation 2.3, we obtain,

$$E' < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} | \Psi \rangle + \int [V'_{ext}(r) - V_{ext}(r)] \rho(r) dr \quad (2.4)$$

If we add together Equations 2.3 and 2.4, we get the following contradictory inequality.

$$E + E' < E' + E \quad (2.5)$$

The contradiction seen in the above inequality shows that two systems with different potentials cannot have the same non-degenerate ground state density. Therefore, if the ground state charge density is specified, it determines the ground state Hamiltonian H and wavefunction Ψ of the system; hence all properties of the system can be obtained. The most important conclusion of the first HK theorem is that the ground state wavefunction $\Psi[\rho]$ and the energy $E[\rho]$ can be considered functionals of the ground state density ρ . The Hamiltonian is defined as follows,

$$\hat{H} = \hat{T} + \hat{U} + \hat{V}_{ext} \quad (2.6)$$

where $\hat{T}$ is the kinetic energy, $\hat{U}$ is the electron–electron interaction energy, and $\hat{V}_{ext}$ is the potential energy from the external field due to positively charged nuclei. The operators $\hat{T}$ and $\hat{U}$ are universal operators, while $\hat{V}_{ext}$ is system dependent. The energy functional is,

$$E[\rho] = F[\rho] + V[\rho] = \langle \Psi[\rho] | \hat{H} | \Psi[\rho] \rangle = F[\rho] + \int V_{ext}(r) \rho(r) dr \quad (2.7)$$

where $F[\rho]$ is a universal functional independent of the number of particles and external potential.

$$F[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{U} | \Psi[\rho] \rangle \quad (2.8)$$

Unfortunately, although the first HK theorem proves that a functional of the electron density exists that can be used to solve the Schrödinger equation, the theorem says nothing about the functionals.

The second HK theorem defines the property of functionals. The density that minimizes the variational total energy of the functional is the true ground state density corresponding to the solution of the Schrödinger equation. If the true functional $F[\rho]$ form was known, then we could vary the density until the energy from the functional is minimized, giving us a prescription for finding the relevant density. Since $\rho(r)$ of any system uniquely determines all ground state properties, then each property, including the total energy functional, can be expressed as a functional of $\rho(r)$. This variational principle is used in practice with approximate forms of the functional.

The functional $F[\rho]$ includes all internal energies of the interacting electronic system, and it must be universal because treatment of the kinetic and internal potential energies is same for all systems and the energies are functionals of the density ρ .

Let us imagine a system with the ground state density $\rho(r)$ corresponding to external potential $V_{ext}(r)$, the HK functional is equal to the expectation value of the hamiltonian in the unique ground state, which has wavefunction Ψ .

$$E = E[\rho] = \langle \Psi | \hat{H} | \Psi \rangle \quad (2.9)$$

According to the variational principle, a different density, say $\rho'(r)$, which corresponds to a different wavefunction Ψ' , will necessarily give an greater energy E' than E .

$$E = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = E' \quad (2.10)$$

Thus, the energy given by Equation 2.7 in terms of the HK functional evaluated for the correct ground state density $\rho(r)$ is indeed lower than for any other density $\rho'(r)$. As a result, if the functional $F[\rho]$ was known, then by minimizing the total energy of the system with respect to variations in the density $\rho(r)$, one would find the exact ground state density and its corresponding energy.

In 1965, the transformation of DFT from a theoretical framework to a practical computational tool took place with an approach proposed by Kohn and Sham. [113] The Kohn–Sham (KS) approach is to replace the original interacting many–body problem with a non–interacting (independent) particle equations that can be solved

more easily. Since the KS system assumes the electrons as non-interacting, the density can be written as

$$\rho(r) = \sum_i^N |\psi_i(r)|^2 \quad (2.11)$$

where ψ_i 's are the single particle wavefunctions known as KS orbitals that are also the lowest energy eigenfunctions, which are obtained by solving the one electron Schrödinger equation of non-interacting system under an effective potential V_{eff} .

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r) \quad (2.12)$$

The KS theory proposed the idea of replacing the kinetic energy of the interacting electrons with that of an equivalent non-interacting system and the universal functional $F[\rho]$ rewritten as

$$F[\rho] = T_S[\rho] + \frac{1}{2} \iint \frac{\rho(r)\rho'(r)}{|r-r'|} dr dr' + E_{xc}[\rho] \quad (2.13)$$

where $T_S[\rho]$ is the kinetic energy functional of the non-interacting electrons, the second term is the Hartree energy, and the $E_{xc}[\rho]$ is the exchange–correlation energy functional in that includes the kinetic correlation ignored in $T_S[\rho]$ and all other many–body effects of exchange and correlation.

If we rewrite the HK energy expression for the KS fictitious auxiliary non-interacting system by substituting $F[\rho]$ into the Equation 2.7, we obtain the KS functional as

$$E_{KS}[\rho] = T_S[\rho] + \int V_{ext}(r)\rho(r)dr + \frac{1}{2} \iint \frac{\rho(r)\rho'(r)}{|r-r'|} dr dr' + E_{xc}[\rho] \quad (2.14)$$

thus we have expressed the energy functional in terms of KS orbitals which minimize the kinetic energy under the fixed density constraint.

The KS orbitals satisfy the single–electron the Equation 2.12 and the effective potential $V_{eff}(r)$, which ensures the density of fictitious non-interacting system is the

same as true density of the interacting system, can be determined by minimizing the KS functional 2.14 by variational principle with respect to density.

$$\frac{\delta}{\delta \rho(r)} \left(E_{KS}[\rho] - \left[\frac{\delta T_S[\rho]}{\delta \rho(r)} + V_{eff}(r) \right] \int \rho(r) dr \right) = 0 \quad (2.15)$$

$$V_{eff}(r) = V_{ext}(r) + \int \frac{\rho'(r')}{|r - r'|} dr' + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} = V_{ext}(r) + V_H(r) + V_{xc}(r) \quad (2.16)$$

Since the effective potential $V_{eff}(r)$ depends on the solutions of the single-particle KS equations through the density, the KS equations should be solved by iterative self-consistent calculations in order to ensure that the density used to construct the effective potential coincides with that obtained from the solutions of the equation via Equation 2.11.

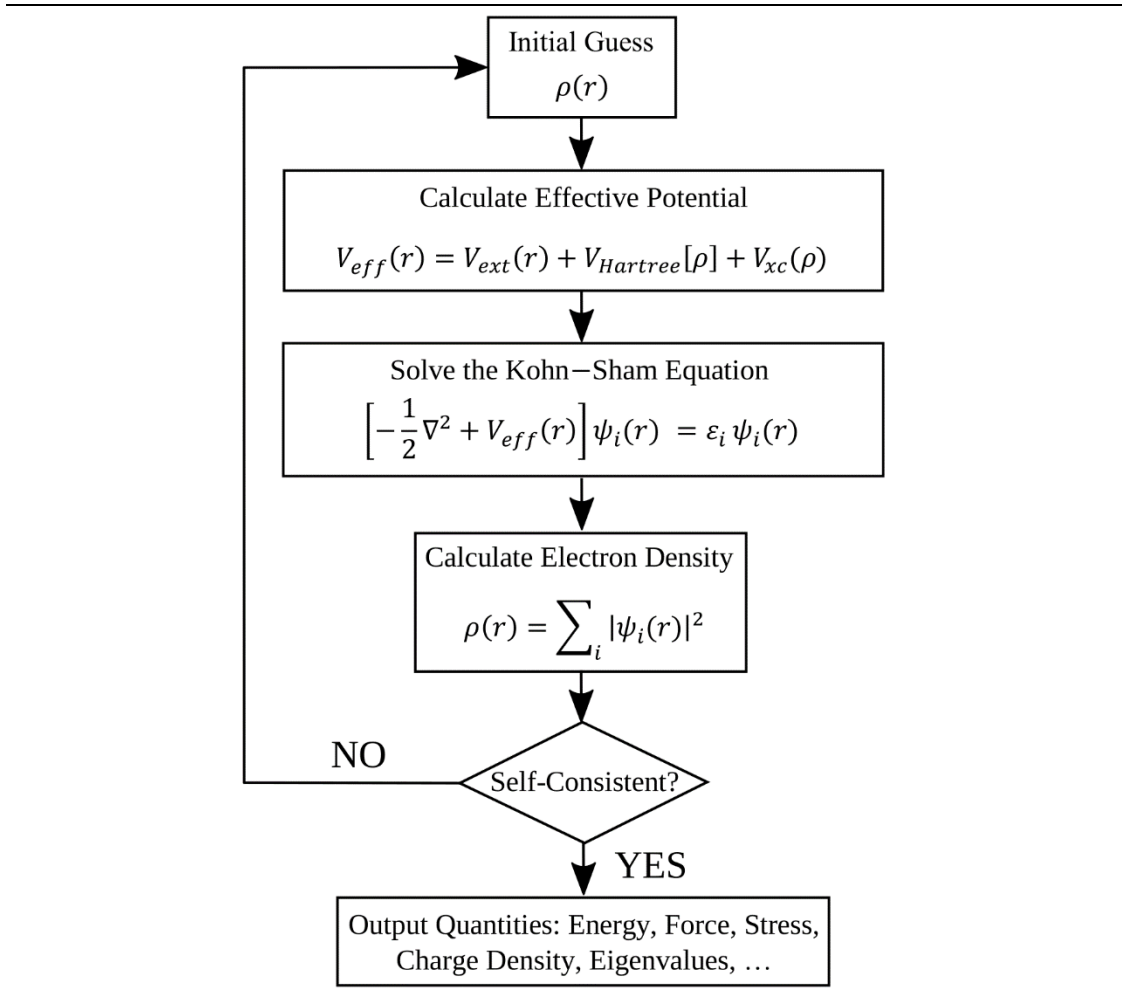


Figure 2.1: Schematic representation of the self-consistent solution of the Kohn-Sham equations.

The iterative algorithm is shown in Figure 2.1. Initially, a trial charge density $\rho(r)$ is defined and the effective potential $V_{eff}(r)$ is calculated. Using the obtained effective potential $V_{eff}(r)$, single-particle wavefunctions are calculated from the KS equation and thus the charge density of the system is determined. The cycle is continued until the difference between the calculated and the initially estimated charge density is equal or within the tolerance limits, thus obtaining a self-consistent solution. Once the charge density is determined, the quantities describing the system such as energy, force, stress, eigenvalues, etc. can be calculated.

The main problem with DFT is that the *exact* functionals for exchange and correlation are still not derived. As mentioned above, DFT is based on the Hohenberg–Kohn theorems. However, in practice, the Kohn–Sham formulation is used within some approximations to calculate exchange and correlation potentials. The first of these approximations is the local density approximation proposed by Kohn and Sham in 1965.

2.1.1. Local Density Approximation (LDA)

Local density approximation (LDA) has long been used to calculate the exchange–correlation energy. [113, 122] The main idea of LDA is the assumption of locally homogeneous electron gas in the inhomogeneous electron gas and used for exchange correlation corresponding to the homogeneous electron gas. In the local density approach, the exchange–correlation energy is expressed as in Equation 2.17 for homogeneous electron gas.

$$E_{xc}^{LDA}[\rho(r)] = \int \rho(r) \varepsilon_{xc}^{LDA}[\rho(r)] dr \quad (2.17)$$

The local spin–density approximation (LSDA) is a generalization of the LDA to include electron spin,

$$E_{xc}^{LSDA}[\rho^\uparrow(r), \rho^\downarrow(r)] = \int \rho(r) \varepsilon_{xc}^{LSDA}[\rho^\uparrow(r), \rho^\downarrow(r)] dr \quad (2.18)$$

where ε_{xc}^{LDA} is the exchange energy density. In the LDA, the exchange–correlation energy (E_{xc}^{LDA}) can be written as the sum of the exchange (E_x^{LDA}) and correlation (E_c^{LDA}) terms as in Equation 2.19.

$$E_{xc}^{\text{LDA}}[\rho] = E_x^{\text{LDA}}[\rho] + E_c^{\text{LDA}}[\rho] \quad (2.19)$$

The exchange term for homogeneous electron gas is analytically given as the Dirac expression in Equation 2.20. The correlation term can be calculated parametrically.

$$E_x^{\text{LDA}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho(r)^{4/3} dr \quad (2.20)$$

LDA exchange–correlation functionals are used successfully, especially in bulk metallic systems, where can be modeled as effective free electrons. However, it underestimates bond length and band gap in molecules, semiconductors, insulators and ionic crystals. Thus, some corrections are required within the LDA in order to better description of the mechanic and electronic properties.

2.1.2. Generalized Gradient Approximations (GGA)

Another approach is used to describe the exchange–correlation is generalized gradient approximation (GGA). [123] While the LDA gives good results for constant charge density, it is insufficient in systems such as atoms and molecules where charge density changes rapidly. GGA is an approximation that includes gradient corrections on LDA exchange correlations to describe better the electronic and geometric properties of molecules and clusters. GGA is known as a semi–local approach. In this approximation, the exchange–correlation function is developed by adding the gradient of the charge density $\nabla\rho(r)$.

$$E_{xc}^{\text{GGA}}[\rho^\uparrow(r), \rho^\downarrow(r)] = \int \rho(r) \varepsilon_{xc}[\rho^\uparrow(r), \rho^\downarrow(r), |\nabla\rho^\uparrow(r)|, |\nabla\rho^\downarrow(r)|] dr \quad (2.21)$$

GGA improves results in calculating properties such as bond lengths, binding energies, electronic band gaps, etc., of molecular geometries and ground state energies compared to LDA. Nevertheless, both GGA and LDA underestimate the electronic bandgap of semiconductors, insulators, and half–metals. Since the potentials of the LDA and GGA functionals are independent of the orbitals, the standard DFT and exchange functionals cannot describe the electronic properties of transition and rare earth metal ions that have partially filled *d* and *f* orbitals and

strong correlation interactions. Therefore, various corrections and methods have been developed to overcome the deficiency of the standard DFT, where exchange potentials cannot be determined exactly.

2.1.3. Strong Correlation Effect and DFT+ U Method

The DFT+ U approach, which is based on the Hubbard model, has been formulated for an accurate calculation of the ground state electronic properties of systems that have (locally d and f orbitals) strong correlation interactions. With the addition of the Hubbard U term, the DFT+ U method gives better results in estimating properties such as bandgap and magnetic moment than the standard DFT approximations.

The DFT+ U method is based on adding a Hubbard-like Hamiltonian to describe the on-site interactions of strongly correlated electronic state of a system. The first formulation for the DFT + U approach was made by Anisimov et al. [114] Due to its ease of use, the commonly used rotational invariant form was introduced by Liechtenstein and Dudarev. [118] According to this formulation, the total energy is defined as in Equation 2.22.

$$E_{\text{DFT}+U} = E_{\text{DFT}}[\rho] + E_U[n^\sigma] - E_{\text{DC}}[n^\sigma] \quad (2.22)$$

where n^σ is the density matrix. E_{DFT} represents the corrected DFT total energy functional, E_U is the Hubbard Hamiltonian term to model the contribution correlated states and E_{DC} is the double-counting term. The latter has to be subtracted from E_{DFT} because the interaction energy is also taken into account by E_U term. According to Dudarev's rotational invariant approach, the energy can be written as in Equation 2.23.

$$E_{\text{DFT}+U} = E_{\text{DFT}} + \frac{(\bar{U} - \bar{J})}{2} \sum_{\sigma} \left[\left(\sum_i \rho_{ii}^{\sigma} \right) - \left(\sum_{i,i'} \rho_{ii'}^{\sigma} \rho_{i'i}^{\sigma} \right) \right] \quad (2.23)$$

where $\rho_{ii'}^{\sigma}$ is the density matrix of correlated electrons, U is the on-site correlation, and J is the interatomic exchange term. According to the Dudarev formulation only

the $U = \bar{U} - \bar{J}$ difference is meaningful. The total energy is expressed in terms of the Kohn-Sham eigenvalues ϵ

$$E_{\text{DFT+U}} = E_{\text{DFT}}[\epsilon] + \frac{(\bar{U} - \bar{J})}{2} \sum_{\sigma, i, i'} \rho_{ii'}^{\sigma} \rho_{i'i}^{\sigma} \quad (2.24)$$

where the last term represents the double counting correction. Orbital energies ϵ_i are obtained by derivatives of total energy $E_{\text{DFT+U}}$ with respect to orbital occupations n_i

$$\epsilon_i = \frac{\partial E_{\text{DFT+U}}}{\partial n_i} = \epsilon_{\text{LDA}} + (\bar{U} - \bar{J}) \left[\frac{1}{2} - n_i \right] \quad (2.25)$$

The Equation 2.25 shows that the occupied orbital energies decrease by $-(\bar{U} - \bar{J})/2$, while the energies of unoccupied orbitals increase by $+(\bar{U} - \bar{J})/2$ with respect to the DFT orbital energies. Thus, with the shifted energies of orbitals, the gap between the occupied and empty orbitals widens up to approximately $(\bar{U} - \bar{J})$ by moving away from the Fermi energy level.

2.1.4. Heyd–Scuseria–Ernzerhof (HSE) Hybrid Functional

In order to improve description of the electronic structure, it is necessary to go beyond the LDA and GGA approaches. One way is to calculate the exchange and correlation energies in DFT with the contribution from the *exact* exchange and correlation energies obtained from the HF theory. Exact exchange energy functionals are obtained by using Kohn–Sham orbitals instead of charge density. Hybrid exchange functionals are generally obtained as a result of linear combination of exchange functionals obtained from DFT with HF exchange E_{x}^{HF} functionals.

In the range-separated hybrid Heyd–Scuseria–Ernzerhof (HSE) functionals, a certain amount of HF exchange energy is added to the exchange energies obtained from standard DFT approaches. However, due to the slow damping of the long-range part of the HF exchange term, the electron–electron interaction is divided into short and long-range to avoid long-term integral calculations. [120] The correlation term is still derived from the GGA approximation. The Coulomb operator has been reconstructed as in Equation 2.26.

$$\frac{1}{r} = S_{\omega}(r) + L_{\omega}(r) = \frac{\text{erfc}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r} \quad (2.26)$$

where $r = |r - r'|$ and ω is the range separation screening parameter that defines the characteristic distance ($2/\omega$) where short-range interactions are neglected. Error functions, $\text{erf}(\omega r)$ and $\text{erfc}(\omega r)$ are defined in Equation 2.27.

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \text{ and } \text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt \quad (2.27)$$

The optimum value of the screening parameter ω has been empirically determined as $0.2 \text{ \AA}^{-1}$. [121] While the contribution of the long-range exchange terms of HF and DFT exchange energies is neglected due to its small size and taking a long time to calculate, the correlation energy is obtained from DFT.

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{DFT,SR}}(\omega) + E_x^{\text{DFT,LR}}(\omega) + E_c^{\text{DFT}} \quad (2.28)$$

where α is the mixing parameter. The value of the mixing parameter is determined as 1/4 by perturbation theory. [117]

2.2. Computational Details

The predictions were obtained from first principles calculations based on the density functional theory (DFT), which were carried out using the VIENNA ab initio simulation package (VASP) [115] together with its projector-augmented wave (PAW) potential database. We carried out spin-polarized density-functional calculations within either the local density approximation (LDA) using the functional of Ceperley and Alder [116] or the generalized gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof [117] (PBE) with and without Hubbard U correction for on-site Coulomb interactions [118]. In vertical heterostructures, we also employed PBE in combination with the semiempirical dispersion (D3) correction. [119] Hence, the van der Waals interaction is taken into account through the PBE+D3 scheme. The hybrid DFT calculations were carried out with the HSE06 functional. [120, 121] The states in the electron configurations $3d 4s$, $3d 4s$, $4d 5s$, $3p 3d 4s$, $5s 5p$, and $3s 3p$ for iron (Fe), nickel (Ni), molybdenum (Mo), vanadium (V), tellurium (Te), and sulfur (S), respectively, were treated as

valence states. Bloch states of electrons are expressed by plane wave basis sets with a kinetic energy cutoff of 400 eV (in geometry optimizations as well as band-structure and DOS calculations) or 300 eV (in molecular dynamics simulations). Increasing the latter to 600 eV for the FeTe₂ monolayer resulted in a variation of 0.25 meV in the total energy per formula unit and yielded no variation in the magnetic moment, both of which imply a high level of convergence with respect to the cutoff energy. Convergence criterion for the electronic self-consistency was set up to 10^{-6} eV. Geometry optimizations were performed by relaxing the ionic positions until the residual forces on atoms were reduced to be smaller than 0.01 eV/Å. Monolayer TMDCs and lateral heterostructures are treated using the supercell geometry with a sufficient vacuum spacing between layers to prevent coupling between the repeating images in the neighboring cells. The vacuum spacing of 20 Å is determined by convergence tests. Brillouin zones were sampled using the Monkhorst-Pack scheme [121], where the k -point mesh is adjusted according to the size of cells in the direct space. Ab-initio molecular dynamics (MD) simulations were performed at temperature 500 K with the aid of a Nosé-Hoover thermostat [125], integrating the equations of motion via the Verlet algorithm with a time step of 2 fs.

In Section 3.1, calculations were performed within the local spin density approximation (LSDA) using the Ceperley-Alder (CA) exchange-correlation functional.

In Section 3.2, we carried out spin-polarized density-functional calculations within either the local density approximation (LDA) using the functional of Ceperley and Alder or the generalized gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof (PBE) combined with the semiempirical dispersion (D3) correction.

In Sections 3.3 and 3.4, comparative analysis of the results of semilocal and hybrid DFT calculations, performed within the local density approximation (LDA) with Ceperley-Adler functional or the generalized gradient approximation with Perdew-Burke-Ernzerhof (PBE) functional with and without Hubbard U correction for on-site Coulomb interaction and using the Heyd-Scuseria-Ernzerhof (HSE) functional, respectively. Spin polarization was taken into account in these calculations, some of which were repeated with spin-orbit coupling for the sake of comparison.

3. RESULTS AND DISCUSSIONS

3.1. Planar Heterostructures of Transition–Metal Dichalcogenides: MoTe₂/NiTe₂

In this section, we investigate planar composite structures formed from the stripes of transition–metal dichalcogenides joined commensurately along their zigzag or armchair edges can attain different states in a two–dimensional (2D), single–layer, 2D or one–dimensional (1D) nonmagnetic metal and semiconductor. Widening of stripes induces metal–insulator transition through the confinements of electronic states to adjacent stripes, that results in the metal/semiconductor junction with a well–defined band lineup. Linear bending of the band edges of the semiconductor to form a Schottky barrier at the boundary between the metal and semiconductor is revealed. Unexpectedly, strictly 1D metallic states develop in a 2D system along the boundaries between stripes, which pins the Fermi level. Through the δ –doping of a narrow metallic stripe one attains a nanowire in the 2D semiconducting sheet or narrow band semiconductor. A diverse combination of constituent stripes in either periodically repeating or finite–size heterostructures can acquire critical fundamental features and offer device capacities, such as Schottky junctions, nanocapacitors, and resonant tunneling double barriers. These predictions are obtained from first–principles calculations performed in the framework of density functional theory.¹

3.1.1. 2D Single Layer Transition–Metal Dichalcogenides: MoTe₂ and NiTe₂

Since composite structure of semiconducting (*S*) and metallic (*M*) S_p/M_q can be viewed as the periodically repeating stripes of the nanoribbons of constituents, the electronic structures of 2D constituents, MoTe₂ and NiTe₂, are essential for our analysis. The calculated band structure of constituent 2D SL MoTe₂ and NiTe₂ will serve as references in this section.

1. The Section 3.1 and its subsections are adapted from Aras M., Kılıç Ç., Ciraci S., (2017), “Planar Heterostructures of Single–layer Transition Metal Dichalcogenides: Composite Structures, Schottky Junctions, Tunneling Barriers, and Half Metals”, Physical Review B, 95 (7), 075434.

In Figure 3.1(a) the top and side views of the atomic structure of these 2D SL transition–metal dichalcogenides are shown. A single layer consists of three atomic planes, where the planes of metal atoms are capped by the plane of chalcogen atoms from either side. The width of the single layer is denoted by Δ . The value of Δ is calculated to be 3.59 Å and 2.92 Å, for 2D SL MoTe₂, and NiTe₂, respectively. The rectangular unit cell, which is suitable for the present study of composite structures has fundamental translation vectors $\vec{a}$ and $\vec{b}$. The values of optimized lattice constants are $a = 3.46$ Å and $b = 6.0$ Å for MoTe₂, and $a = 3.59$ Å and $b = 6.22$ Å for NiTe₂. One-fourth of the corresponding Brillouin zone with symmetry directions are also shown.

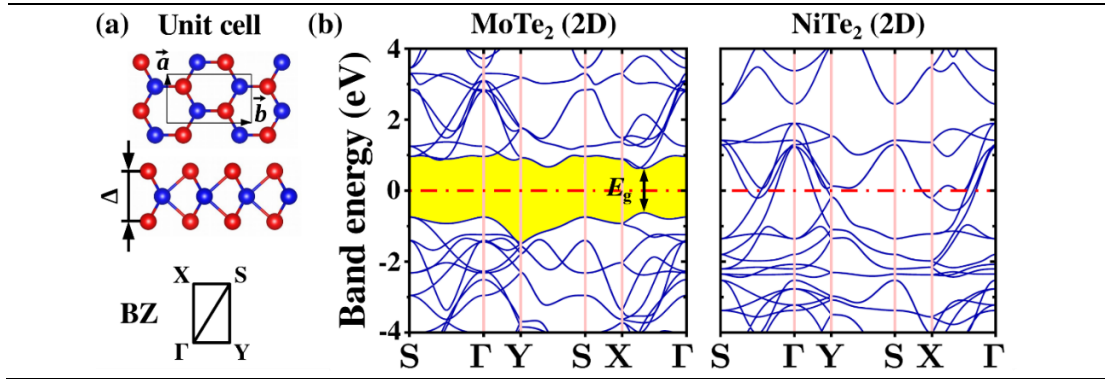


Figure 3.1: (a) Top and side views of the optimized atomic structure of 2D SL transition–metal dichalcogenides, MoTe₂ and NiTe₂. The layer thickness is denoted by Δ . The rectangular unit cell is delineated and has lattice constants a and b . (b) The electronic energy bands are calculated within the LSDA using the optimized atomic structures. The zero of energy of the semiconducting MoTe₂ is set at its intrinsic Fermi level.

The cohesive energy per formula unit is calculated from the expression

$$E_C[2D - MX_2] = E_T[M] + 2E_T[X] - E_T[2D - MX_2] \quad (3.1)$$

in terms of the total energies (E_T) of free transition metal atom M , and chalcogen atom X , and the optimized total energy of MX_2 . Accordingly, the cohesive energies (E_C) of MoTe₂ and NiTe₂ are 15.64 eV and 12.98 eV, respectively. The formation energy (E_f) of a 2D SL MX_2 at $T = 0$ K relative to the parent three–dimensional (3D) bulk crystals, is

$$E_f[2D - MX_2] = E_C[2D - MX_2] - E_C[2D - MX_2] \quad (3.2)$$

Three-dimensional bulk crystals of MX_2 are layered structures, where the interlayer attractive interaction is dominated by weak van der Waals interaction. Therefore, the formation energies of $MoTe_2$ and $NiTe_2$ at $T = 0$ K are small, but negative. While $E_C > 0$ indicates cohesion relative to free atoms, $E_f < 0$ implies that 2D SL MX_2 corresponds to local minimum on the Born–Oppenheimer surface. The stability of these 2D, SL structures were demonstrated earlier theoretically [56].

Two-dimensional $MoTe_2$ is a stable nonmagnetic semiconductor with the direct fundamental band gap of $E_g = 1.25$ eV occurring along the Γ –X direction. The hybrid functional method [120, 121] is applied to correct the electronic band structure, whereby the fundamental band gap increased only by 0.09 eV. Earlier studies on 2D SL transition–metal dichalcogenides, in particular on MoS_2 , showed that their electronic structures can be predicted successfully by LSDA. Since corrections by hybrid functional is small, but is time consuming for composite systems comprising several atoms, we carried out only LSDA calculations on optimized structure in the rest of the Section 3.1. When spin orbit coupling included the degenerate bands at the top of the valence band split only by ~ 0.2 eV. As for the other 2D constituents, 2D $NiTe_2$ is a nonmagnetic metal.

In following subsections, we will treat periodic and finite-size composite structures of transition–metal dichalcogenide MX_2 stripes commensurately joined along their zigzag (Z) or armchair (A) edges. We start by describing our atomistic model and examining the stability of the foregoing composite structures against thermal excitations.

3.1.2. Atomistic Model and Stability

The atomistic model of the composite structure of S_p/M_q with two asymmetric boundaries, I_I and I_{II} along their zigzag and armchair boundaries, are shown in Figures 3.2(a) and 3.2(d), respectively. Along the x –direction the heterostructure extends to infinity (without any edge) in terms of stripes of $MoTe_2$ and $NiTe_2$. The y –direction is perpendicular to zigzag or armchair boundaries, along which the stripes of constituents repeat periodically. Hence, the 2D structure consisting of three parallel atomic planes, where the plane of metal atoms is capped by two Te atomic planes, has a 2D rectangular lattice, with lattice constants $a||x$ and $b||y$. Here one should note the dramatic differences in dimensionality between the present in–plane

heterostructure and the well-known bulk heterostructures [126, 127] or the heterostructures between different van der Waals solids [28]. In the latter systems, the interface is planar; electrons in metallic interfaces exhibit a 2D quantization with staircase-like density of states in terms of jumps of $m^*/\pi\hbar^2$ per unit area. Whereas in the present in-plane heterostructures the interface is 1D and metallic electrons at the interface display a density of states inversely proportional to the square root of energy, $1/\sqrt{E}$.

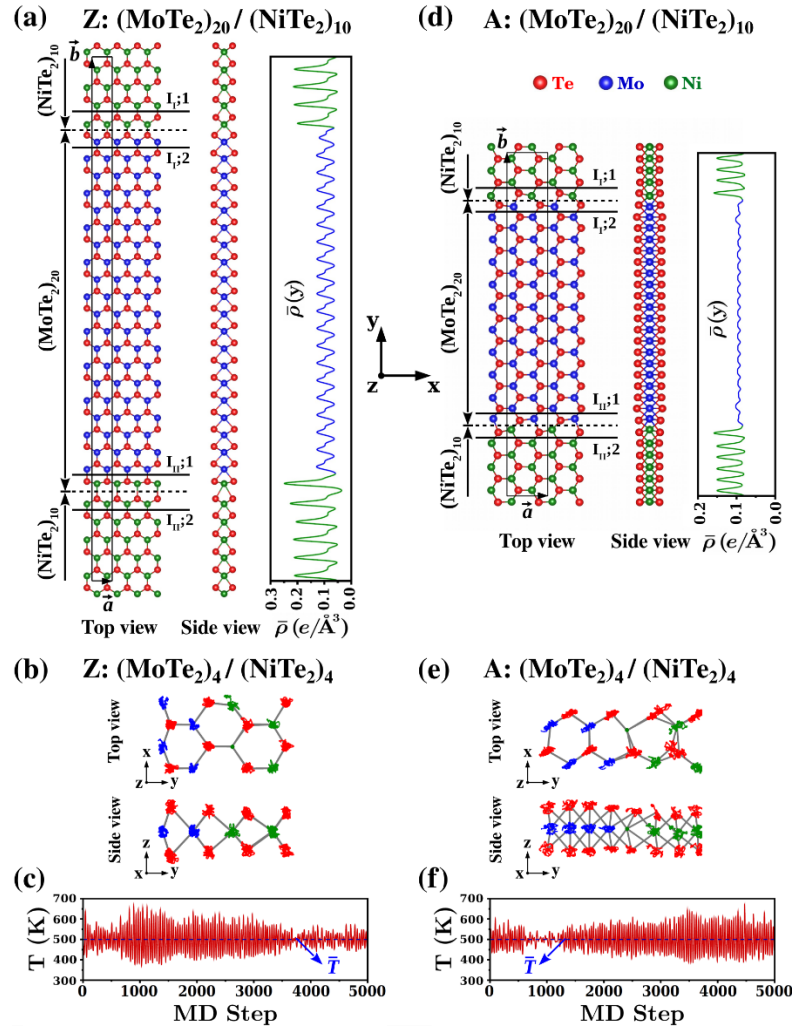


Figure 3.2: (a) Top and side views of atomistic model of SL, in-plane composite structures $Z:S_p/M_q$ with $p = 20$, $q = 10$. The 2D rectangular unit cell with Bravais lattice vectors $\vec{a}$ and $\vec{b}$ is delineated by thin lines. Two types of boundaries having zigzag edge geometry between NiTe₂ and MoTe₂ stripes are indicated by I_I and I_{II} . The xz -plane averaged self-consistent charge density $\bar{\rho}(y)$ corresponds to the optimized structure. (b) Trajectories of atoms $Z:S_p/M_q$ in the xy - and yz -planes attained from the average position of atoms in each 100 steps in the course of ab initio MD iterations at $T = 500$ K. (c) Variation of the temperature T and average temperature $\bar{T}$ versus MD steps running at $T = 500$ K. (d)–(f) Same for $A:S_p/M_q$.

Small lattice mismatches, $\Delta a/a \sim 0.03$, induce small strains in MoTe_2 , NiTe_2 stripes. For A: and Z: S_p/M_q composites with large p and q the strain ϵ induced by the lattice mismatch is inhomogeneous, and hence attains different values in different regions of the composite structure. In Table 3.1, we present the calculated strain values for A: and Z: S_{20}/M_{10} .

Table 3.1: Calculated values of the local strain ϵ (in %) at different regions (as indicated in the first row) of two composite structures A: and Z: S_{20}/M_{10} with S (MoTe_2) and M (NiTe_2). Strain values are deduced from changes of bond lengths $d_{X-\text{Te}}$ ($X = \text{Mo}, \text{Ni}$ or Te) relative to those of parent 2D SL constituents.

		Center of S	Center of M	I_I (S side)	I_I (M side)	I_{II} (S side)	I_{II} (M side)
A: S_{20}/M_{10}	$d_{\text{Mo-Te}}$	0.4	—	1.0	—	1.7	—
	$d_{\text{Ni-Te}}$	—	− 0.7	—	7.4	—	1.8
	$d_{\text{Mo-Te}}$	0.8	1.4	5.7	5.8	5.6	6.0
Z: S_{20}/M_{10}	$d_{\text{Ni-Te}}$	0.3	—	0.5	—	− 1.1	—
	$d_{\text{Te-Te}}$	—	− 0.6	—	− 3.1	—	2.4
	$d_{\text{Mo-Te}}$	− 0.1	1.6	− 6.0	2.8	− 6.2	− 1.3

The values in Table 3.1 indicate that the center of semiconducting (S) stripes is usually under tensile strain, whereas metallic (M) stripes are under compressive strain. Induced strains at the boundary regions are asymmetric and complex. We should address the questions of whether the in-plane composite can grow and remain stable despite the small lattice mismatch and inhomogeneous strain induced therefrom. To this end, we first calculate cohesive energies relative to free atoms, formation energies relative to 2D SL constituents, and also formation energies relative to nanoribbons E_{jf} . In Table 3.2, the values calculated for periodic and finite-size composites are presented.

Table 3.2: The calculated values of the average cohesive energy E_C (eV per pair), the formation energy E_f per cell at $T = 0$ K relative to 2D SL constituents (eV per cell), and the junction formation energy E_{jf} at $T = 0$ K relative to the corresponding nanoribbons (eV per cell).

System	E_C (eV)	E_f (eV)	E_{jf} (eV)
A: S_2 / M_2	14.01	− 1.35	
A: S_2 / M_{10}	13.39	− 1.19	
A: S_{10} / M_2	15.12	− 1.14	
A: S_{10} / M_{10}	14.29	− 1.11	5.39
A: S_{20} / M_2	15.35	− 1.33	
A: S_{20} / M_6	15.01	− 1.01	
A: S_{20} / M_{10}	14.74	− 1.26	5.26
Z: S_2 / M_2	14.21	− 0.55	
Z: S_2 / M_{10}	13.44	− 0.59	
Z: S_{10} / M_2	15.14	− 0.91	
Z: S_{10} / M_{10}	14.31	− 0.73	4.31
Z: S_{20} / M_2	15.36	− 1.10	
Z: S_{20} / M_6	15.02	− 0.66	
Z: S_{20} / M_{10}	14.75	− 0.89	4.15
A: $M_2 - S_{10} - M_2$	14.73	− 2.43	
A: $M_6 - S_{10} - M_6$	14.07	− 3.59	
A: $M_{10} - S_{10} - M_{10}$	12.58	− 3.72	4.65
A: $M_{10} - S_{10}$	14.14	− 4.19	1.46
A: $M_{20} - S_{20}$	14.24	− 4.34	3.06
Z: $M_2 - S_{10} - M_2$	14.75	− 2.08	
Z: $M_6 - S_{10} - M_6$	14.15	− 1.72	
Z: $M_{10} - S_{10} - M_{10}$	12.64	− 1.75	4.29
Z: $M_{10} - S_{10}$	14.24	− 2.19	2.85

All composite structures have positive cohesive energy relative to free atom energies. On the other hand, the formation energies relative to 2D SL constituents have negative values. Their magnitudes are small for periodic composite structures, but become large for finite-size junctions because of free edges adjacent to vacuums.

Negative formation energies indicate that formation of composite systems unfavorable relative to 2D bare constituents. Under these circumstances, can composite structures form (grow) despite the negative formation energy? This question is answered by the calculations of junction formation energy. Here, the energies of two free standing stripes (nanoribbons) are compared with the energy of the composite formed from these stripes. The junction formation energies E_{jf} of periodic and finite composite structures are positive in Table 3.2. Accordingly, the growth of a composite is favorable energetically, if one type (say M) of stripe continues to grow commensurately after the formation (or growth) of the other type (say S) of stripe.

As for the question of whether a composite structure corresponds to a local minimum and remains stable under strain, it can be answered by the analysis of dynamical and thermal stability. In the dynamical stability, positive frequencies of all modes should be ensured at $T = 0$ K. This, however, does not ensure that the given composite structure corresponds to a deep minimum, and hence sustains thermal excitations. In this respect, the thermal stability can be more critical. In this study, the stability of a composite structure is tested by finite-temperature ab initio MD simulations. After all, a structure which is dynamically unstable, becomes also unstable at low temperature MD simulations.

Results of our thermal stability tests on composite structures are summarized in Figures 3.2(b) and 3.2(e), where the trajectories of atoms of Z : and $A:S_4/M_4$ heterostructures in the xy - and yz -planes are shown. These trajectories are obtained from the position of atoms (averaged over every 100 MD steps) in the course of MD iterations. The fluctuations and average of temperatures throughout 5000 steps are also shown in Figures 3.2(c) and 3.2(f), respectively. The tendency of the atoms to restore their equilibrium positions at a temperature (500 K) considerably higher than room temperature indicates that the in-plane heterostructures are stable and can sustain applications at room temperature.

3.1.3. $MoTe_2/NiTe_2$ Composite Structures: δ -Doping

We focus on the electronic structure of A : and $Z:S_p/M_q$ composite structures. Our results are summarized by the energy bands presented in Figure 3.3. Composite structures (or line compounds) $Z:S_2/M_2$ and $A:S_2/M_2$ are metals. The situation with

$p = 2$, but large q or vice versa can be viewed as if one of the 2D constituent is δ -doped by the other along the x -direction. For example, δ -doping of the wide semiconducting MoTe_2 stripe by the narrow metallic NiTe_2 stripe, which are commensurately joined along their zigzag edges is modeled by $\text{Z:S}_{20}/\text{M}_2$. Even if the resulting composite structure is seemingly metallic in momentum space, the metallic states are confined to the narrow NiTe_2 stripe. The wide MoTe_2 stripes continue to be semiconducting. Energy bands projected to the bonds in the unit cell demonstrate that the metallic bands occurring in the band gap of MoTe_2 are actually separated from the semiconducting stripe and display a 1D character having the density of states $D(E) \sim 1/\sqrt{E}$. Conversely, the same δ -doped composite with the armchair boundary, namely $\text{A:S}_{20}/\text{M}_2$ is a narrow band gap semiconductor in Figure 3.3, where even the narrow M stripe has a narrow band gap. This difference between Z and A edges is explained by the fact that the M stripes of the armchair edged composite is narrower than the zigzag edged ones even if they have the same value of q . However, the narrow band gap is closed by increasing the width of the M stripe. For example, $\text{A:S}_{20}/\text{M}_6$ is metallized. Metallic NiTe_2 lines can be considered as interconnect in MoTe_2 -based nanoelectronics. On the other hand, wide M stripes δ -doped by narrow S stripes, namely $\text{Z:S}_2/\text{M}_{20}$ and $\text{A:S}_2/\text{M}_{20}$ continue to be metallic.

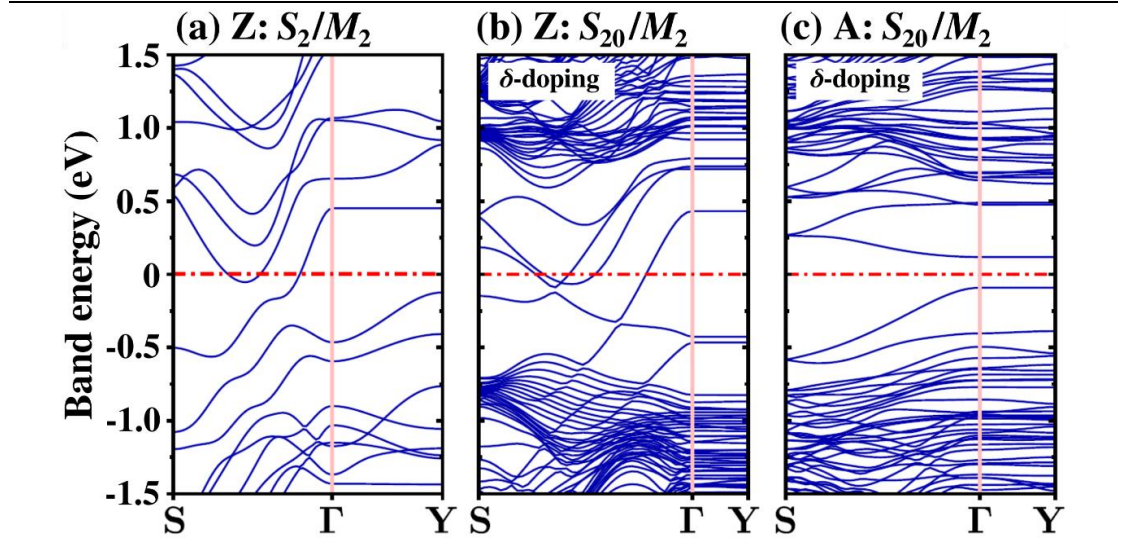


Figure 3.3: Energy bands of specific composite structures. (a) $\text{Z:S}_2/\text{M}_2$, a line compound of MoTe_2 and NiTe_2 , showing a metallic state. (b) $\text{Z:S}_{20}/\text{M}_2$, stripes of semiconducting $(\text{MoTe}_2)_{20}$ which are δ -doped by narrow metallic $(\text{NiTe}_2)_2$ stripes along their zigzag edges. Metallic bands are localized in the M stripe. (c) $\text{A:S}_{20}/\text{M}_2$, in which stripes of semiconducting $(\text{MoTe}_2)_{20}$ are δ -doped by narrow metallic $(\text{NiTe}_2)_2$ stripes along their armchair edges is a narrow band gap semiconductor.

For both small p and q , the composites display properties different from constituent 2D compounds. However, as the S or M stripe is widened with increasing p or q , the properties of wide stripes approach those of respective parent 2D constituents, except the boundary region. Under this circumstance, electronic states are confined to either one of these stripes to construct periodically repeating metal–semiconductor junctions. Briefly, p and q function as parameters to design in–plane composite nanostructures with diverse electronic properties. Under the lateral electric field perpendicular to the boundary of a finite–size composite, A: or Z: M_q – S_p – M_q , metallic stripes at either side of the insulating stripe are charged with opposite polarity and hence store energy. This system operates as an in–plane nanocapacitor [73], and can be viewed as a critical element in atomically thin circuits [73]. As discussed in forthcoming sections, in the similar finite–size composite, the band gap of the S_p stripe acts as a tunneling barrier with well–defined barrier height between two adjacent M_q . Also, the combination M – S – M units can operate as a double barrier resonant tunneling (DBRT) device.

3.1.4. MoTe₂/NiTe₂ Heterostructure: Schottky Barrier

Having outlined critical features of the composite structures, let us now focus on the in–plane, periodic heterostructures with large p and q , for example, Z: S_{20}/M_{10} . Despite significant deformations at the I_I boundary and the formation energy relative to constituent nanoribbons is $E_{jf} = 4.15$ eV per cell, the formation of junctions of individual constituent nanoribbons or S and M stripes is favored. Once the ribbons are joined commensurately, space–charge regions form at the boundaries as demonstrated in Figure 3.4 and determine the bending and lineup of band edges in compliance with the models proposed earlier [23, 128, 129], depending on whether charged impurities are located near I_I and I_{II} .

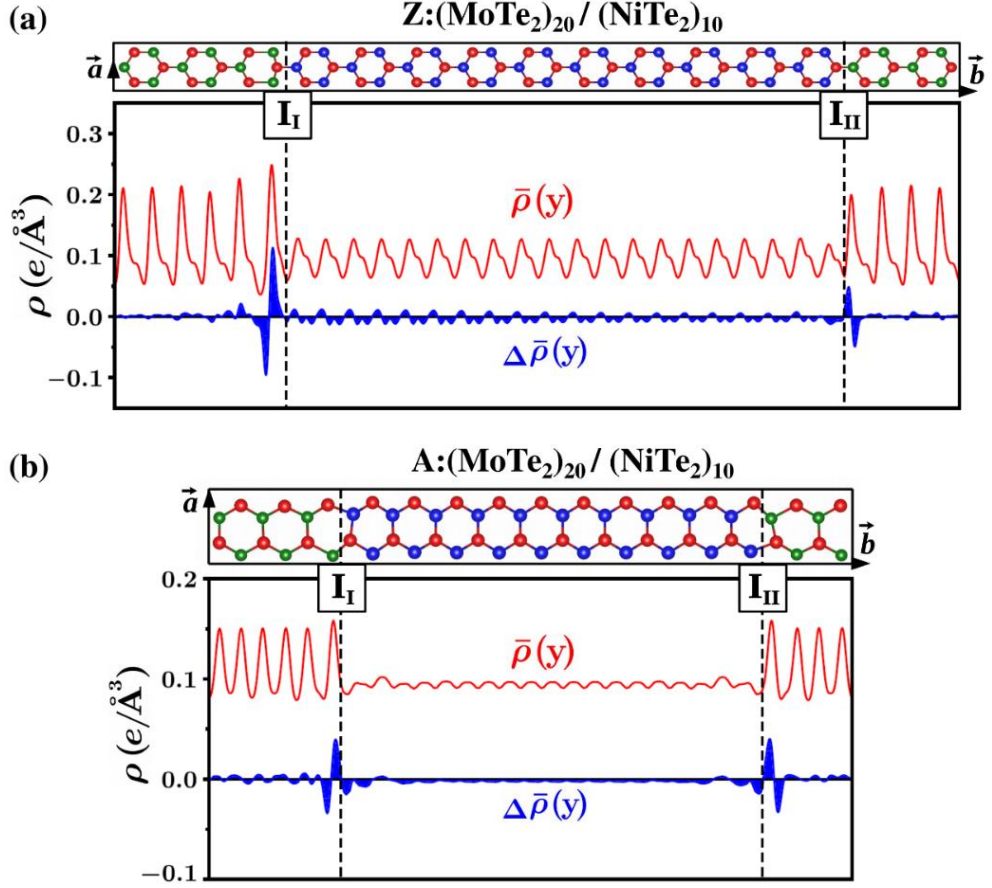


Figure 3.4: The xz -plane averaged charge density $\bar{\rho}(y)$ and charge transfer $\Delta\bar{\rho}(y)$ in Z:S₂₀/M₁₀ (a) and in A:S₂₀/M₁₀ (b). $\Delta\bar{\rho}(y)$ is computed by subtracting the sum of charge densities of 2D SL MoTe₂ and 2D SL NiTe₂ from the charge density of the heterostructure. The upper panels show optimized atomic configurations of each composite structure with two boundaries I_I and I_{II}. The blue (green) and red balls represent Mo (Ni) and Te atoms, respectively. The total charge transfer at the boundaries is $-0.8e$ and $-1.1e$ in Z:S₂₀/M₁₀ and A:S₂₀/M₁₀, respectively.

In the absence of charged impurities as in the present study the bending has to be linear. [23, 128, 129] In Z:S₂₀/M₁₀, Schottky barriers develop in compliance with Figure 3.4(a). The xz -plane averaged potential $\bar{V}(y)$ and the macroscopic average potential [130, 131] $V_{\text{macro}}(y)$ show changes of potential at the boundaries, and also indicate an asymmetry between two different types of boundaries, I_I and I_{II}. The variation of the band gap in direct space, thus the occurrence of alternating metallic and semiconducting zones along the y -direction, is revealed by the densities of states projected to Mo-Te and Ni-Te bonds located at different positions of the unit cell (LDOS) as shown in the insets of Figure 3.5(a). While LDOS in the MoTe₂ stripe has a band gap of 1.25 eV, it is metallic in the NiTe₂ stripe; the Fermi level is pinned by high density of states located near the center of the band gap at I_{II}.

This information is, however, absent in the band structure of $Z:S_{20}/M_{10}$ in momentum space, which displays a metallic state. Separation of semiconducting and metallic regions can also be revealed by the analysis of the contributions of different Mo–Te and Ni–Te bonds in the different band states of the whole heterostructure. While several bands cross the Fermi level in the first panel of Figure 3.5(c), in the second panel the contribution of a Mo–Te bond to the bands is absent in the gap.

This means that while the states in the MoTe_2 –region stripe develop an energy gap, the metallic states of the NiTe_2 region with energy coinciding with this gap cannot propagate in the MoTe_2 region; rather they decay and slightly penetrate to it. This situation is characteristic of a metal–insulator transition in a 2D metallic system. Notably, specific NiTe_2 states, which can match to the momentum and energy of MoTe_2 states in the valence and conduction band continua can propagate along k_y without confinement.

In view of the earlier theories [130, 131], we calculated the energy position and the Schottky barrier height. To this end, we first determined energies of E_{CB} and E_{VB} of 2D SL MoTe_2 from its $V_{\text{macro}}(y)$. We marked these energies in Figure 3.5(a) from the calculated $V_{\text{macro}}(y)$ fixing the conduction and valence band edges. This way, the linear variation of $V_{\text{macro}}(y)$ at the boundaries is reflected to linear band bending. Notably, the energies of the band edges in the direct space in Figure 3.5(a) are in fair agreement with the edges deduced from the edges in LDOS calculated at Mo–Te bonds in the S stripe. At the end the Schottky barrier energies are found to be $E_S = 1.03$ and 1.07 eV (for I_I and I_{II} , respectively) for $Z:S_{20}/M_{10}$ in Figure 3.5. Because of asymmetry of the charge transfer across I_I and I_{II} boundaries, a small tilt of band edges, due to the tilt of $V_{\text{macro}}(y)$, is noticed.

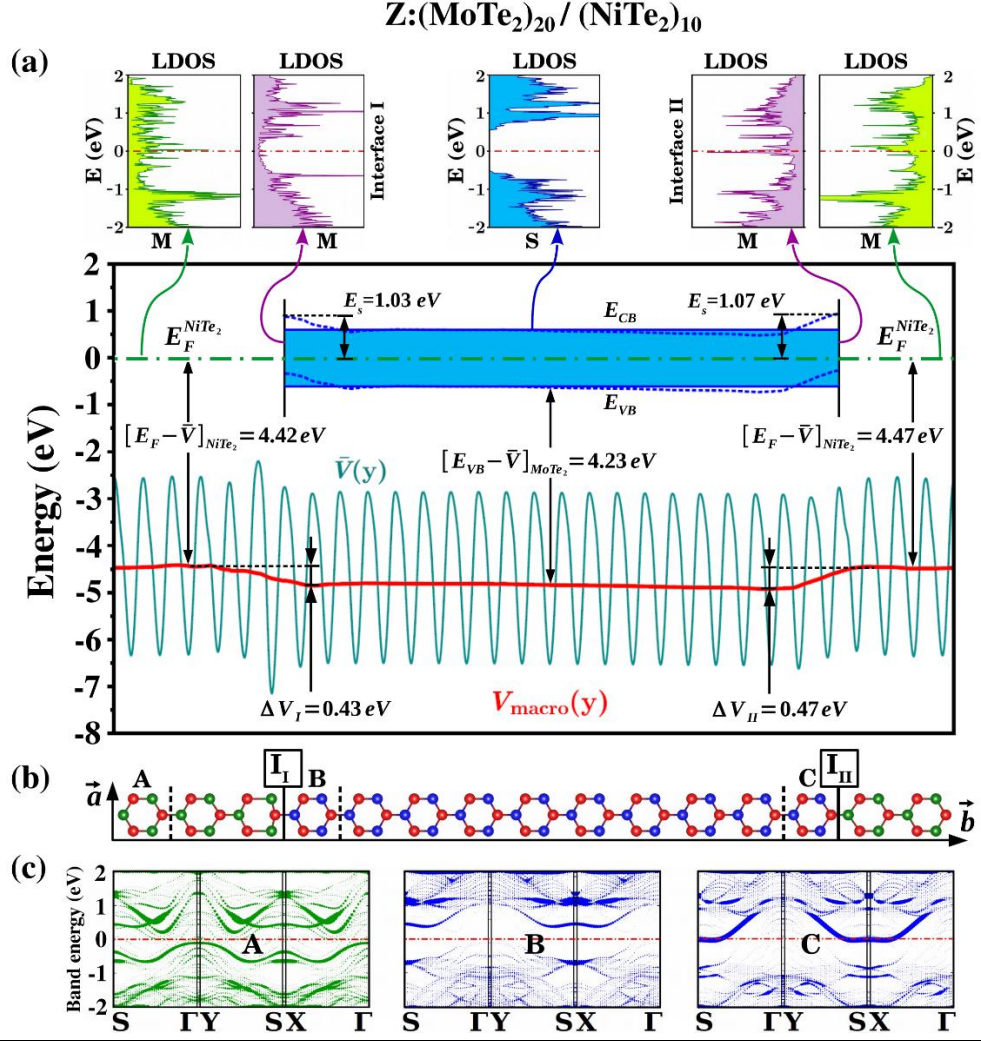


Figure 3.5: Z:(MoTe₂)₂₀/(NiTe₂)₁₀ (or Z:S₂₀/M₁₀) heterostructure. (a) The xz -plane averaged potential $\bar{V}(y)$, (in turquoise) and the macroscopic average potential $V_{\text{macro}}(y)$ (in red). The alignment and bending of VB and CB edge energies with respect to the Fermi level E_F (marked by the dash-dotted line) is shown. The Schottky barrier height E_s relative to E_F is depicted. The local densities of states (LDOS) in the vicinity of E_F are shown at *metallic M*, *semiconducting S*, and boundary regions by insets. (b) Optimized atomic configuration of Z:S₂₀/M₁₀ is described by blue (green) and red balls representing Mo (Ni) and Te atoms, respectively. $\vec{a}$ and $\vec{b}$ are the lattice translation vectors of the 2D rectangular cell of the heterostructure. (c) Energy bands weighted by the contribution of particular bonds designated in (b) by A, B, and C. Thicker bands denote higher contribution.

As seen in Figures 3.6(a)–(c), Schottky junctions form also at the boundaries of A:S₂₀/M₁₀. In contrast to the Z-type boundary, the potential profiles, viz. $V_{\text{macro}}(y)$, at I_I and I_{II} [cf. Figure 3.6(a)] are virtually identical in the A-type boundary. Thus the Schottky barrier height is estimated to be $E_s = 1.12$ eV for both I_I and I_{II} in A:S₂₀/M₁₀.

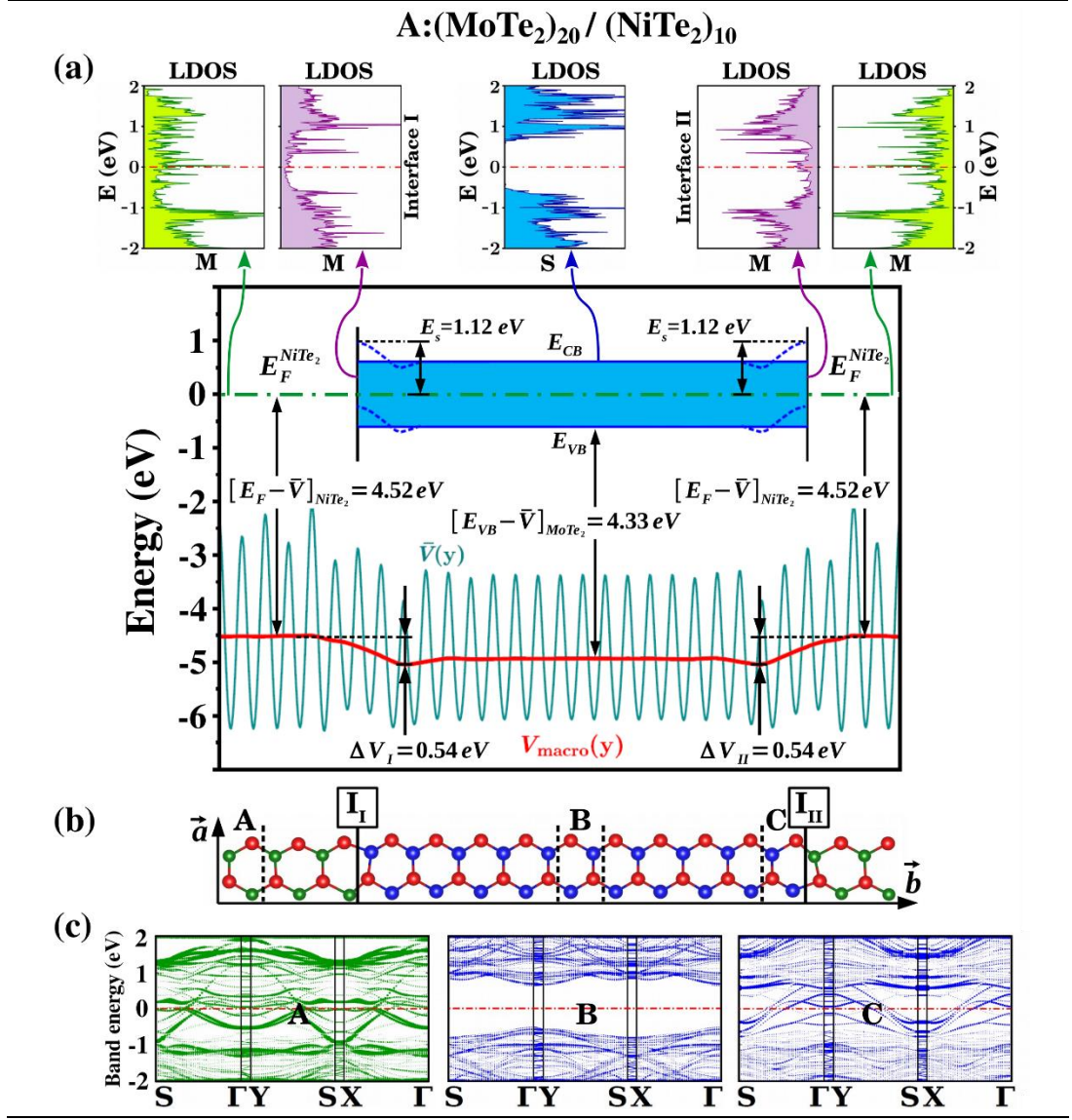


Figure 3.6: A:(MoTe₂)₂₀/(NiTe₂)₁₀ (or A:S₂₀/M₁₀) heterostructure. (a) The xz -plane averaged potential $\bar{V}(y)$ (in turquoise) and the macroscopic average potential $V_{\text{macro}}(y)$ (in red). The alignment and bending of VB and CB edge energies with respect to the Fermi level E_F (marked by the dash-dotted line) is shown. The Schottky barrier height E_s relative to E_F is depicted. The local density of states (LDOS) in the vicinity of E_F is shown at *metallic M*, *semiconducting S*, and boundary regions in the insets. (b) Optimized atomic configurations of A:S₂₀/M₁₀ is described by blue (green) and red balls representing Mo (Ni) and Te atoms, respectively. $\vec{a}$ and $\vec{b}$ are the lattice translation vectors of the 2D rectangular cell of the heterostructure. (c) Energy bands weighted by the contribution of particular atoms indicated in (b) by A, B, and C.

The band structures and the isosurfaces of charge densities $\rho_{nk}(r) = \psi_{nk}^*(r)\psi_{nk}(r)$ of specific states indicated by A, B, C, D, and E therein are presented in Figure 3.7. Despite the fact that several bands seemingly cross the Fermi level in k space and hence imply a metallic state, the charge density plots confirm the

confinement of specific states as discussed above. States of energy bands $E_n(k)$ in the gap region are confined to NiTe_2 stripes and to the boundaries. In Figure 3.7(a), the isosurfaces of the states A and B in the valence and conduction band edge are confined to the S stripe. In contrast, specific states in the gap are confined to the M stripe. The charge density isosurfaces of the states C and D deserve special attention. These states form the bands in the gap, which have high dispersion along the Γ -X direction parallel to the stripes. The minimum of the band of C is above the Fermi level and corresponding states are localized at the boundary I_I , mainly at the Mo-Te bond. The band states D is also highly dispersive along k_x , but is localized strongly along the y -axis at the boundary I_{II} , mainly at Mo-Te bonds; the Fermi level is pinned by this band. Both C and D states are reminiscent of the interface or metal-induced gap states [24, 127, 133, 134] in 3D metal-semiconductor junctions. Here, these states are, however, strictly 1D metallic states in a strictly 2D SL system.

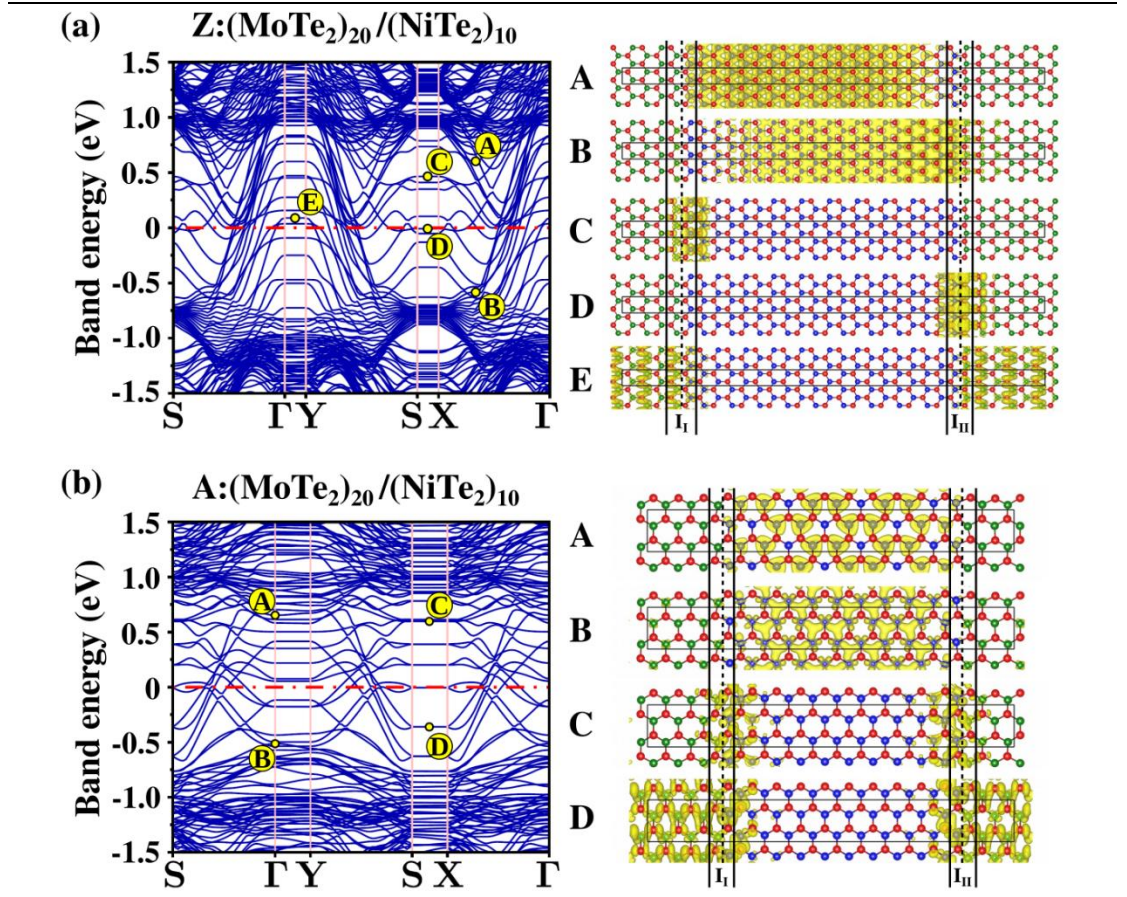


Figure 3.7: (a) (Left) Energy band structure of $\text{Z}:\text{S}_{20}/\text{M}_{10}$ in momentum space. (Right) Isosurfaces of charge densities of the selected band states A, B, C, D, and E. The isosurface charge density is $0.5 \times 10^{-3} e/\text{\AA}^3$. (b) Same for $\text{A}:\text{S}_{20}/\text{M}_{10}$.

In Figure 3.7(b), the $A:(\text{MoTe}_2)_{20}/(\text{NiTe}_2)_{10}$ in-plane heterostructure exhibits similar behaviors. The A and B states at the edges of CB and VB of the semiconducting MoTe_2 stripe are confined to this region. The C state of the dispersive bands in the band gap is confined to the boundaries I_I and I_{II} and is strictly one-dimensional. The band state indicated by D originates from NiTe_2 stripes and is 2D for large q .

3.1.5. Single Metal–Semiconductor Junction and Tunneling Barrier

In a finite system consisting of one S stripe joined M stripe, for example, $Z:M_{10}-S_{10}$, one can attain a 1D metal–semiconductor junction with a single Schottky barrier as shown in Figure 3.8. This system appears as a single stripe composed of S and M stripes and capped by vacuum from both sides. The optimized atomic configuration is presented in Figure 3.8(a). Specific regions of interest are indicated by numerals ①–⑥. The bands contributed by the bonds in regions ①–③ in the NiTe_2 stripe cross the Fermi level and hence attribute a metallic state. In contrast, in regions ⑤ and ⑥ in the MoTe_2 stripe a band gap is opened indicating a semiconducting state. The common Fermi level is located almost at the middle of the gap. This finite-size system mimics a single Schottky barrier despite the unsaturated bonds at either edge facing the vacuum. Plane averaged potential $\bar{V}(y)$ shows differences at the edges. The edge effects can be eliminated through the saturation by specific atoms. The level of average potential shifts down by 0.42 eV at the semiconducting side.

A tunneling barrier is constructed by commensurately joined $(\text{NiTe}_2)_{10}-(\text{MoTe}_2)_{10}-(\text{NiTe}_2)_{10}$ (or $M_q-S_p-M_q$) stripes capped by vacuum from both sides. While NiTe_2 stripes remain metallic, a gap opens in the MoTe_2 stripe in between. Metallic states see the edge of the conduction band of the semiconducting stripe, which is aligned 1.1 eV above the Fermi level as a tunneling barrier of $\Phi_B = 1.1$ eV. As a result, metallic states cannot propagate in the semiconducting stripe, but they can tunnel from the left side to the right side. The width w and height Φ_B of the barrier can be tuned by the width of MoTe_2 or by p . For $p = 2$, Φ_B does not occur, and is considered as a δ -doping. However for $p \geq 5$ a well-defined barrier of significant width starts to form.

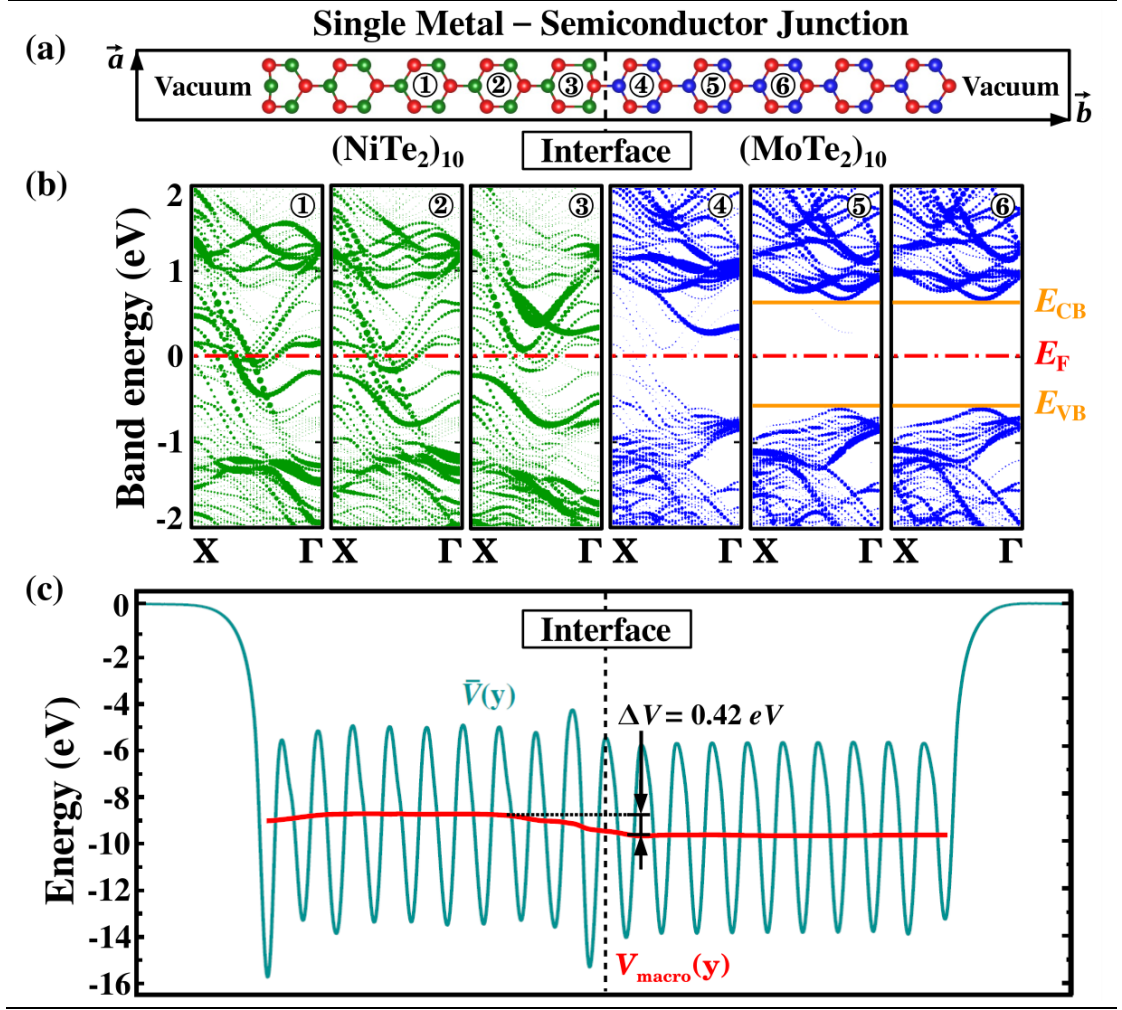


Figure 3.8: A finite-size metal-semiconductor junction Z:(NiTe₂)₁₀–(MoTe₂)₁₀. (a) The atomic configuration and vacuum space at both sides. Numerals indicate specific regions and Mo–Te or Ni–Te bonds in the junction. (b) Contributions of specific regions are indicated by numerals in (a) to the energy bands. Thicker bands denote higher contribution. Bands are metallic at the NiTe₂ side, but a gap is opened in the MoTe₂ side. In panels ⑤ and ⑥ no states exist between E_{CB} and E_{VB} . (c) xz-plane averaged electronic potential and its average $V_{macro}(y)$.

A resonant tunneling double barrier (RTDB) device can be constructed by the extension of the tunneling barrier in Figure 3.9(d) through the combination $M_q-S_p-S_t-S_p-M_q$, where S_t is as shown in Figure 3.9(e). Here S_t is an SL MX_2 stripe having narrow band gap and nearly lattice matched to the S stripe. Trigonal NiSe₂, hexagonal WTe₂ or CrTe₂ fit to these descriptions [56] and form a quantum well between two S stripes. Confined electronic states in this well mediate very fast tunneling time from the left M stripe to the right M stripe. The character of this device can be determined by S , t , and p .

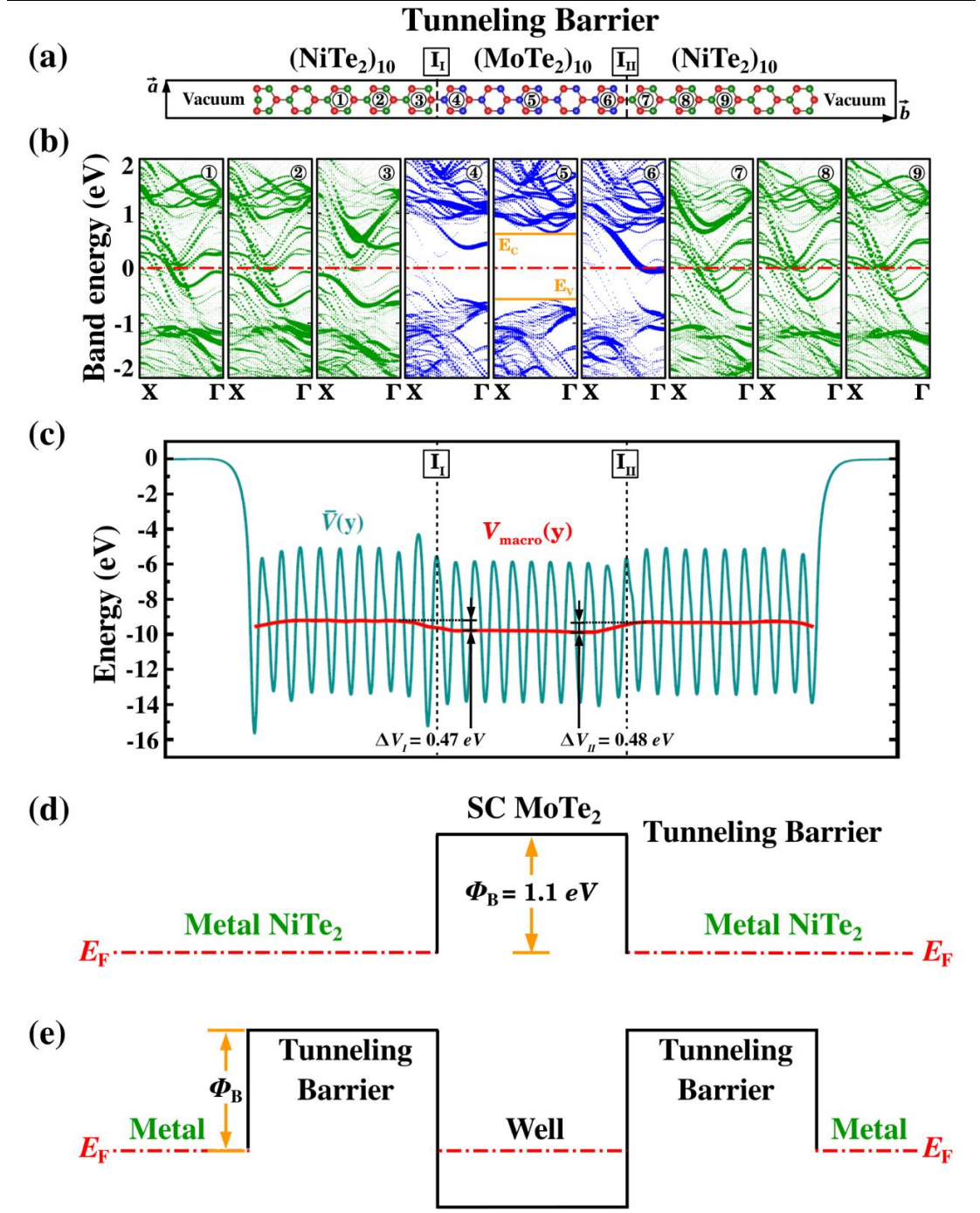


Figure 3.9: $(\text{NiTe}_2)_{10}$ – $(\text{MoTe}_2)_{10}$ – $(\text{NiTe}_2)_{10}$ (or M_q – S_p – M_q) junction functioning as a tunneling barrier between two metal electrodes also as a nanocapacitor. (a) The optimized atomic configuration with boundaries I_I and I_{II} . Numerals indicate specific regions and Mo–Te or Ni–Te bonds. (b) Contributions of specific regions indicated by numerals in (a) to the energy bands. Thicker bands denote higher contribution. Bands are metallic at the NiTe_2 side, but a gap is opened in the MoTe_2 side. (c) xz –plane averaged electronic potential $\bar{V}(y)$, and its average $V_{\text{macro}}(y)$. (d) Schematic description of the tunneling barrier with barrier energy Φ_B between two metals at both sides. (e) Formation of RTDB structure with M_q – S_p – S_t – S_p – M_q , where S_t denotes hexagonal or trigonal SL transition–metal dichalcogenides stripe with narrow band gap.

3.2. Lateral and Vertical Heterostructures of Transition Metal Dichalcogenides of MoTe₂/NiTe₂

In this section, we investigate periodic lateral and vertical heterostructures of transition metal dichalcogenides (TMDCs). Lateral heterostructures are constructed by the alternating metallic and semiconducting single-layer stripes of TMDCs joined commensurately along their armchair edges and attain different states depending on the widths of constituents. While these heterostructures acquire a composite character with metallic state for narrow stripes, large stripes lead to the confinement of electronic states and function as metal/semiconductor junctions with a tunable Schottky barrier. The interface or boundary between constituent stripes has finite extension and allows charge transfer between them. On the other hand, the weak van der Waals interaction between layers sets the features of vertical heterostructures. Their interfaces are sharp: metal/semiconductor junction and Schottky barrier developed thereof can be induced even within a few layers. In the absence of dopants, we find minute charge transfer across the interface with negligible band bending in vertical heterostructures. The δ -doping of the semiconducting constituent by the metallic one forms strictly two-dimensional metallic electrons in a three-dimensional layered semiconductor and leads to crucial directionality effects and quantization of conductance. Our work unveils significant differences between lateral and vertical heterostructures.²

3.2.1. Atomistic Models and Energetic Stability

Our atomistic models of the lateral and vertical heterostructures are described in Figure 3.10. Along the x -direction of the lateral ones in Figures 3.10(a)–(b) the constituent stripes, SL MoTe₂ and NiTe₂, extend to infinity (without any edge); the y -direction is perpendicular to the armchair edges, along which two different stripes repeat alternately and periodically. In the xy -plane, the heterostructure has a 2D rectangular lattice and each constituent consists of three parallel atomic planes, where the plane of metal atoms (Mo or Ni) is capped by two Te atomic planes.

2. The Section 3.2 and its subsections are adapted from Aras M., Kılıç Ç., Ciraci S., (2018), “Lateral and Vertical Heterostructures of Transition Metal Dichalcogenides”, The Journal of Physical Chemistry C, 122 (3), 1547–1555.

The interfaces (or boundaries) between two commensurately joined constituent stripes, I_1 and I_2 , are 1D. The lateral heterostructures are repeated periodically along the z -direction with a vacuum spacing of 20 Å in a three-dimensional (3D) orthorhombic lattice. Small lattice mismatches between constituents induce inhomogeneous small strains in the heterostructures, which can easily be compensated.

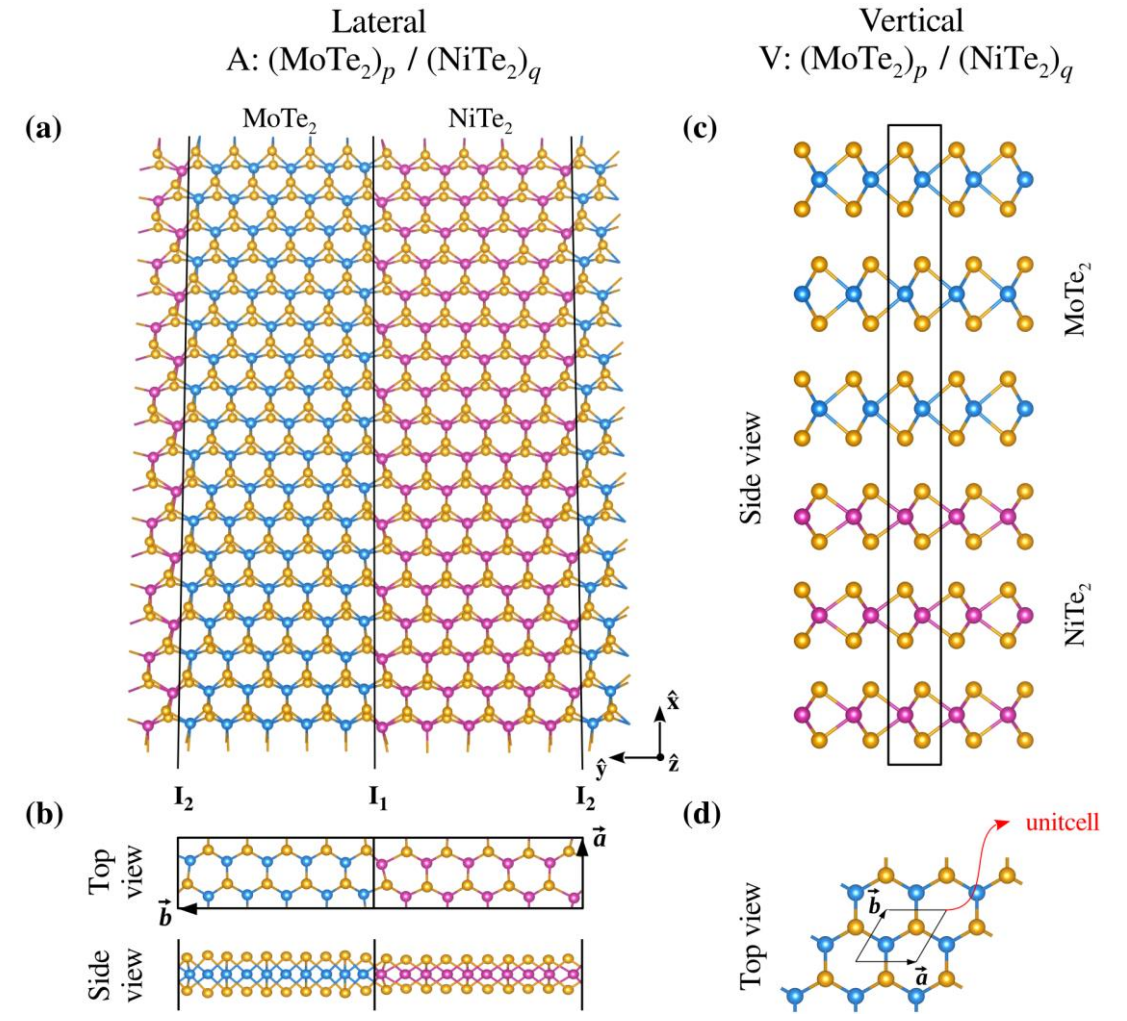


Figure 3.10: (a) Top and (b) side views of atomistic model of SL, lateral heterostructure A:(MoTe₂)_p/(NiTe₂)_q with $p = 10$ and $q = 10$. Blue, magenta, and gold balls indicate Mo, Ni, and Te atoms, respectively. Two-dimensional rectangular unit cell with Bravais lattice vectors $\vec{a}$ and $\vec{b}$ is also shown. I_1 and I_2 are interfaces (or boundaries) between different constituent TMDC stripes along the armchair edges. (c) Side view of the vertical heterostructure V:(MoTe₂)_p/(NiTe₂)_q with $p = 3$ and $q = 3$. (d) Top view. Three-dimensional hexagonal unit cell is delineated in side and top views.

Vertical heterostructures are produced by layer-by-layer stacking of 2D SL constituents, which interact weakly with adjacent layers. A vertical stack of p layers of one constituent is followed by a stack of q layers of the other constituent as shown in Figure 3.10(c). This stacking sequence repeats periodically and continuously with a 3D hexagonal lattice. The definition of the cohesive energy E_C and formation energy E_f , which are used to specify the energetics, are presented in the *Appendix A*. We note that cohesive energy is given relative to constituent atoms, and E_C indicates cohesion. The formation energy is given relative to 3D layered bulk parent crystals, which constitute global minima. Accordingly, heterostructures with slightly negative formation energies are stable in local minima on the Born–Oppenheimer surface.

Before we start to study heterostructures, we note that whereas 2D SL NiTe₂ is a nonmagnetic metal, 2D SL MoTe₂ is a semiconductor with a direct band gap. Earlier it was shown that LDA predicts the fundamental band gaps of SL TMDCs close to the measured values. [135] Also, earlier experimental and LDA band gaps of TMDCs such as MoS₂, MoSe₂, WS₂, and WSe₂ were shown to be in agreement. [136] The band gap of SL MoTe₂ is calculated using LDA to be direct, and $E_g = 1.25$ eV. This value is in agreement with the experimental value of 1.10 eV. [137] This band gap increased to only 1.34 eV by applying the correction using hybrid functionals. [120, 121] On the other hand, the band gap decreased slightly to 1.15 eV in calculations using PBE+D3. Given this relatively small variation in the band gap, the lateral heterostructures consisting of a single layer are treated within the LDA. However, the van der Waals (vdW) interaction is taken into account for the vertical heterostructures through the PBE+D3 approach. [119] We did not apply the GW correction, since it is not feasible computationally for the large systems we are treating and also is known to overestimate the band gaps of SL TMDCs. [135]

In Tables 3.3 and 3.4 we summarize optimized values of cohesive energy, formation energy, optimized lattice constants, and fundamental bandgaps of lateral and vertical heterostructures $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ and $V:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$, respectively. Values of 3D crystals, trilayers, bilayers, and monolayers are presented as Table B1.1 in *Appendix B*.

Table 3.3: Optimized values of lateral heterostructure $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ for $1 \leq p = q \leq 10$, values of average cohesive energy $\bar{E}_C$, average formation energy $\bar{E}_f$, two-dimensional rectangular lattice constants a and b , and fundamental bandgap E_g .

Composite (p/q)	$\bar{E}_C$ (eV)	$\bar{E}_f$ (eV)	a (Å)	b (Å)	E_g (eV)
A:(1/1)	13.780	-0.707	5.966	3.444	
A:(2/2)	13.893	-0.594	6.083	7.025	
A:(3/3)	14.049	-0.438	6.054	10.486	
A:(4/4)	14.119	-0.369	6.090	14.065	
A:(5/5)	14.128	-0.360	6.067	17.515	0.426
A:(6/6)	14.143	-0.344	6.098	21.123	0.778
A:(7/7)	14.151	-0.336	6.089	24.608	0.962
A:(8/8)	14.158	-0.329	6.073	28.050	1.053
A:(9/9)	14.164	-0.323	6.076	31.572	1.124
A:(10/10)	14.172	-0.315	6.074	35.065	1.173

Table 3.4: Optimized values of vertical heterostructure $V:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$, values of average cohesive energy $\bar{E}_C$, average formation energy $\bar{E}_f$, superlattice constants $a = b$ and c , interface spacing d_{int} , and fundamental indirect bandgap E_g .

Composite (p/q)	$\bar{E}_C$ (eV)	$\bar{E}_f$ (eV)	$a = b$ (Å)	c (Å)	d_{int} (Å)	E_g (eV)
V:(1/1)	11.988	-0.075	3.589	12.797	3.108	
V:(2/2)	12.012	-0.051	3.581	25.910	3.227	
V:(3/3)	12.019	-0.044	3.579	38.887	3.271	0.641
V:(4/4)	12.023	-0.040	3.528	51.667	3.203	0.657
V:(5/1)	12.734	-0.032	3.528	41.192	3.306	0.722
A:(1/5)	11.328	-0.033	3.651	36.239	3.105	

3.2.2. Lateral Heterostructures of $\text{MoTe}_2/\text{NiTe}_2$

The electronic structure of 2D SL MoTe_2 and NiTe_2 as well as the energetics and thermal stability of zigzag or armchair edged lateral heterostructures were discussed in Section 3.1.2. In this section, we consider features which were not treated earlier. Moreover, we contrast these features with those of the vertical heterostructures.

The armchair edged lateral heterostructures $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ have large cohesive energies in the range of $E_C = 14$ eV per formula unit, but negative formation energies in the range of $E_f = -0.4$ eV. However, the growth of a heterostructure from two freestanding constituent stripes is favored, since the formation of junction is exothermic due to saturation of dangling bonds at the boundaries. The electronic structures of these heterostructures made of the periodic junctions of semiconducting and metallic stripes of MoTe_2 and NiTe_2 of different widths exhibit diverse features. The most interesting feature is that they are metallic in both momentum and direct space for small p and q ; these heterostructures can be considered as a composite structure or a special alloy. However, electronic states are confined in different constituent stripes as p and q increase and constituent stripes start to display the electronic properties of their parent 2D TMDCs. Namely, the heterostructure changes from metal to metal–semiconductor junction, as indicated in Figure 3.11.

For $p = q \geq 5$, a band gap starts to open in the MoTe_2 stripe, which is enlarged as p increases, while NiTe_2 remains a metal. This band gap in the MoTe_2 stripe constitutes a potential barrier for the metallic states of NiTe_2 , and causes them to be confined between two MoTe_2 stripes. Hence, the heterostructure starts to function as a metal–semiconductor junction for $p = q \geq 5$, but the semiconducting stripe assumes the electronic properties of 2D MoTe_2 for $p \sim 10$. The charge can be transferred across the boundaries I_1 and I_2 , whereby the edges of the conduction and valence bands in direct space are bent.

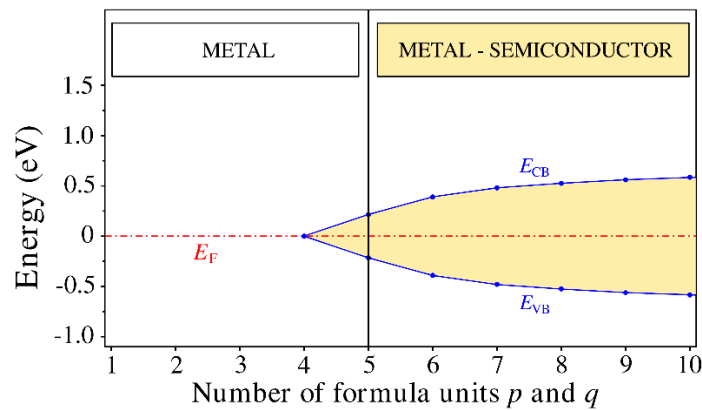


Figure 3.11: Transition from metal to metal–semiconductor junction with increasing $p = q$ in $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ heterostructure. The band gap between the conduction E_{CB} and valence band E_{VB} edges at the center of MoTe_2 is shaded. The zero of energy is set at the Fermi level E_F .

The confinement of electrons in adjacent stripes leading to a metal–semiconductor transition through phase separation in direct space and eventually the formation of Schottky barrier will now be discussed in detail. In Figure 3.12, the unit cell, Brillouin zone (BZ), energy bands projected to Te–Mo–Te and Te–Ni–Te units in the heterostructures, and corresponding projected densities of states of $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ for $p = q = 1$ and $p = q = 5$ are shown. The energy bands projected to Te–Mo–Te and Te–Ni–Te units are of particular importance, since they show the contribution of these units to the states of any band.

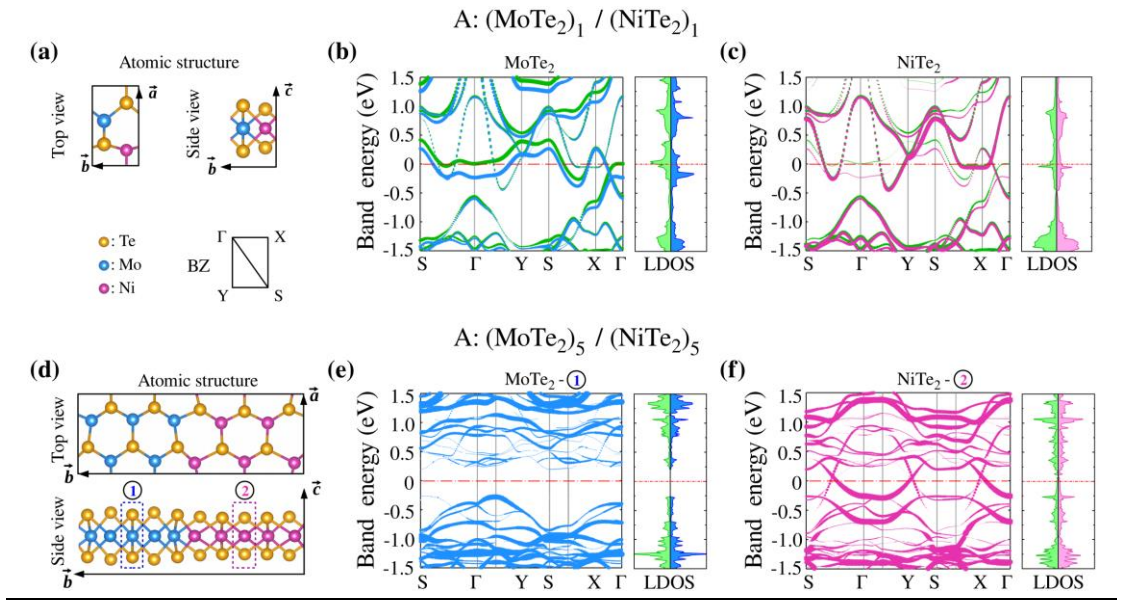


Figure 3.12: $A:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$ lateral heterostructure. (a) Unit cell with 2D rectangular lattice and corresponding Brillouin zone, BZ. (b) Bands projected to the Te–Mo–Te unit in the unit cell and corresponding asymmetric spin-polarized projected densities of states. (c) Bands projected to the Te–Ni–Te unit in the unit cell with spin-polarized projected densities of states. (d–f) Same for $A:(\text{MoTe}_2)_5/(\text{NiTe}_2)_5$. Bands are projected to the Te–Mo–Te and Te–Ni–Te units in the labeled unit cells. Zero of energy is set to the common Fermi level.

For $p = q = 1$, both Te–Mo–Te and Te–Ni–Te units contribute to the density of states (DOS) at the Fermi level and attribute a metallic character to the heterostructure. Additionally, the spin-polarized DOS is asymmetric at the MoTe_2 side, but the resulting net magnetic moment is negligible. The situation for $A:(\text{MoTe}_2)_5/(\text{NiTe}_2)_5$, however, is rather different. The contribution of a Te–Mo–Te unit at the center of the MoTe_2 stripe to the bands at the Fermi level ceases, while the contribution of a Te–Ni–Te unit at the Fermi level continues. This is the initial stage for the onset of the metal–semiconductor transition.

The electronic phase separation and band lineup leading to Schottky barrier formation is completed in $A:(\text{MoTe}_2)_{10}/(\text{NiTe}_2)_{10}$, where the band gap at the MoTe_2 stripe approaches the value of the fundamental band gap of 2D SL MoTe_2 as shown in Figure 3.13. The plane averaged electronic potential energy and its average value $\bar{V}(y)$ shown in Figure 3.13(b) are different in different stripes. $\bar{V}(y)$ is nearly flat inside each stripe, but its value changes smoothly and linearly across the boundary. This is in compliance with the Schottky–Mott theory. [23, 128]

In Figure 3.13(c), DOSs projected to different Te–cation–Te units indicated by the numerals are shown. The band gap is opened inside the central MoTe_2 stripe, but it is closed by approaching the boundaries. However, the NiTe_2 stripe is metallic with finite DOS at the common Fermi level. This is the demonstration of a metal–semiconductor transition, whereby a totally metallic heterostructure $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ with $p = q \leq 4$ changes to a semiconductor in the MoTe_2 side and forms a Schottky barrier for $p = q = 10$. This transition occurs with the confinement of electronic states to one of the constituents. At the end each stripe transforms gradually to its parent 2D SL structure with increasing p and q . Owing to the symmetry of the boundaries, $\bar{V}(y)$ is not tilted inside the semiconducting side of the heterostructure.

To determine the Schottky barrier, we first obtain the energy band diagram in direct space. To this end, the energies of the valence band edge, E_{VB} , and the conduction band edge, E_{CB} , relative to $\bar{V}(y)$ are retrieved from SL 2D MoTe_2 . In spite of the fact that this is a rather rigorous method for very wide MoTe_2 stripes, E_{VB} and E_{CB} can conveniently be determined directly from the LDOS by projecting the DOS to the Te–Mo–Te unit at the center of the stripe as illustrated in Figure 3.13(c). This way effects due to confinement of carriers in the stripe are taken into account. Then, following the methods developed earlier for 3D junctions, [131, 138] and by marking these band edges relative to $\bar{V}(y)$, one can draw the band diagram indirect space. Here the premise is that the energies of E_{VB} and E_{CB} will remain invariant across the MoTe_2 stripe. Accordingly, owing to the linear variation of $\bar{V}(y)$ near boundaries, the band edges are bent at the interface. By definition, the Schottky barrier energy E_S is the energy from the common Fermi level to E_{CB} at the interface, which is taken to be sharp. Based on this construction, the Schottky barrier is calculated to be $E_S = 1.03$ eV. We note that the value of E_S depends on the widths of stripes, or p and q , but it converges to a value for a very wide stripe.

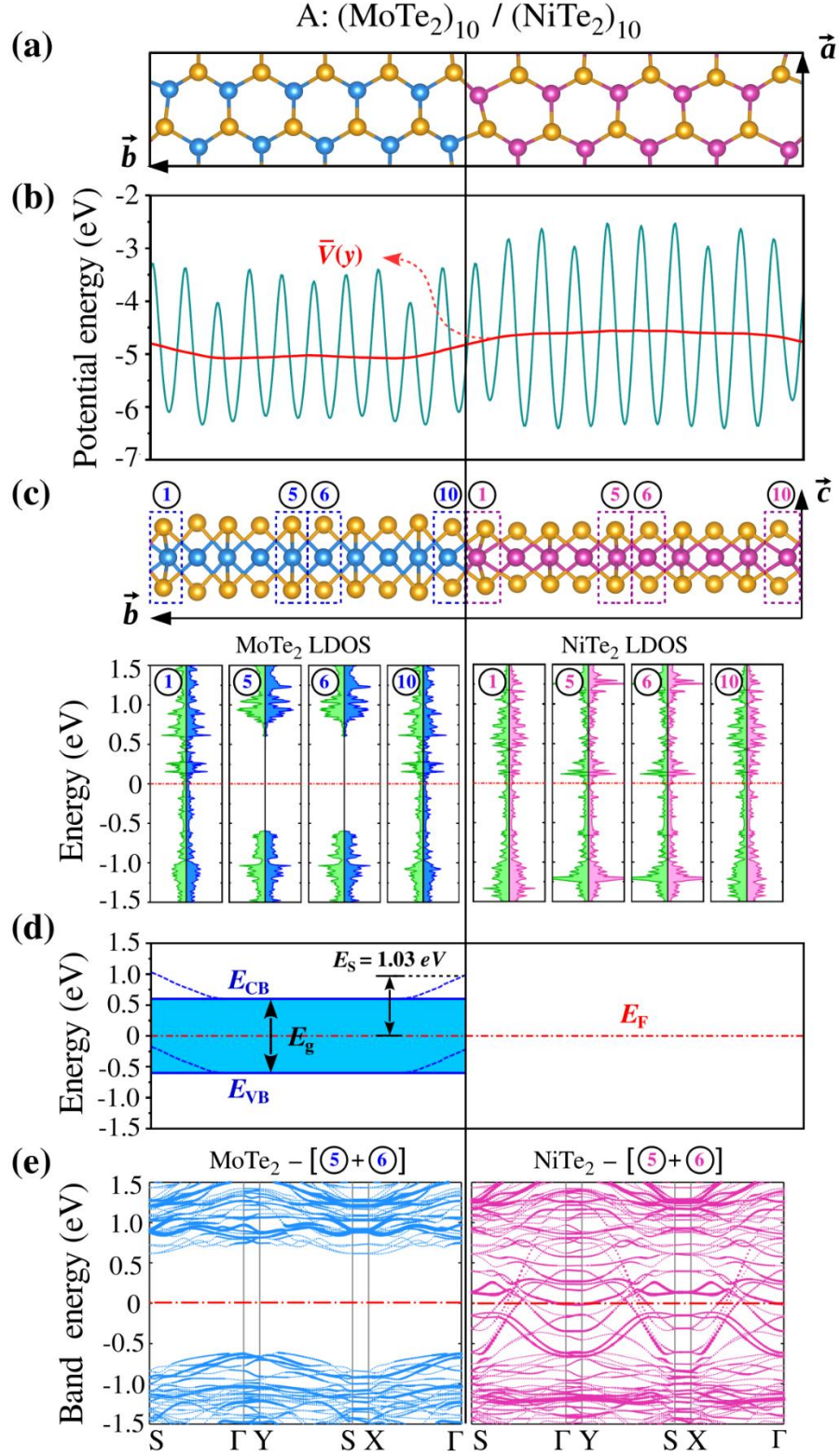


Figure 3.13: Heterostructure A:(MoTe₂)₁₀/(NiTe₂)₁₀. (a) Unit cell with lattice vectors. (b) Plane averaged electronic potential energy and its average along y -direction, $\bar{V}(y)$. (c) Spin-polarized densities of states projected to Te-Mo-Te and Te-Ni-Te units in the labeled unit cells. (d) Formation of metal (NiTe₂ stripe)-semiconductor (MoTe₂ stripe) junction with band lineup and Schottky barrier. (e) Bands projected to the Te-Mo-Te and Te-Ni-Te units in the unit cells specified in (c).

The physical explanation of pinning of the Fermi level and bending of bands is as follows: Upon the opening of a band gap inside the MoTe₂ stripe, metallic NiTe₂ states have to decay inside MoTe₂ when their energies coincide with the gap. This way, excess electronic charge is accumulated at the MoTe₂ side close to the boundary, which in turn, bends $\bar{V}(y)$ near the boundaries. Metallic states of NiTe₂ decaying toward MoTe₂ and pinning the Fermi level is reminiscent of the metal induced states (MIGS) proposed for 3D bulk metal–semiconductor junctions [24, 132].

At this point another point worth emphasizing concerns the width of the interface: Our results show that the boundary or interface between metal and insulator is not sharp; a distance corresponding to a few MoTe₂ units is needed at each boundary to recover the semiconducting side of the heterostructure. This situation marks the dramatic difference between present 2D lateral and 3D bulk metal–semiconductor junctions. In this respect, crucial aspects one should take into account are the dimensionality, thickness, and width of the in–plane lateral structure. Our calculations indicate the following crucial features:

- (i) The boundary region between metallic and semiconducting stripes cannot be sharp, but has a finite extension.
- (ii) The energy band diagram in the direct space cannot be uniform across the semiconducting stripe; the band gap can be closed in the boundary region because of metallic states penetrating the semiconducting side.

Under these circumstances, the Schottky barrier of in–plane, lateral heterostructures can be determined directly from LDOS calculated at the atoms across the semiconducting stripe. One should keep in mind that an uncertainty is involved in determining band edges from LDOS in this direct method. In Figure 3.13(e), the Schottky barrier determined from LDOS appears to be reduced to ~ 0.7 eV.

3.2.3. Vertical Heterostructures of MoTe₂/NiTe₂

The vertical heterostructures are constructed by stacking 2D SL MoTe₂ and NiTe₂ layers as described in Figures 3.10(c)–(d). For a better understanding of heterostructures involving multilayer stacking of constituents, we first consider the

variation of the electronic structures of NiTe_2 and MoTe_2 in single layer (SL), bilayer (BL), trilayer (TL), and periodic multilayer (ML) bulk forms. In forming bilayer, trilayer, and multilayer structures, interlayer distance and stacking geometry are fully optimized including vdW interaction. We found that NiTe_2 remained metallic in SL and ML forms. However, the situation is critical for the semiconducting MoTe_2 as shown in Figure 3.14. The monolayer structure of MoTe_2 is a semiconductor with a direct band gap of 1.15 eV occurring at the K-point of hexagonal BZ. In the bilayer, the band gap is slightly reduced and becomes indirect. It occurs between the maximum of the valence band at the Γ -point and the minimum of the conduction band along the Γ -K direction. By stacking one more layer in TL, the gap continues to reduce, but remains indirect. Finally, in 3D layered MoTe_2 the band gap is indirect and saturates at 0.75 eV. Apparently, the fundamental band gap of MoTe_2 slabs reduces with an increasing number of layers and changes from direct to indirect. Our results are in fair agreement with the band gaps deduced from monolayers and multilayers of MoTe_2 . These results may have important implications in the context of band tunability which reflects the electronic properties of vertical heterostructures.

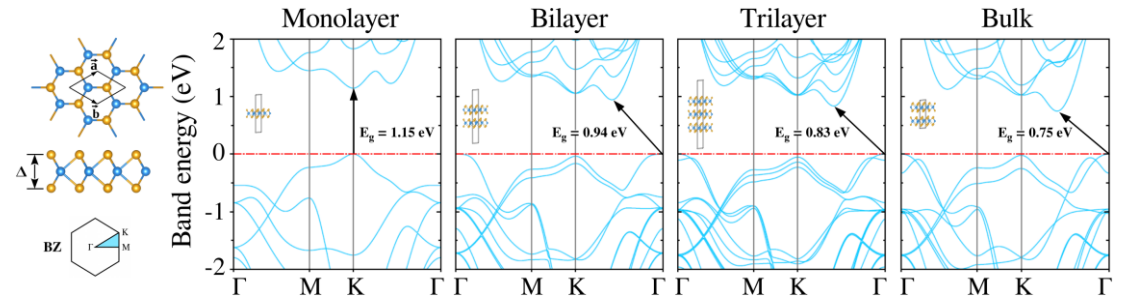


Figure 3.14: Electronic energy band structure of monolayer, bilayer, trilayer, and periodic bulk MoTe_2 . The zero of energy is set at the top of the valence band.

In a vertical heterostructure, $\text{V}:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$, p and q are crucial parameters, which control the electronic properties. Confinements leading to electronic phase separation can take place for large $p = q \geq 2$. Additionally, as revealed in the above discussion, the electronic properties of the MoTe_2 side depend also on p . For the sake of comparison with lateral heterostructures, we first consider $\text{V}:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$ where alternately SL MoTe_2 and NiTe_2 are stacked. While this stacking is reminiscent of lateral and metallic $\text{A}:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$, in the vertical one, as shown in Figure 3.15(a), metallic and semiconducting regions start to

be separated in the direct space and acquire only minute state density at the MoTe₂ unit. Apparently, the weak vdW interaction between adjacent SL MoTe₂ and NiTe₂ layers cannot couple the states of these two layers. In Figure 3.15(b), the projected bands and LDOS of V:(MoTe₂)₃/(NiTe₂)₃ indicate that a well-defined metal–semiconductor junction is formed: the MoTe₂ side appears as a semiconductor with an indirect band gap of 0.64 eV, while the NiTe₂ side remains metallic in Figure 3.15(b). This feature of vertical vdW heterostructures becomes even more critical in δ -doping, where one SL TMD can be implemented in the thick slab constructed by the other SL TMD. In Figure 3.15(c), an SL MoTe₂ is placed on top of every vertically stacked five SL NiTe₂'s to form V:(MoTe₂)₁/(NiTe₂)₅. This construction results in one layer of 2D semimetal in a thick metallic NiTe₂ slab. Accordingly, the vertical conductivity of such a device is limited while the lateral 2D conductivity remains high. Conversely, in V:(MoTe₂)₅/(NiTe₂)₁, a strictly 2D sheet of metallic zone is generated in a semiconducting slab having a band gap of 0.72 eV. Electrons confined in this 2D metallic sheet may exhibit interesting dimensionality effects and quantization. [139–143] In particular, the conductance G is quantized; it changes in steps of quantum of conductance with changes in Fermi energy; each band dipping in the Fermi level opens a conduction channel. Although it is not resolved from LDOS of δ -doped NiTe₂, the state density projected to the 2D metallic layer shows a staircase behavior in steps of $m/\pi\hbar^2$ per unit area [144]. Also, specific bands projected to NiTe₂ in Figure 3.15(d) dip into the Fermi level and increase the electron density under compressive strain. Eventually, conductance $G_{\parallel}$ jumps by the quantized value, $2e^2/\hbar$. Such a behavior can be used as a device function.

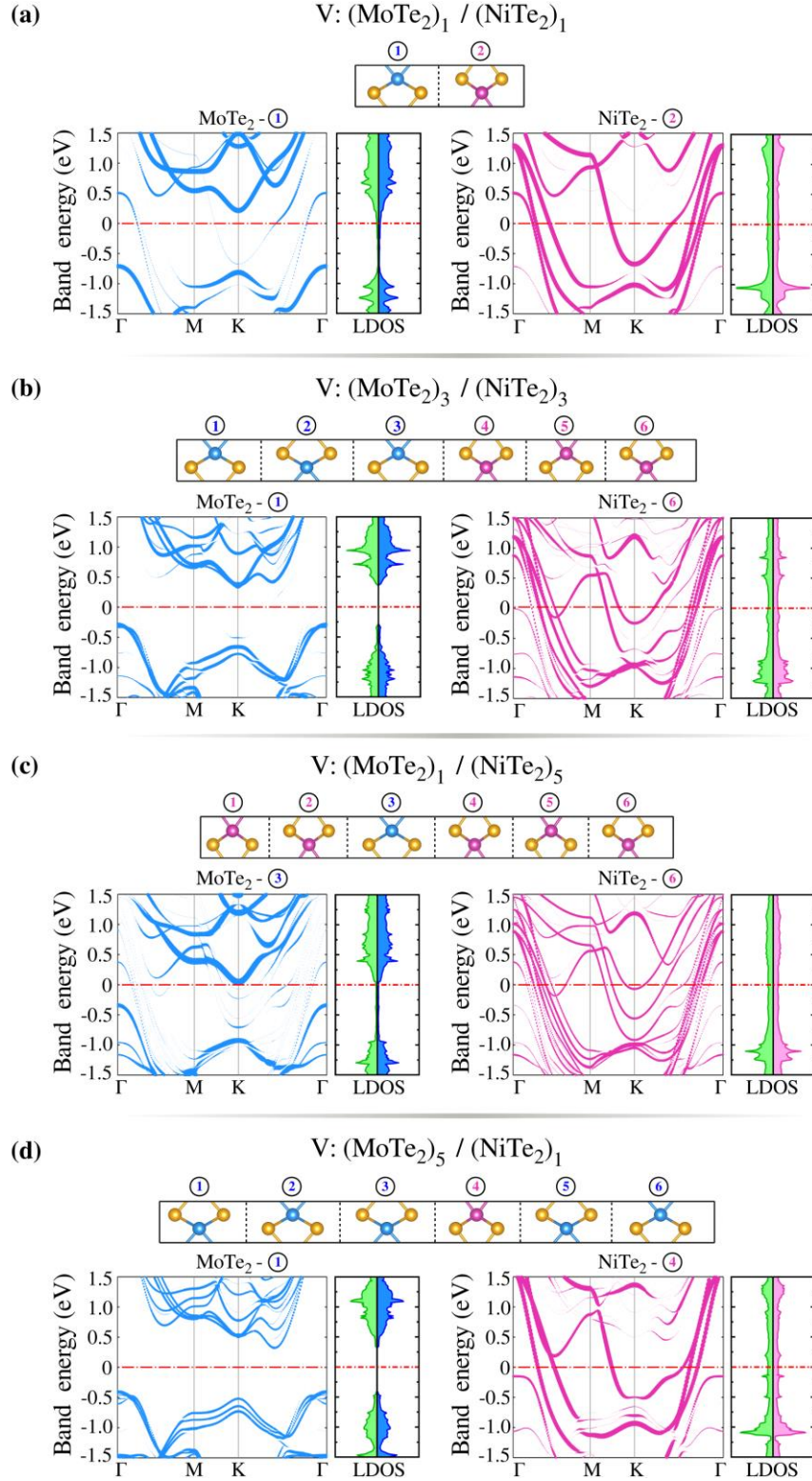


Figure 3.15: (a) $V:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$ heterostructure. Unit cell, energy bands, and corresponding state densities projected to adjacent Mo–Te₂ and Ni–Te₂ pairs. (b) $V:(\text{MoTe}_2)_3/(\text{NiTe}_2)_3$ heterostructure with a well-defined metal–insulator junction. (c) $V:(\text{MoTe}_2)_1/(\text{NiTe}_2)_5$. δ -doping of NiTe₂ slab by a single sheet of MoTe₂. (d) $V:(\text{MoTe}_2)_5/(\text{NiTe}_2)_1$. δ -doping of semiconducting MoTe₂ slab by a single sheet of metallic NiTe₂.

Crucial differences are observed between the vertical heterostructure $V:(\text{MoTe}_2)_4/(\text{NiTe}_2)_4$ in Figure 3.16 and the lateral in-plane heterostructure $A:(\text{MoTe}_2)_{10}/(\text{NiTe}_2)_{10}$ in Figure 3.13, which become apparent in the electronic potential energy diagrams. For example, in the electronic potential energy diagram of the vertical heterostructures, one recognizes high potential energy regions between the adjacent layers. Due to the latter, the conduction phenomena in vertical heterostructures may become directional. The DOS projected to Te–cation–Te units shown in Figure 3.16(c) distinguishes two domains in the heterostructure. In the stack of MoTe_2 the empty conduction band states are separated from filled valence band states by a fundamental band gap of 0.66 eV. In contrast, the DOS projected to Ni–Te₂ pairs are all metallic in the adjacent stack of four NiTe_2 layers. This behavior indicates a periodic metal–semiconductor junction. Similar behavior occurs also in a non-periodic single junction. The energy band diagram can be constructed in the direct space by joining conduction and valence band edges of each Te–Mo–Te unit. Here the interface between metallic and semiconducting regions is sharp. Since the charge transfer from the MoTe_2 side to the NiTe_2 side is minute in the absence of dopants near the interface layers, the bending or tilting of bands in direct space is negligible. However, three features are of importance:

- (i) At the MoTe_2 side the band gap is slightly reduced at the interface. This is in compliance with the recent predictions. [144]
- (ii) The largest gap at the MoTe_2 side is smaller than the band gap of 2D SL MoTe_2 . This is in compliance with Figure 3.14. The energy bands projected to Mo–Te₂ and Ni–Te₂ units at different locations of the unit cell show the formation of semiconductor–metal junction with a Schottky barrier of $E_S = 0.3$ eV.
- (iii) Spin-polarized LDOSs are symmetric, and the whole system is nonmagnetic. It should also be noted the bands are expected to bend down in the case of *n*-type MoTe_2 stack, where excess carriers spill to NiTe_2 .

Our calculations reveal that periodic lateral and vertical heterostructures formed by semiconducting SL MoTe_2 and metallic SL NiTe_2 constitute two different class of composite materials exhibiting diverse electronic properties depending on the composition (extension) of the constituents. The predicted properties herald novel artificial materials, which can be crucial for 2D electronics.

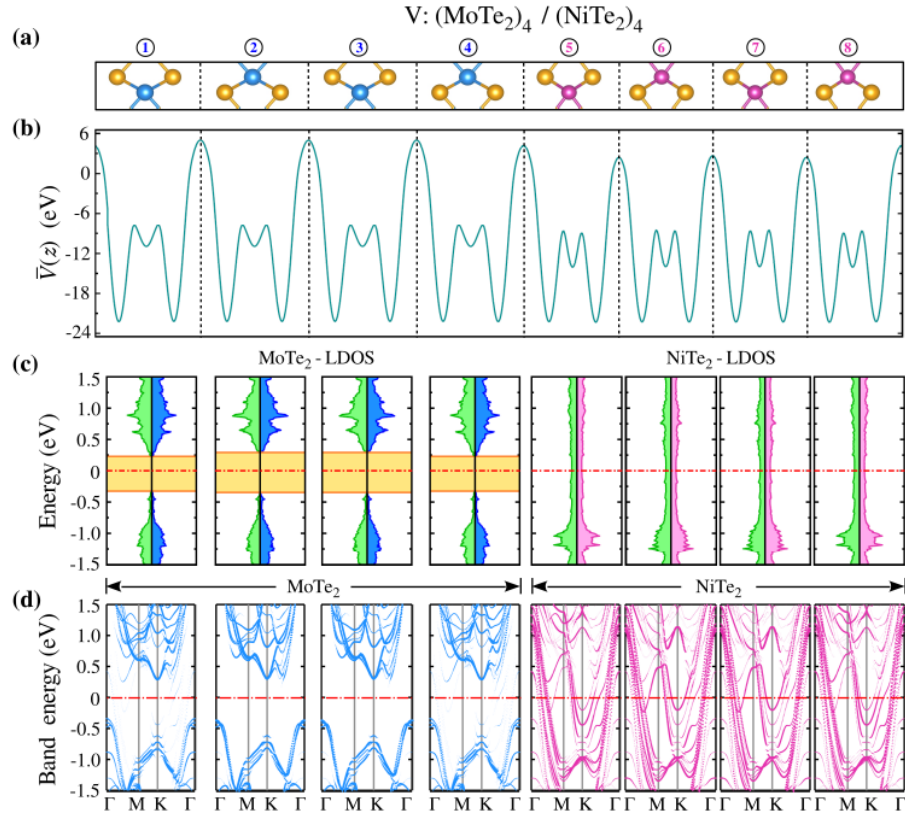


Figure 3.16: V:(MoTe₂)₄/(NiTe₂)₄ heterostructure. (a) The unit cell and chalcogen–cation–chalcogen units are specified by numerals. (b) Plane averaged electronic potential $\bar{V}(z)$. (c) Densities of states projected to chalcogen–cation–chalcogen units. The fundamental band gap at MoTe₂ side is shaded. (d) Bands projected to chalcogen–cation–chalcogen units.

In armchair edged, in-plane, lateral heterostructures, the coupling between different constituents is strong because of covalent + ionic Mo–Te and Ni–Te bonds crossing the boundaries. For small p and q , namely for narrow stripes of constituents, the heterostructure is a composite metal. Upon widening of stripes, $p \geq 5$, a band gap is opened in the MoTe₂ side. Electrons of metallic NiTe₂ having energies coinciding with the band gap decay into the semiconducting side and pin the Fermi level. This way the metallic region penetrates the semiconductor and charge can transfer across the boundaries between two constituents. The boundaries have finite width, but are symmetric. The average electronic potential energy, which is rather flat and horizontal in the stripes, changes linearly across the boundary; no sawtooth-like tilting occurs. For finite size semiconducting stripes, the band edges can conveniently be retrieved from the density of states projected to the chalcogen–metal–chalcogen units in the unit cell. This way, confinement effects are taken into account. For wide stripes, one can attain the fundamental band gap of 2D SL MoTe₂. Energies of band

edges relative to the average potential of SL 2D MoTe₂ should coincide with those obtained directly from the LDOS at the center of the wide stripe. Our calculations indicate that the band gap is not uniform, but it is closed in the vicinity of the boundary. According to earlier methods developed initially for 3D heterostructures, Schottky barrier energy would be determined as the energy from the Fermi level to the edge of the conduction band, which follows the electronic potential energy $\bar{V}(z)$ and bends as shown by the dashed curve in Figure 3.13(d). However, we found that band edges traced this way in the direct space deviate near the boundary from the ones determined directly using LDOS. This situation constitutes the dramatic effect of dimensionality.

Vertical heterostructures obtained by the periodic stacking of constituent 2D MoTe₂ and NiTe₂ layers behave rather differently from the armchair edged lateral heterostructure. The van der Waals interaction, albeit weak, is the main cause of the differences. The vertical heterostructure with $p = q = 1$ exhibits semimetallic character along the z -direction with minute state density at the Te–Mo–Te unit, which is a good metal in the xy -plane. For $p = q \geq 2$ semiconducting and metallic phases are separated and metal–semiconductor junction is formed. The interface is sharp and planar; band bending is negligible for undoped MoTe₂ stacks. The plane averaged electronic potential, $\bar{V}(z)$, is relatively high between two adjacent layers, which may limit the conductivity along the z -direction. The Schottky barrier is calculated as the energy from the Fermi level to the conduction band edge. The fundamental band gap at the semiconductor side is narrower as compared to lateral heterostructure, since the band gap of MoTe₂ decreases and changes from direct to indirect by going from monolayer to bilayer and multilayers.

The δ -doping is even more interesting in vertical structures. We predict that, by replacing one sheet of NiTe₂ multilayer slab with MoTe₂ monolayer, the structure acquires directional features: Along the z -direction it is a semimetal with the conduction band of MoTe₂ touching the Fermi level and hence has poor perpendicular conductivity, $\sigma_{\perp}$, but it is a good metal and has good lateral conductivity $\sigma_{\parallel}$ in the NiTe₂ slab. Conversely, by replacing one sheet of the MoTe₂ slab by NiTe₂ monolayer, one can attain a strictly 2D metallic sheet within a semiconductor. Staircase-like densities of states and quantized conductance and also other features related to the dimensionality can be attained and exploited in 2D device applications.

3.3. Magnetic Ground State in FeTe₂, VS₂, and NiTe₂ Monolayers

Our analysis based on the results of hybrid and semilocal density–functional calculations with and without Hubbard U correction for on–site Coulomb interactions reveals the true magnetic ground states of three transition–metal dichalcogenide monolayers, viz., FeTe₂, VS₂, and NiTe₂, which comprise inhomogeneous magnetic moment configurations. In contrast to earlier studies considering only the magnetic moments of transition–metal atoms, the chalcogen atoms by themselves have significant, antiparallel magnetic moments owing to the spin polarization through p – d hybridization. The latter is found to be true for both H – and T –phases of FeTe₂, VS₂, and NiTe₂ monolayers. Our predictions show that the FeTe₂ monolayer in its lowest–energy structure is a half–metal, which prevails under both compressive and tensile strains. Half metallicity occurs also in the FeTe₂ bilayer but disappears in thicker multilayers. The VS₂ monolayer is a magnetic semiconductor; it has two different band gaps of different character and widths for different spin polarization. The NiTe₂ monolayer, which used to be known as a nonmagnetic metal, is indeed a magnetic metal with a small magnetic moment. These monolayers with intriguing electronic and magnetic properties can attain new functionalities for spintronic applications.³

3.3.1. Inhomogeneous Spin Arrangement: Antiparallel Magnetic Moments at Chalcogen Atoms

We used 1×1 supercells based on the 2D monolayer unit cells (with one MX_2 unit), including a vacuum spacing of 20 Å between periodic images of the monolayer along the direction perpendicular to the monolayer. We performed structural optimizations where the equilibrium value of the 2D lattice constants was determined via minimization of the total energy and the ionic positions were relaxed until the residual forces on atoms were reduced to be smaller than 10^{-2} eV/Å. The Brillouin zone sampling was done using $12\times 12\times 1$ (FeTe₂ and NiTe₂) or $18\times 18\times 1$ (VS₂) k –point meshes generated according to the Monkhorst–Pack scheme [121].

3. The Section 3.3 and its subsections are adapted from Aras M., Kılıç Ç., Ciraci S., (2020), “Magnetic Ground State in FeTe₂, VS₂, and NiTe₂ Monolayers: Antiparallel Magnetic Moments at Chalcogen Atoms”, Physical Review B, 101 (5), 054429.

Using the optimized structures, we performed electronic structure calculations in order to obtain the magnetic and electronic states of FeTe₂, VS₂, and NiTe₂. The density derived electrostatic and chemical (DDEC) spin partitioning technique [147, 148] was employed to divide the magnetic moment μ_{tot} per formula unit among the constituent atoms M and X , which was preferred to ensure $\mu_{\text{tot}} = \mu_M + 2\mu_X$.

In order to assess the stability of the magnetic ground state of FeTe₂, we scanned a variety of competing magnetic configurations generated by using 2×2 supercells (SCs) that contain four FeTe₂ units, and computed the total energy E_{SC} using HSE for a range of fixed values of the supercell magnetic moment M_{SC} . We also studied the variation of E_{SC} with the total magnetic moments of the Fe and Te sublattices in order to identify the character of exchange interactions between the Fe–Fe, Fe–Te, and Te–Te atom pairs.

Earlier studies based on dynamical and thermal stability analysis have ensured the stability of the FeTe₂ (e.g., Refs. [56, 79]), VS₂ (e.g., Refs. [56, 149, 150]), and NiTe₂ (e.g., Refs. [42, 56]) monolayers in both H and T structures with trigonal prismatic and octahedral coordination, respectively. As one can see from Table 3.5, regardless of the method of calculation, for FeTe₂ and VS₂ (NiTe₂) monolayers, the H (T) phase has lower energy for FeTe₂ and VS₂ (NiTe₂) monolayers. Therefore, we present the results for H –FeTe₂, H –VS₂, and T –NiTe₂ mono– and multi–layers, and also mention some results for the higher–energy structures for comparison.

Table 3.5: The difference between the optimized total energies, ($E_H - E_T$, in meV per formula unit) of H – and T –phases for FeTe₂, VS₂, and NiTe₂ monolayers.

Monolayer	LDA	PBE	HSE
FeTe ₂	–44	–14	–65
VS ₂	–18	–41	–59
NiTe ₂	+281	+224	+334

The LDA and PBE calculations with $U = 0$ fail to yield the true magnetic ground state and electronic structure for the FeTe₂ monolayer, both of which result in a ferromagnetic metallic state with non–integer values of the magnetic moment. After adding a Hubbard U term to either LDA or PBE functional, a band gap starts to open in the density of states (DOS) of minority spins for $U > 1.5$ eV. Notably, both PBE+ U and LDA+ U with $U = 2$ eV predict a small band gap of the minority spin

states but a metallic state for majority spins. The net (total) magnetic moment is calculated to be $\mu_{\text{tot}} = 2\mu_B$ using both methods. As U increases, the band gap of minority spin states increases, but μ_{tot} remains fixed at $2\mu_B$. The HSE calculations also predict $\mu_{\text{tot}} = 2\mu_B$, and a band gap of 1.77 eV, which is wider than that of LDA even with $U = 5$ eV. Nevertheless, except for the value of the minority band gap, the PBE+ U and HSE calculations yield quite similar electronic structures as seen in Figure 3.17, and also produce the same integer value for the magnetic moment. This agreement between the DFT+ U and HSE results (qualitative for the spin-polarized electronic structure and minority band gap) demonstrates that semilocal DFT calculations, where strong correlations needed for the proper description of d electrons of transition metals are missing, would not necessarily yield the correct magnetic ground state of MX_2 monolayers. The integer values of μ_{tot} (associated with either the magnetic semiconductor or half-metallic behavior) are important and pave the way for a variety of spintronic applications. Apparently, such an important property of bare MX_2 monolayers could have been skipped if the electron–electron interaction was not treated properly.

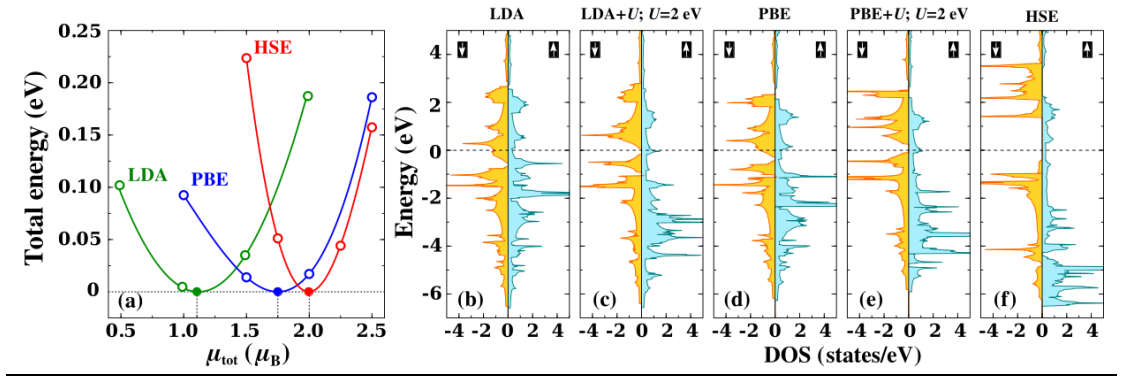


Figure 3.17: Magnetic ground state of FeTe_2 monolayer in H structure predicted by hybrid, semilocal DFT, and DFT+ U calculations. (a) The total energies as a function of the magnetic moment per formula unit μ_{tot} , obtained from the LDA ($U = 0$), PBE ($U = 0$), and HSE calculations. (b)–(f) The densities of states (DOS) of the minority (spin-down, $\downarrow$) and majority (spin-up, $\uparrow$) states of FeTe_2 within various approximations for the electron–electron interaction.

The magnetic ground state of three transition-metal dichalcogenide monolayers, viz., FeTe_2 , VS_2 , and NiTe_2 , calculated with HSE are characterized by plotting the isosurfaces of the spin density $\rho_s(r) = \rho^\uparrow(r) - \rho^\downarrow(r)$ in Figure 3.18(a), where $\rho^\uparrow(r)$ and $\rho^\downarrow(r)$ denote the charge density of spin-up and spin-down states,

respectively. It is seen that the charge densities localized around the transition–metal and chalcogen atoms originate from states of different spin polarizations. Thus, contrary to earlier assumptions which assign the net magnetic moment only to the transition–metal atoms, the chalcogen atoms by themselves have a significant magnetic moment in opposite polarization. The latter is further elaborated by dividing the total magnetic moment μ_{tot} among the constituent atoms to yield $\mu_{\text{tot}} = \mu_M + 2\mu_X$, which is done by the DDEC spin partitioning technique [147, 148]. The alignment of local magnetic moments (μ_M and μ_X) is shown in Figure 3.18(b), which is reminiscent of ferrimagnetic order. Hence, the magnetic ground state in MX_2 monolayers here, some of which were identified earlier as ferromagnetic [151–155], comprise inhomogeneous magnetic moment configurations owing to significant magnetic moments at chalcogen atoms antiparallel to those at transition–metal atoms. We believe that this is an important, insofar fundamental, conclusion, conveying the correct magnetic ground state of FeTe_2 , VS_2 , and NiTe_2 monolayers. This conclusion arrived at in the absence of the spin–orbit coupling shows, contrary to prevailing assumptions [57], that the magnetic order in 2D MX_2 –based materials need not be attributed to the magnetocrystalline anisotropy.

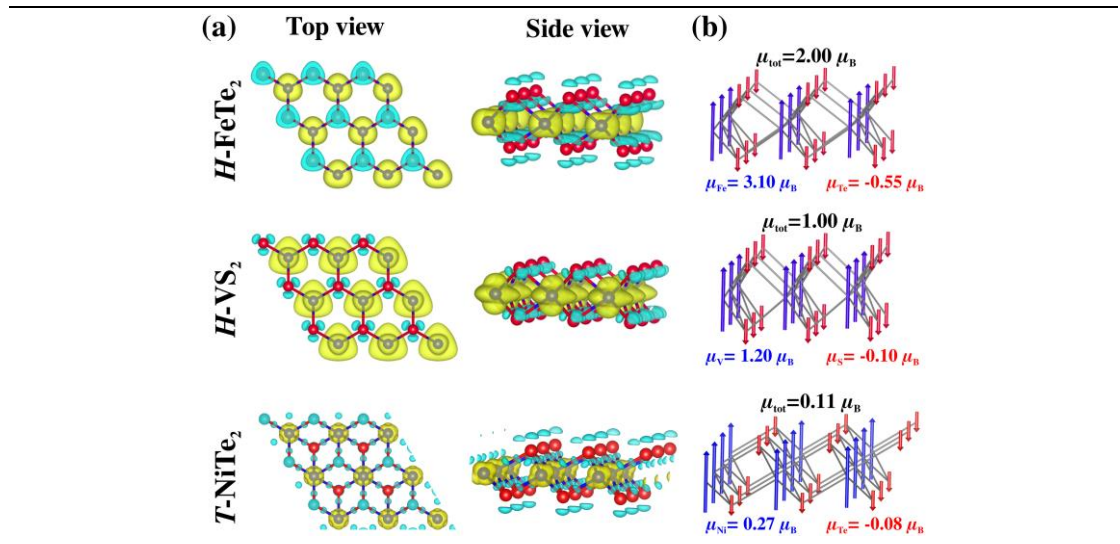


Figure 3.18: (a) Top and side views of the isosurfaces of the HSE–calculated spin density $\rho_S(r)$ for FeTe_2 , VS_2 , and NiTe_2 monolayers in their lowest–energy structures, corresponding to the isovalues of +0.01, +0.0075, and +0.005 (yellow) and –0.01, –0.0075, and –0.005 (cyan) $\mu_B/\text{\AA}^3$, respectively. (b) Local magnetic moments μ_M and μ_X calculated at the transition–metal (M) and chalcogen (X) atoms, respectively. The blue and red arrows (located at the M and X atom sites, respectively) are drawn, not to scale, to indicate opposing spin polarization of the transition–metal and chalcogen atoms.

Figure 3.19(a) displays the bar plots of μ_{tot} and its transition-metal and chalcogen components, i.e., μ_{M} and $2\mu_{\text{X}}$, respectively, for comparing the results obtained at five levels of approximations. It is seen that the DFT+ U and HSE calculations yield either the same or very close values for μ_{tot} of FeTe₂ and VS₂ monolayers, which makes it clear that μ_{tot} is substantially underestimated in the semilocal DFT calculations.

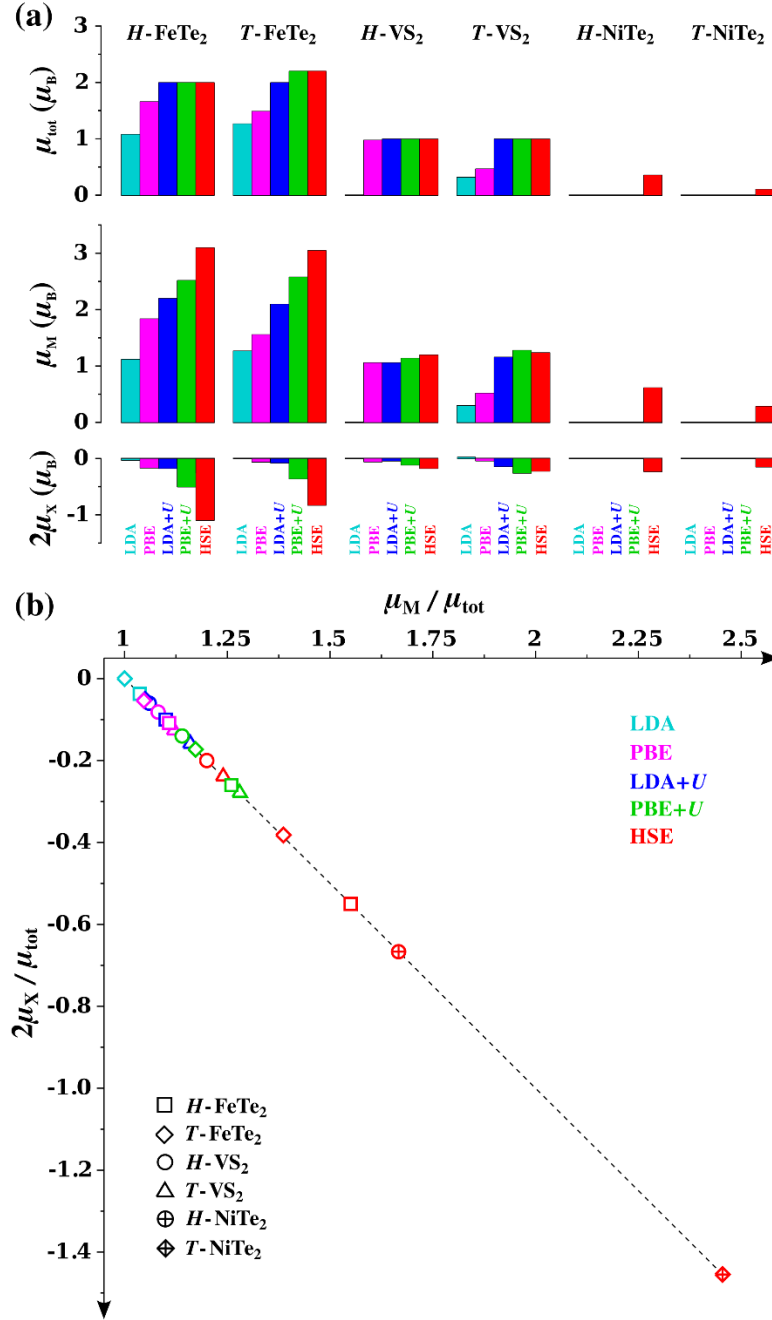


Figure 3.19: (a) The bar plots of μ_{tot} and its components μ_{M} and $2\mu_{\text{X}}$, obtained at five levels of approximation, i.e., LDA, PBE, LDA+ U , PBE+ U , and HSE. (b) The plot of $2\mu_{\text{M}}/\mu_{\text{tot}}$ with respect to $\mu_{\text{M}}/\mu_{\text{tot}}$.

Similarly, whereas the semilocal DFT calculations with $U = 0$ yield a negligibly small μ_X (cf. Refs. [151, 155]), the DFT+ U and HSE results show that μ_X is indeed not negligible compared to μ_{tot} . This is seen better in Figure 3.19(b), where the ratios μ_M/μ_{tot} and $2\mu_X/\mu_{\text{tot}}$ are plotted with respect to each other, which signify the M and X contributions to the magnetic moment, respectively. On the other hand, it can be likely that μ_M and μ_X are both overestimated in the DFT+ U and HSE calculations even though they yield a more reliable value for μ_{tot} , which is supported by the linear correlation between $2\mu_X/\mu_{\text{tot}}$ and μ_M/μ_{tot} in Figure 3.19(b). Furthermore, it is known that the magnetic moment of transition-metal atoms in their elemental metallic solids can be substantially overestimated by HSE, corresponding to an error as high as 35% for elemental Ni solid [156]. Contrary to the latter, the HSE calculations for half metals such as GdN can yield magnetic moments in close agreement with experiment [156]. Fortunately, the metallic NiTe₂ monolayer provides a useful example for the assessment of the HSE-calculated magnetic moments. The HSE calculations yield small but nonzero values for both μ_{Ni} and μ_{Te} , indicating an antiparallel alignment of the Ni and Te moments, whereas $\mu_{\text{Ni}} = \mu_{\text{Te}} = 0$ in all other (LDA, PBE, LDA+ U , and PBE+ U) calculations [cf. Figure 3.19(a)]. Experimental studies on single-crystalline NiTe_x bulk samples [80] as well as NiTe_x nanorods [81], both with chemical bonding reminiscent of that in the T -NiTe₂ monolayer, show that the magnetic moment of NiTe_x decreases with increasing x . Even if this behavior is attributable to the presence of diamagnetism in NiTe_x nanorods [81], an antiparallel alignment of the Ni and Te moments is inferred from it because the diamagnetism was not detected in bulk NiTe₂ single crystals [80]. As long as neither semilocal DFT nor DFT+ U calculations yield an antiparallel alignment of μ_{Ni} and μ_{Te} as in experimental and HSE results, we think that the hybrid rather than other DFT calculations produce reliable estimates for the atomic moments in the NiTe₂ monolayer

The stability of the magnetic ground state of FeTe₂ depicted in Figure 3.18(b) is assessed by comparing the total energies E_{SC} of a variety of competing magnetic configurations generated by using 2×2 supercells, as shown in Figure 3.20. It is to be noted that various types of magnetic configurations where the magnetic moments of the second-neighbor Fe atoms are parallel (the red symbols) or antiparallel (the green and blue symbols in Figure 3.20) are included, which were obtained via minimization of the total energy. It is seen from the HSE-calculated energy profile

plotted in Figure 3.20 that $M_{\text{SC}} = 0$ and $M_{\text{SC}} = 4\mu_{\text{B}}$ configurations have almost the same energy that is 0.19 eV higher than the energy of the configuration corresponding to $M_{\text{SC}} = 8\mu_{\text{B}}$. Hence, the $M_{\text{SC}} = 8\mu_{\text{B}}$ configuration with magnetic order as shown in Figure 3.18(b) has the lowest energy, which is then the magnetic ground state in FeTe₂. It should also be noticed that the system needs to overcome large energy barriers of 0.87 and 1.12 eV in order to have a transition from this configuration to the $M_{\text{SC}} = 4\mu_{\text{B}}$ and $M_{\text{SC}} = 0$ configurations, respectively. For VS₂ and NiTe₂ monolayers, the HSE calculations using 2×2 supercells predict that the antiferromagnetic state has an energy higher than that of the ground state by 0.58 and 0.15 eV, respectively.

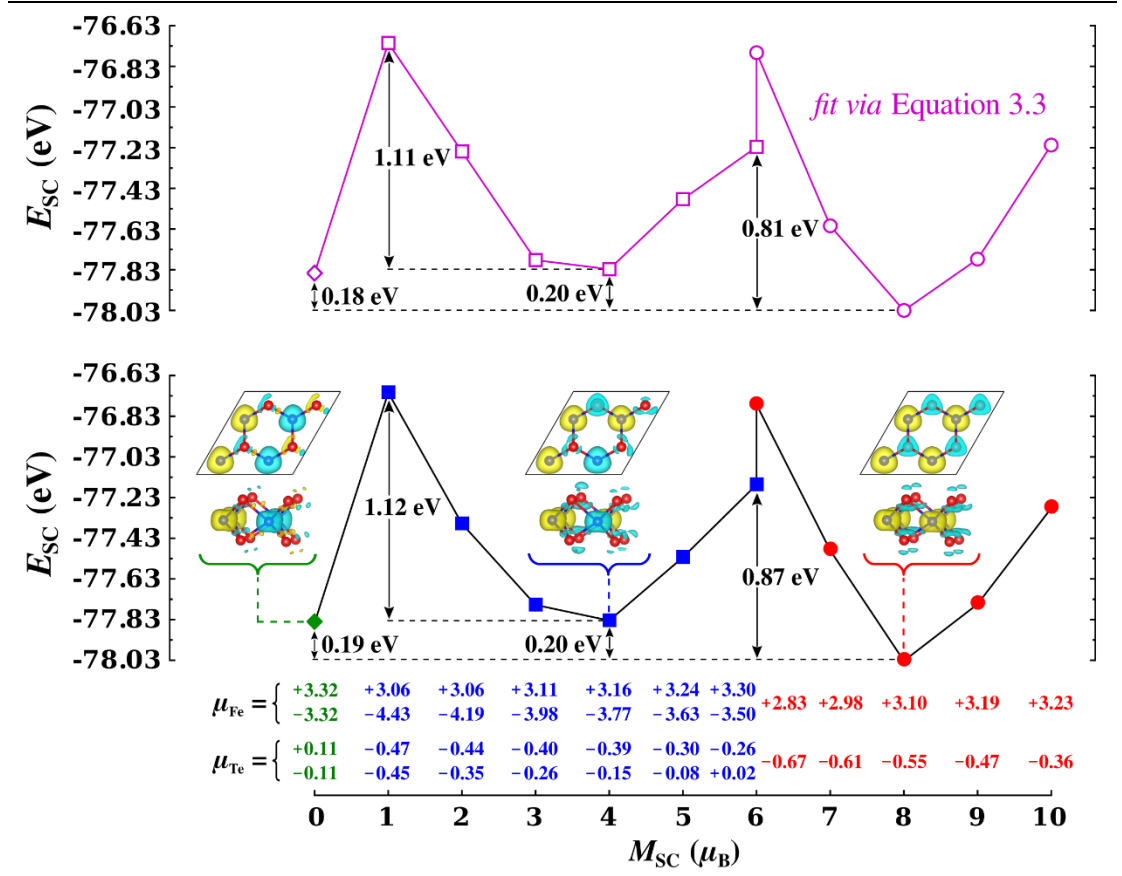


Figure 3.20: The variation of the supercell total energy E_{SC} with the supercell magnetic moment M_{SC} . The solid and open symbols represent the HSE-calculated and fitted points, respectively. The solid lines connecting the calculated as well as fitted points are drawn to guide the eye. The isosurfaces of the spin density for the $M_{\text{SC}} = 0\mu_{\text{B}}$, $4\mu_{\text{B}}$, and $8\mu_{\text{B}}$ configurations are shown as insets.

In order to identify the character of exchange interactions between the Fe–Fe, Fe–Te, and Te–Te atom pairs, we study the variation of the total energy also with the total magnetic moments of the Fe and Te sublattices. A parametrization of E_{SC} as a function of $M_{\text{Fe}} = \Sigma_{\text{Fe}} \mu_{\text{Fe}} / \mu_{\text{B}}$ and $M_{\text{Te}} = \Sigma_{\text{Te}} \mu_{\text{Te}} / \mu_{\text{B}}$ according to

$$\begin{aligned}
 E_{\text{SC}} &= E_0 + E_2 + E_4 \\
 E_2 &= -1/2 (\gamma_{11} M_{\text{Fe}}^2 + 2\gamma_{12} M_{\text{Fe}} M_{\text{Te}} + \gamma_{22} M_{\text{Te}}^2) \\
 E_4 &= g_1 M_{\text{Fe}}^4 + g_2 M_{\text{Fe}}^3 M_{\text{Te}} + g_3 M_{\text{Fe}}^2 M_{\text{Te}}^2 + g_4 M_{\text{Fe}} M_{\text{Te}}^3 + g_5 M_{\text{Te}}^4
 \end{aligned} \tag{3.3}$$

is presented in magenta in Figure 3.20. The inclusion of the E_2 and E_4 terms in Equation 3.3 are in line with the Néel [158, 159] and Landau [161, 162] theories, respectively. As seen from their values in Figure 3.20, the local magnetic moments μ_{Fe} and μ_{Te} exhibit significant variation among the scanned magnetic states, which is indicative for non-Heisenberg exchange interactions [83, 162]. Thus, we took into account not only the usual *bilinear* exchange interactions (through E_2) but also *biquadratic* exchange interactions [163, 164] (through E_4), which enabled us to obtain a satisfactory parametrization. A weighted fit yields $\gamma_{11} = -0.108$, $\gamma_{12} = -0.305$, $\gamma_{22} = -0.848$, $g_1 = -0.001$, $g_2 = -0.013$, $g_3 = -0.053$, $g_4 = -0.096$, $g_5 = -0.062$, and $E_0 = -77.847$ eV, where the biquadratic coefficients turn out to be much smaller than the bilinear coefficients. It should be noted that the fit via Equation 3.3 is numerically quite satisfactory since it reproduces not only the energy differences among the $M_{\text{SC}} = 0\mu_{\text{B}}$, $4\mu_{\text{B}}$, and $8\mu_{\text{B}}$ configurations but also the barrier heights accurately, as indicated in Figure 3.20. Since the mean-field (γ) coefficients and the exchange (J) constants are usually of the same sign [160], having $\gamma_{11}, \gamma_{12}, \gamma_{22} < 0$ means that the exchange couplings between the Fe–Fe, Fe–Te, and Te–Te atom pairs are antiferromagnetic (i.e., negative). Negative exchange coupling between its constituent atoms may facilitate the use of the FeTe₂ monolayer in spin transfer applications. This finding also reminds us of spinel ferrites (decomposed into the sublattices A and B) in which the A–A, A–B, and B–B antiferromagnetic interactions lead to ferrimagnetic order [158, 164, 165]. It is nevertheless to be noted that antiferromagnetic Fe–Fe and Te–Te interactions in the FeTe₂ monolayer obtained from the above fit contrast with the ground state predicted from the HSE calculations.

It has been customary to deduce the exchange coupling constants from the energy differences between antiferromagnetic configurations and the magnetic ground state and to estimate the transition temperature to paramagnetic state via either a mean-field expression for Curie temperature T_C or Monte Carlo simulations, which was also done for the VS_2 monolayer [152, 153, 166] and nanoribbons [167], and the FeTe_2 monolayer [154]. As seen from the predicted values of T_C collected in Table B1.4 of *Appendix B*, the estimates scatter considerably, which can partly be attributed to different approximations for electron–electron interaction. In contrast with these efforts, our findings indicate that this type of approach is in fact not adequate for MX_2 monolayers that have a magnetic ground state with antiparallel alignment of local magnetic moments at M and X atoms, which are not describable by classical Heisenberg or Ising models owing to the non-Heisenberg character of the exchange interactions in these systems. The latter is manifested by the substantial variation of the local magnetic moments μ_M and μ_X among the scanned magnetic states in Figure 3.20 as mentioned above, which is also clear from the values of μ_M and μ_X in Table 3.6. It should, for example, be noticed that the magnitude of the local moments of vanadium in the VS_2 monolayer in the antiferromagnetic state is $0.58 \mu_B$, which is substantially smaller than $\mu_V = 1.2\mu_B$ for the magnetic ground state. A significant reduction of μ_X in the antiferromagnetic state is also noticeable. It is also revealing to note that a satisfactory parametrization of E_{SC} as a function of the sublattice magnetic moments within a mean-field approximation for the Heisenberg Hamiltonian is not obtained even if the non-Heisenberg character of the exchange interactions in the MX_2 monolayer is overlooked, as analyzed in Figure 3.21.

Table 3.6: The HSE-calculated values of the local magnetic moments μ_M and μ_X in antiferromagnetic ($M_{\text{SC}} = 0$) and magnetic ground ($M_{\text{SC}} \neq 0$) states.

Monolayer	$M_{\text{SC}} (\mu_B)$	$\mu_M (\mu_B)$	$\mu_X (\mu_B)$
$H\text{-FeTe}_2$	8	+ 3.10	– 0.55
	0	± 3.32	± 0.11
$H\text{-VS}_2$	4	+ 1.20	– 0.10
	0	± 0.58	± 0.02
$T\text{-NiTe}_2$	0.44	+ 0.27	– 0.08
	0	± 0.27	± 0.02
$H\text{-NiTe}_2$	1.44	+0.60	– 0.12
	0	± 0.49	± 0.02

In Figure 3.21, the fit with $E_{\text{SC}} = E_0 + E_2$ is represented with the orange curve and symbols, which yields $\gamma_{11} = -0.072$, $\gamma_{12} = -0.429$, $\gamma_{22} = -0.621$, and $E_0 = -77.837$ eV. This is not satisfactory because (i) the energies of low-energy ($M_{\text{SC}} = 4\mu_{\text{B}}$ and $8\mu_{\text{B}}$) configurations are not accurately reproduced and (ii) there are substantially more pronounced deviations from HSE-calculated points in the vicinity of magnetic ground state ($M_{\text{SC}} = 8\mu_{\text{B}}$). E_2 is identical to the mean-field energy expression based on the Heisenberg Hamiltonian for systems with ferrimagnetic-like order. Thus, the unsatisfactory fit using $E_{\text{SC}} = E_0 + E_2$ reveals that a satisfactory parametrization of E_{SC} as a function of the sublattice magnetic moments within a mean-field approximation for Heisenberg Hamiltonian is not obtained even when the ferrimagnetic-like order, i.e., the antiparallel alignment of M_{Fe} and M_{Te} , is taken into account.

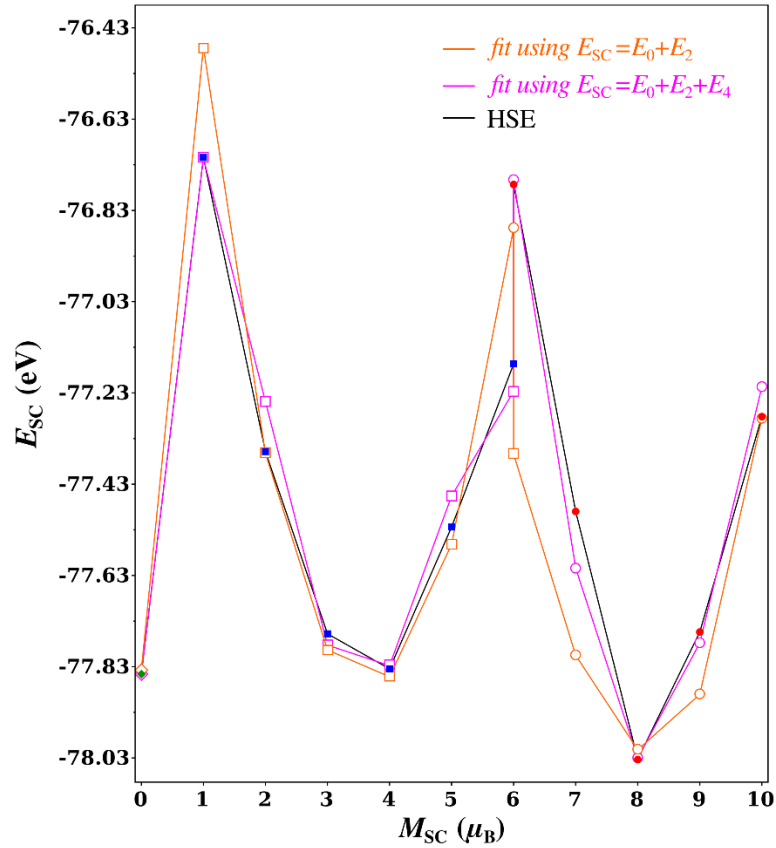


Figure 3.21: A comparison of two parametrizations of E_{SC} as a function of M_{Fe} and M_{Te} using $E_{\text{SC}} = E_0 + E_2 + E_4$ and $E_{\text{SC}} = E_0 + E_2$ with the E_2 and E_4 terms given in Equation 3.3. As in Figure 3.20, the filled and empty symbols represent the HSE-calculated and fitted points, respectively, and the solid lines connecting the calculated and fitted points are drawn to guide eye. The filled symbols, the empty symbols in magenta, and the black and magenta curves are the same as those in Figure 3.20.

In order to examine the effect of SOC on the magnetic order in the $H\text{-FeTe}_2$ monolayer, we present the values of μ_{Fe} and μ_{Te} in Table 3.7, which are obtained from the collinear and noncollinear PBE+ U calculations with and without SOC, respectively, performed by using 2×2 supercells. It is seen that the inclusion of SOC results in a slight increase in M_{SC} for both in-plane and out-of-plane configurations. Corresponding to the latter, μ_{Fe} and μ_{Te} also vary slightly. More importantly, the Fe and Te moments are found to align antiparallel in noncollinear calculations, except for the out-of-plane configuration with $M_{\text{SC}} = 0.023\mu_{\text{B}}$ (where the μ_{Fe} and μ_{Te} vectors deviate slightly from the antiparallel alignment by less than 4). Among the noncollinear configurations, the in-plane configuration with $M_{\text{SC}} = 8.088\mu_{\text{B}}$ is found to have the lowest energy, the energy of which is lower than the energies of out-of-plane $M_{\text{SC}} = 8.064\mu_{\text{B}}$, out-of-plane $M_{\text{SC}} = 0.023\mu_{\text{B}}$, and in-plane $M_{\text{SC}} = 0\mu_{\text{B}}$ configurations by 33, 299, and 384 meV per formula unit, respectively. The latter means that the magnetic anisotropy energy (MAE) is 33 meV per formula unit, which is slightly larger than the predicted value in Ref. [79]. The alignment of the Fe and Te moments in the lowest-energy configuration is antiparallel when SOC is taken into account, which is the same as when SOC is ignored.

Table 3.7: The values of the supercell magnetic moment M_{SC} and the local magnetic moments μ_{Fe} and μ_{Te} for the $H\text{-FeTe}_2$ monolayer, obtained from the collinear and noncollinear PBE+ U calculations with and without spin-orbit coupling (SOC), respectively. Noncollinear configurations are indicated by "In plane" ("Out of plane") in the second column, which means that the magnetization vectors are aligned in (perpendicular to) the monolayer plane.

Method		$M_{\text{SC}} (\mu_{\text{B}})$	$\mu_{\text{Fe}} (\mu_{\text{B}})$	$\mu_{\text{Te}} (\mu_{\text{B}})$
PBE+ U	Collinear	8	+ 2.524	− 0.262
		0	± 3.014	± 0.052
PBE+ U +SOC	In plane	8.064	+ 2.526	− 0.255
		0	± 3.004	± 0.053
	Out of plane	8.088	+ 2.526	− 0.262
		0.023	± 2.961	± 0.056

3.3.2. Electronic Structures of FeTe₂, VS₂, and NiTe₂ Monolayers

Now we examine the electronic structure of FeTe₂, VS₂, and NiTe₂ monolayers in their lowest-energy structures. Figure 3.22 displays majority and minority spin bands of these three monolayers projected to $d_{x^2-y^2}+d_{xy}$, $d_{xz}+d_{yz}$, and d_{z^2} orbitals of transition-metal atoms and p_x+p_y and p_z orbitals of chalcogen atoms.

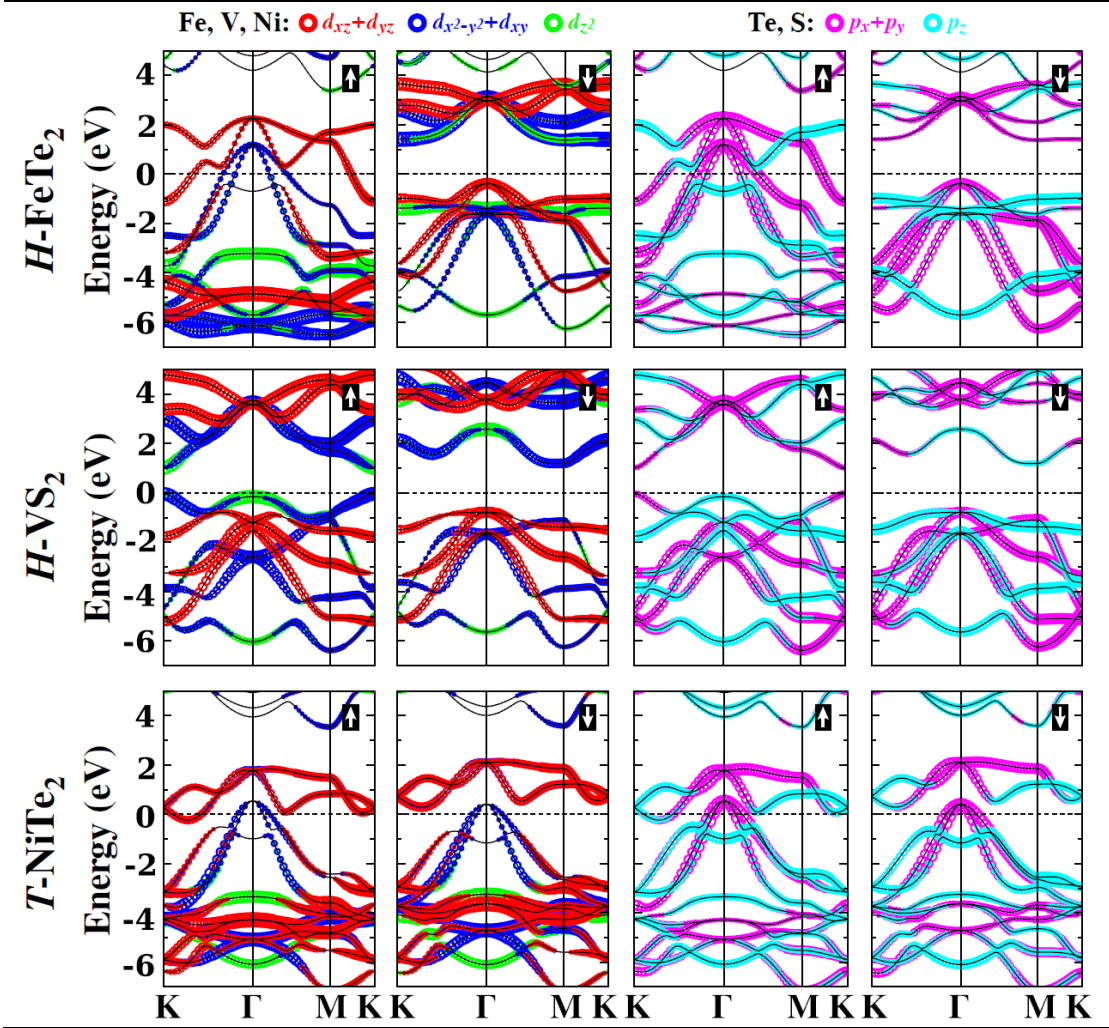


Figure 3.22: Orbital projected bands and state densities of majority ($\uparrow$) and minority ($\downarrow$) spin states, calculated using HSE, for H -FeTe₂ (upper panels), H -VS₂ (middle panels), and T -NiTe₂ (lower panels) monolayers. The open circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition-metal (Fe, Ni, and V) and chalcogen (Te and S) atoms, which are also colored as indicated at the top. The zero of energy is set to the Fermi level for metals and to the energy of the highest occupied spin state for semiconductors.

The majority spin bands of the FeTe₂ monolayer display a metallic behavior with spin-up bands crossing the Fermi level, which are derived mostly from the Te $p_x + p_y$ orbitals with significant contribution from the Fe $d_{x^2-y^2} + d_{xy}$ and $d_{xz} + d_{yz}$ orbitals. The minority spin bands, on the other hand, have an indirect band gap of 1.77 eV. While the top of the valence band at the center of the Brillouin zone slightly below the Fermi energy is derived from the Fe $d_{xz} + d_{yz}$ orbitals, the bottom of the conduction band at the K-point is constructed mostly from the Fe $d_{x^2-y^2} + d_{xy}$ and d_{z^2} orbitals. The Te $p_x + p_y$ orbitals make also a substantial contribution to both the upper valence and lower conduction bands. It seems that the hybridization of the Fe d and Te p orbitals make both the spin-up states around the Fermi level and the spin-down states in the upper valence and lower conduction bands have a significant contribution from the p (d) orbitals of Te (Fe) atoms. This summarized arrangement of spin bands in Figure 3.22 shows, in agreement with previous predictions [79], that the FeTe₂ monolayer with $\mu_{\text{tot}} = 2\mu_B$ is a half-metal. Hence the FeTe₂ monolayer keeps the promise of being a potential spintronic material operating as a spin valve or an active component in 2D MTJs.

The spin-polarized electronic states of the VS₂ monolayer, on the other hand, display a rather different situation, as also noted by others [152, 153, 168]. Both spin-up and spin-down bands open a band gap of different widths. The direct band gap of spin-up bands is 1.06 eV and occurs at the K-point. V d_{z^2} and S $p_x + p_y$ orbitals contribute to the spin-up states at the conduction- and valence-band edges. The indirect band gap of spin-down states is 1.98 eV and occurs between the conduction-band states at the M-point derived from V $d_{x^2-y^2} + d_{xy}$ and S p_z orbitals, and the valence-band states at the Γ -point are derived from V $d_{xz} + d_{yz}$ and S $p_x + p_y$ and p_z orbitals. The VS₂ monolayer is thus an interesting 2D structure with an integer magnetic moment of $\mu_{\text{tot}} = 1\mu_B$ and has two band gaps of different width for different spin polarization; one of them is direct, while the other one is indirect. This is a rare situation and offers critical spintronic applications.

Finally, the NiTe₂ monolayer in Figure 3.22 is metallic for both spin bands, but has spin polarization at the Fermi level and hence a net magnetic moment of $0.11\mu_B$. In earlier studies [9, 10, 56] using only LDA, the NiTe₂ monolayer was predicted to

be a nonmagnetic metal with a perfect symmetry between spin-up and spin-down densities. Apparently, LDA alone failed to determine the ground state of NiTe₂.

In Figure 3.23, the electronic structure of *T*-FeTe₂, *T*-VS₂, and *H*-NiTe₂ monolayers in higher energy structures is given for completeness. A comparison between Figures 3.22 and 3.23 shows that NiTe₂ and VS₂ monolayers are metallic and semiconducting, respectively, regardless of the phase (*H* or *T*). On the other hand, the FeTe₂ monolayer in the *T* structure is metallic, which shows that the half metallicity of FeTe₂ occurs only in the *H* structure.

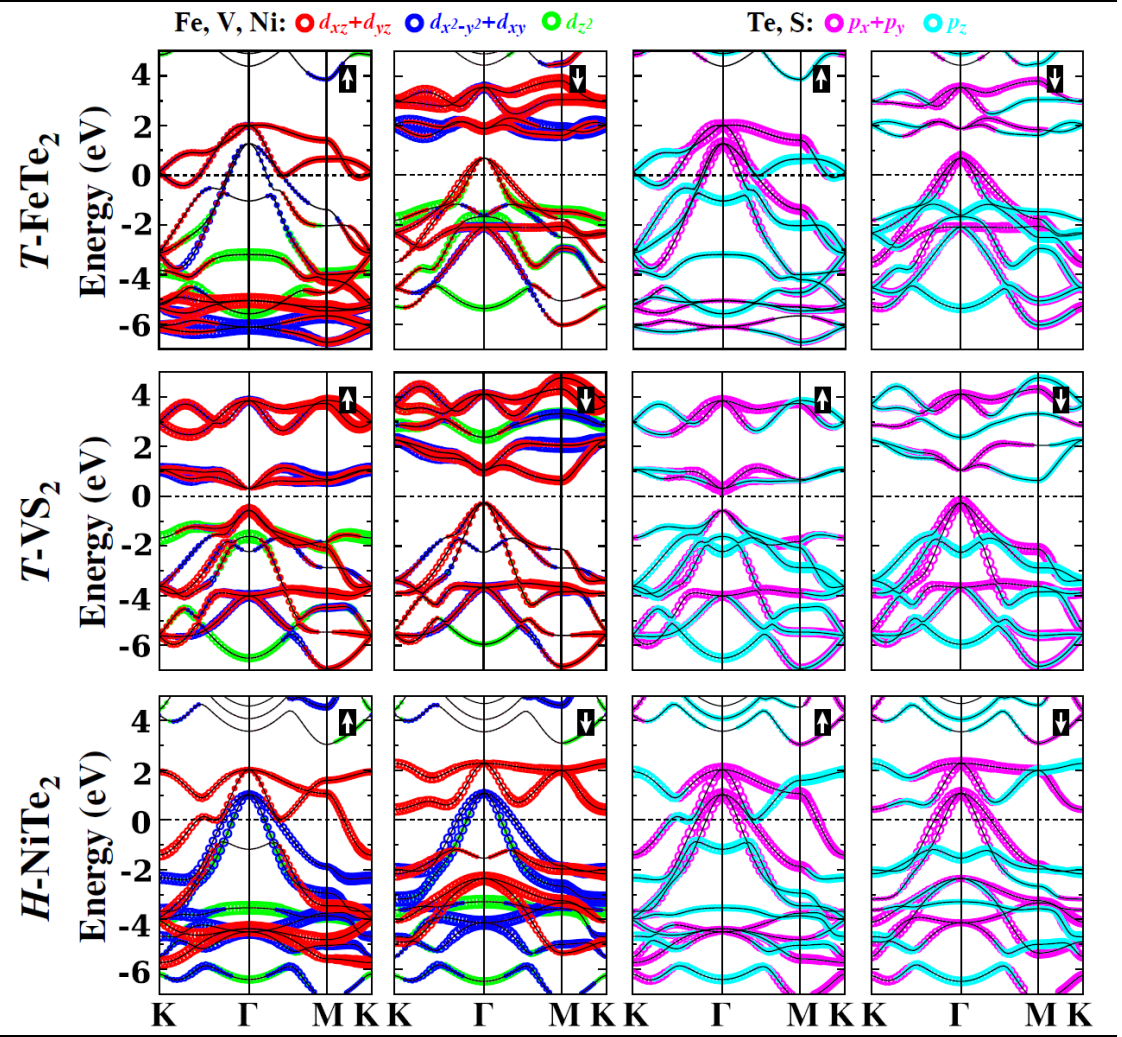


Figure 3.23: Orbital projected bands and state densities majority (↑) and minority (↓) spin states, calculated using HSE, for *T*-FeTe₂ (upper panels), *T*-VS₂ (middle panels) and *H*-NiTe₂ (lower panels) monolayers. The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal (Fe, Ni and V) and chalcogen (Te and S) atoms, which are also colored as indicated at the top. Zero of energy is set to the Fermi level for metals and to the energy of the highest occupied spin-state for semiconductors.

Having set the type of the magnetic ground state and predicted half-metallic state of the H -FeTe₂ monolayer, we now examine two critical issues, which are of fundamental as well as technological importance since they may offer efficient tunability in electronic properties: How do the magnetic ground state and electronic structure vary with *strain* and the *number of layers* in van der Waals FeTe₂ multilayers? Although the T -phase remains the higher-energy phase of the FeTe₂ monolayer for a wide range of strain ($-0.10 \leq \epsilon \leq 0.10$) as shown in Figure 3.24, the results for the T -FeTe₂ monolayer are included in Figure 3.25(a)–(c) for comparison.

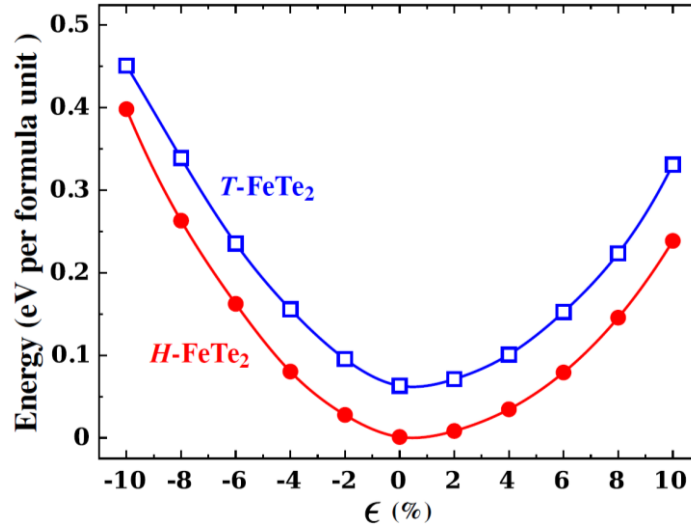


Figure 3.24: The energy versus strain curves for H -FeTe₂ and T -FeTe₂ monolayers. As long as H - and T -phases remain the lower- and higher-energy phases, respectively, *no* phase transition takes place under applied biaxial strain for $(-0.10 < \epsilon < 0.10)$.

In Figures 3.25(a)–(c), 3.26 and 3.27, we present the variation of minority band gap $E_g^\downarrow$, magnetic moment per formula unit μ_{tot} , and magnetic moment of Fe (Te) atoms μ_{Fe} (μ_{Te}) with the applied biaxial strain. It is seen that the half-metallic state of the H -FeTe₂ monolayer determined in equilibrium (i.e., $\epsilon = 0$) subsists as long as $-0.07 < \epsilon$, but transforms almost suddenly to metallic once $\epsilon \leq -0.07$. On the other hand, the metallic state of the T -FeTe₂ monolayer transforms to a half-metallic state once $\epsilon > 0.03$. In the range of strain where the half-metallic state prevails, the total magnetic moment per formula unit is fixed at $\mu_{\text{tot}} = 2\mu_B$ since μ_{Fe} and μ_{Te} increase in reverse directions, which holds true for both H - and T -phases. For the H -FeTe₂ monolayer, these findings point to the fact that its half-metallic state is robust under strain ranging from compressive to tensile.

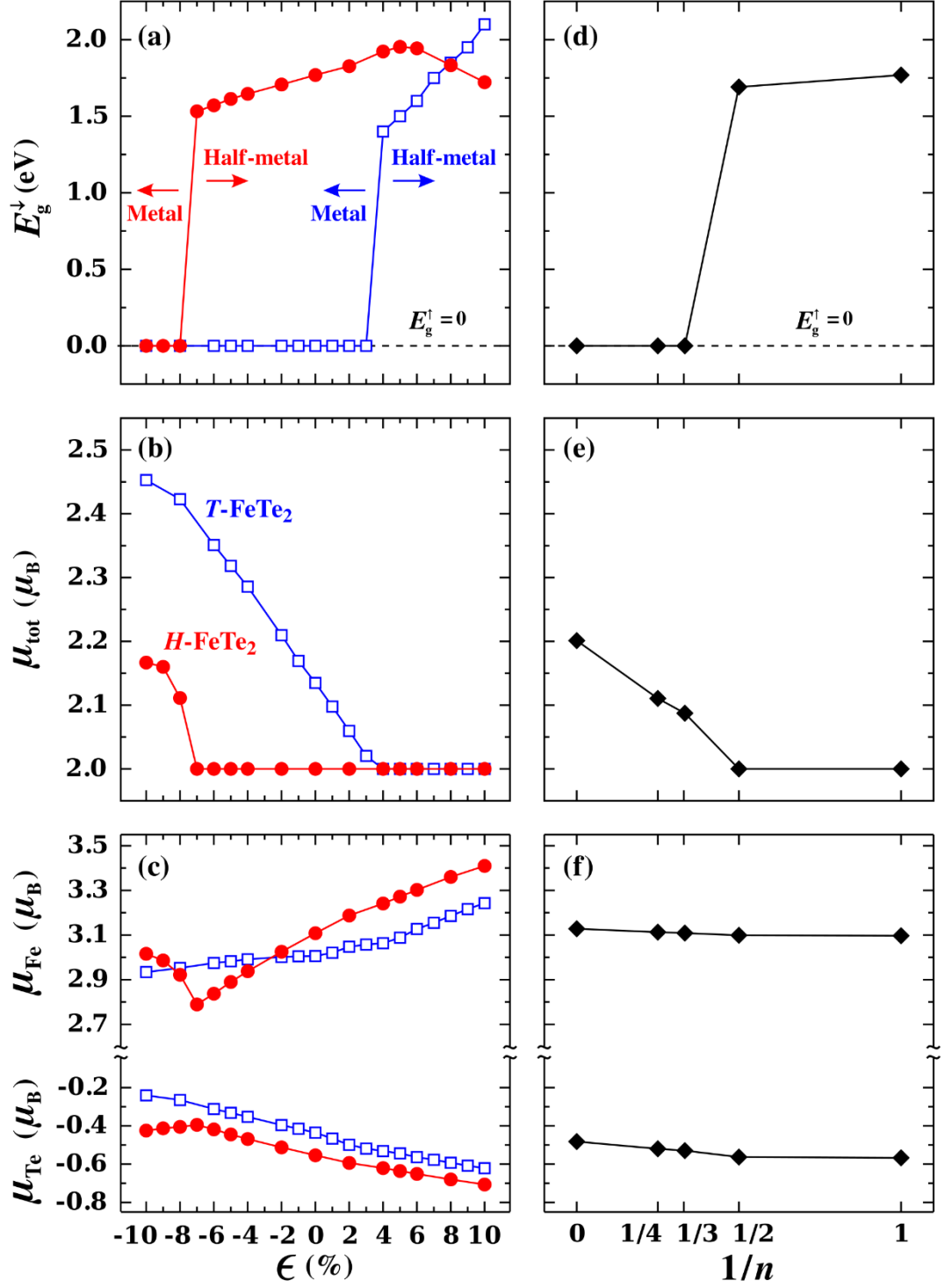


Figure 3.25: The variation of (a) the spin-down band gap $E_g^\downarrow$, (b) the magnetic moment per formula unit μ_{tot} , and (c) the magnetic moments at Fe and Te atoms, μ_{Fe} and μ_{Te} , respectively, with the biaxial strain for $H\text{-FeTe}_2$ (in red) and $T\text{-FeTe}_2$ (in blue) monolayers. (d)–(f) The same with the inverse number of layers $1/n$ for FeTe_2 multilayers.

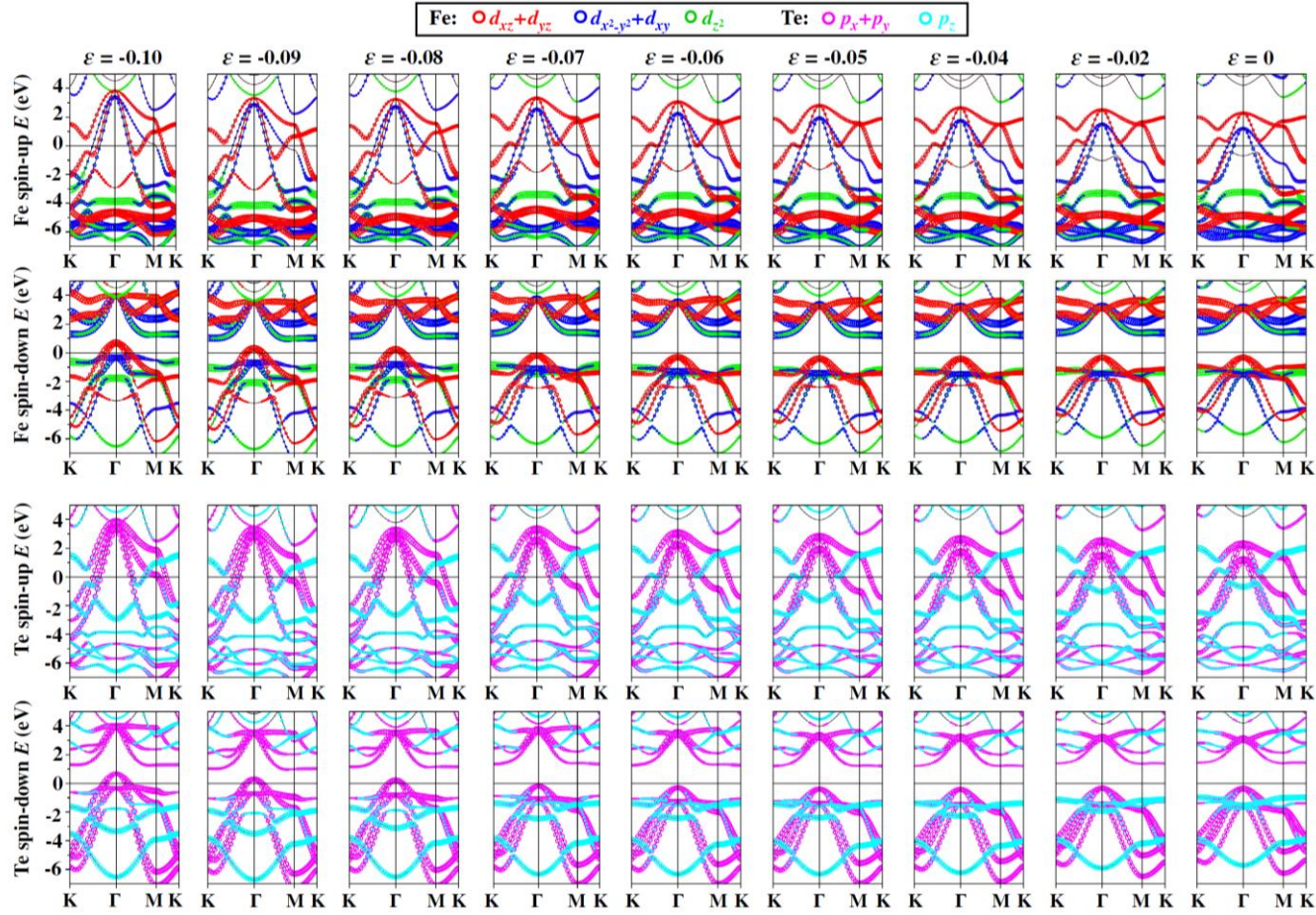


Figure 3.26: Orbital projected majority ($\uparrow$) and minority ($\downarrow$) spin bands, calculated using HSE, for H -FeTe₂ monolayer under biaxial *compressive* strain. The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal Fe, and chalcogen Te atoms, which are also colored as indicated at the top.

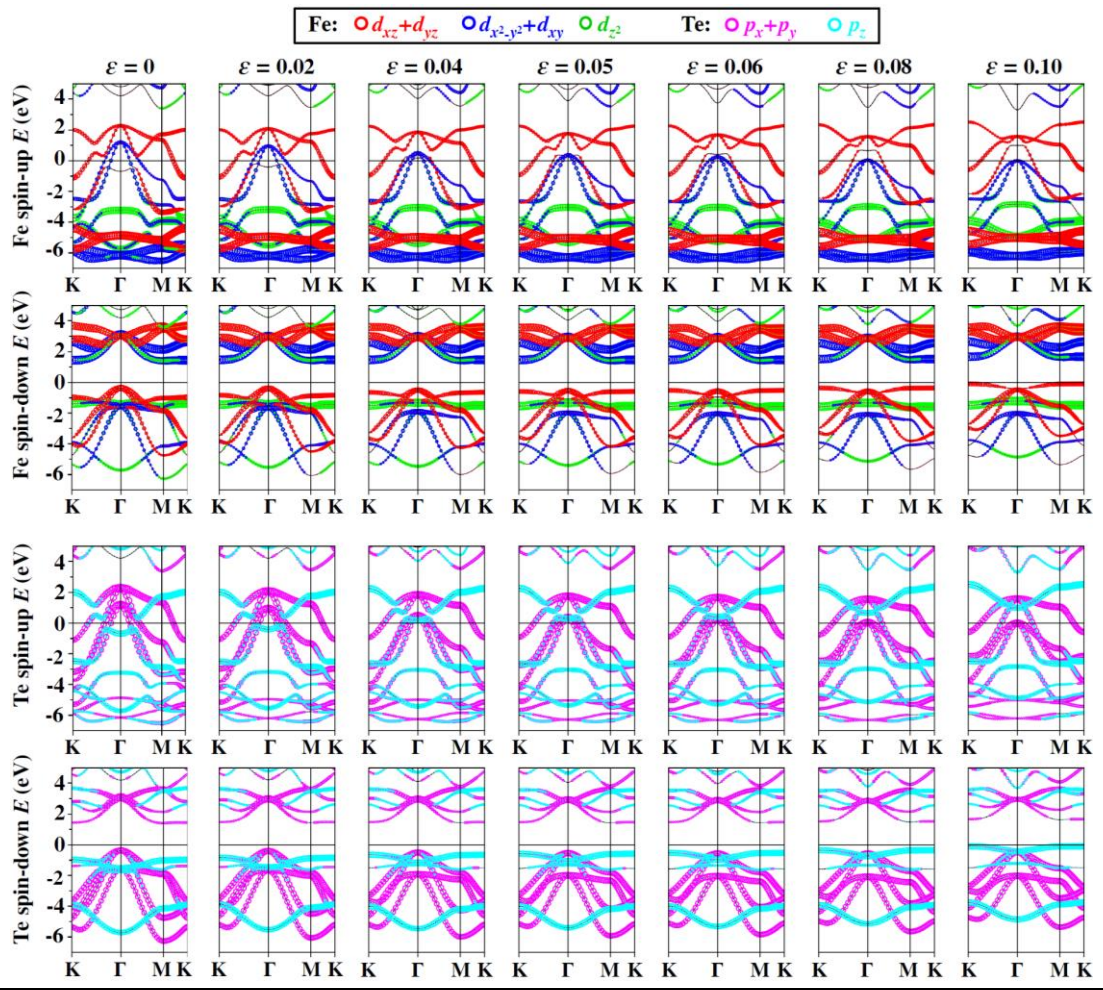


Figure 3.27: Orbital projected majority ($\uparrow$) and minority ($\downarrow$) spin bands, calculated using HSE, for H -FeTe₂ monolayer under biaxial *tensile* strain. The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal Fe and chalcogen Te atoms, which are also colored as indicated at the top.

Our investigation of the electronic and magnetic states of FeTe₂ multilayers of various thicknesses, made of n layers, are summarized in Figures 3.25(d)–(f) and 3.28. We performed the HSE calculations for $n = 1, 2, 3, 4$, as well as for a 3D layered FeTe₂ crystal with optimized structure with vertical stacking geometry corresponding to the energy minimum. The crucial outcome of this investigation is, briefly, that the half-metallic state of FeTe₂ occurs only for $n \leq 2$ (i.e., for monolayer and bilayer), which is destroyed as the multilayer gets thicker since $E_g^\downarrow$ is zero for $n \geq 3$. The slight increase in μ_{tot} for $n > 2$ making the total magnetic moment have a non-integer value signifies a transition from the half-metallic state to a magnetic metal, which renders the FeTe₂ multilayers thicker than bilayer as magnetic metals.

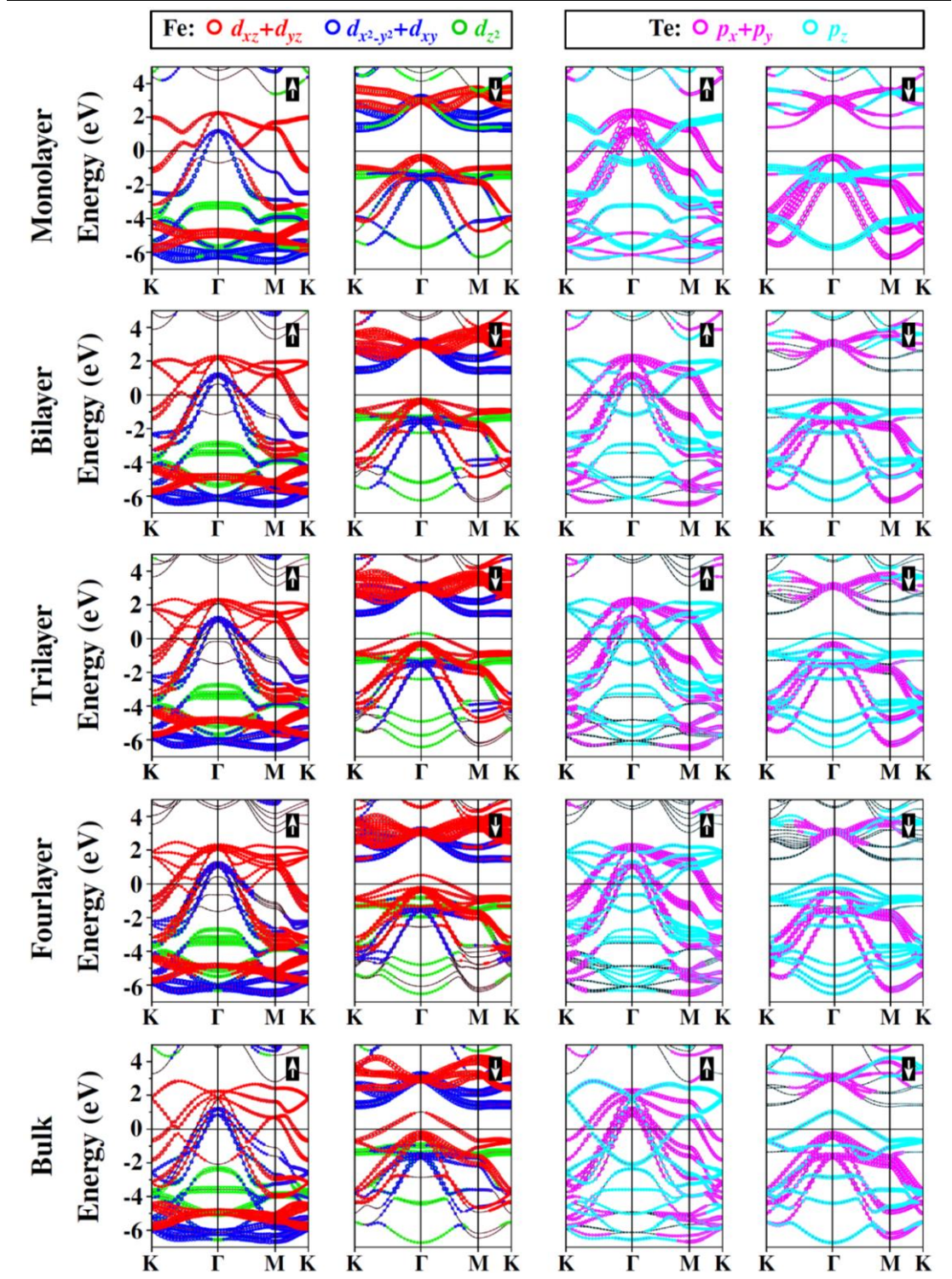


Figure 3.28: Orbital projected majority ($\uparrow$) and minority ($\downarrow$) spin bands, calculated using HSE, for FeTe₂ monolayer, multilayers (bilayer, trilayer, fourlayer) and 3D layered FeTe₂ crystal (bulk). The empty circles used to draw spin bands are resized to be proportional to relative contributions from the orbitals of transition metal Fe and chalcogen Te atoms, which are also colored as indicated at the top.

3.4. Magnetic Heterostructures of Transition–Metal Dichalcogenides: FeTe₂/NiTe₂

Various forms of periodic, lateral and vertical heterostructures constructed from magnetic transition–metal dichalcogenide monolayers, FeTe₂ and NiTe₂, have been investigated by using hybrid density functional calculations. The lateral heterostructures formed from the stripes of these constituents joined along their armchair edges are found to be half–metallic within both constituent stripes with integer number of total magnetic moment per cell; they are semiconductor for spin–down electrons, but metallic for spin–up ones. Additionally, the indirect band gap of these half–metallic structures in the energy range of visible light as well as their normal band–lineup exhibit features which can be tunable with the width of stripes. Normal band line up can lead to the confinement of excess spin down electrons and eventually to the change of dimensionality from two to one. Strong variations of the band gap can be attained by δ –doping. Half metallicity spreads from the FeTe₂ side of the junction to the adjacent NiTe₂ side, which is metallic when stand–alone, through strong Fe–Te–Ni bonds at the boundary. In contrast, in the thin, vertical heterostructures, where the interlayer coupling is rather weak, the half–metallic character is retained only in FeTe₂ side; NiTe₂ side remains a spin polarized metal. Hence, these vertical heterostructures form a semiconductor/metal junction with a Schottky barrier for one spin direction to function as a diode, but a metal/metal junction for the opposite spin direction to function as a conductor. These lateral and vertical heterostructures have inhomogeneous magnetic moment configurations due to p – d hybridization; in both sides of the junction chalcogen atoms have magnetic moments antiparallel to those at transition metal atoms. Functionalities revealed here are rare and can lead to crucial applications.⁴

3.4.1. FeTe₂ and NiTe₂ Monolayers

We performed structural optimizations where the equilibrium value of the 2D lattice constants as well as the lattice constant in the direction perpendicular to the layers were determined via minimization of the total energy and the ionic positions

4. The Section 3.4 and its subsections are adapted from Aras M., Kılıç Ç., Ciraci S., (2020), “Magnetic Heterostructures of Transition Metal Dichalcogenides: Antiparallel Magnetic Moments of Half–Metallic State”, The Journal of Physical Chemistry C, 124 (42), 23353–23360.

were relaxed until the residual forces on atoms were reduced to be smaller than 10^{-2} eV/Å. In order to analyze the stability of the optimized heterostructures, we computed the bond-length strain ε distribution in them with respect to the respective bond lengths in bare FeTe₂ and NiTe₂ monolayers. The Brillouin zone sampling was carried out using $12 \times 8 \times 1$ (lateral heterostructure with $p = q = 1$), $8 \times 8 \times 1$ (lateral heterostructures with $p + q = 4$), $4 \times 8 \times 1$ (lateral heterostructures with $p + q > 4$), $12 \times 12 \times 4$ (vertical heterostructure with $p = q = 1$), and $12 \times 12 \times 2$ (vertical heterostructure with $p = q = 2$) k -point meshes generated according to Monkhorst–Pack scheme [121]. Using the optimized structures, we performed self-consistent field electronic structure calculations in order to obtain the magnetic and electronic states of A:(FeTe₂)_p/(NiTe₂)_q and V:(FeTe₂)_p/(NiTe₂)_q systems with various combination of p and q . The atomic (μ_{Fe} , μ_{Ni} , μ_{Te}) spin moments were computed by dividing the total spin moment μ_{tot} amongst Fe, Ni and Ti atoms according to the density derived electrostatic and chemical (DDEC) spin partitioning technique [147, 148]. Throughout the subsections, the total and atomic spin moments are given in units of Bohr magneton μ_B per cell and atom, respectively.

Before focusing on the lateral and vertical (FeTe₂)_p/(NiTe₂)_q heterostructures, we discuss the stability, magnetic and electronic properties of the free-standing FeTe₂ and NiTe₂ monolayers. Previous studies, (e.g., Refs. [10, 56]), have shown that both FeTe₂ and NiTe₂ monolayers are stable in both H and T structures. The energy difference ($E_H - E_T$) between the H - and T -phases is calculated, using HSE, to be -65 and 334 meV per formula unit for the FeTe₂ and NiTe₂ monolayers, respectively. Indeed, regardless of the level of approximation in DFT, [10] the H and T structure has lower energy for the FeTe₂ and NiTe₂ monolayers, respectively. On the other hand, the occurrence of stable, higher-energy phases in heterostructures cannot be precluded, since the lattice matching and commensurability at interfaces are favored in the course of heterostructure growth. Accordingly, we believe that NiTe₂ can be grown in H -phase at the armchair edge of FeTe₂ nanoribbons. For this reason, we place emphasis on the heterostructures A:(FeTe₂)_p/(NiTe₂)_q with both constituent stripes in H structure.

Based on the results of LDA calculations, ferromagnetic and nonmagnetic ground states were assigned to the FeTe₂ and NiTe₂ monolayers, respectively, in earlier studies [10, 56]. Recently, however, a comparative analysis of the results obtained at five level of approximations [108] revealed that the true magnetic ground

state of FeTe₂ and NiTe₂ monolayers comprises inhomogeneous magnetic moment configurations, and the chalcogen atoms by themselves have significant, antiparallel magnetic moments owing to the spin polarization of chalcogen atoms through p - d hybridization. Furthermore, FeTe₂ monolayer in H structure, which is a half-metal, has an integer magnetic moment of $\mu_{\text{tot}} = 2\mu_{\text{B}}$; the magnetic moments on Fe and Te atoms being $\mu_{\text{Fe}} = 3.10\mu_{\text{B}}$ and $\mu_{\text{Te}} = -0.55\mu_{\text{B}}$. On the other hand, NiTe₂ is a magnetic metal with non-integer magnetic moment of $\mu_{\text{tot}} = 0.36\mu_{\text{B}}$; the magnetic moments on Ni and Te atoms being $\mu_{\text{Ni}} = 0.60\mu_{\text{B}}$ and $\mu_{\text{Te}} = -0.12\mu_{\text{B}}$.

As for the electronic structure, the majority spin bands of the H -FeTe₂ monolayer, which are derived from the Te p_x+p_y and Fe $d_{x^2-y^2}+d_{xy}$ and $d_{xz}+d_{yz}$ orbitals, cross the Fermi level and hence display a metallic character. In contrast, an indirect band gap of 1.77 eV is opened up between the minority spin bands constructed from the states of the valence band maximum at the Γ -point derived from the Fe $d_{xz}+d_{yz}$ and Te p_x+p_y orbitals and the states of the conduction band minimum at the K-point derived from the Fe $d_{x^2-y^2}+d_{xy}$ and d_{z^2} and Te p_x+p_y orbitals. These render the free-standing H -FeTe₂ monolayer to be a half-metal. On the other hand, both majority and minority spin bands of the NiTe₂ monolayer cross the Fermi level, rendering it a magnetic metal with a small magnetic moment.

3.4.2. Armchair Lateral Heterostructures of FeTe₂/NiTe₂

We performed calculations for periodic, lateral heterostructures with armchair boundary, i.e., A:(FeTe₂) _{p} /(NiTe₂) _{q} with $(p,q) = (1,1), (1,3), (2,2), (3,1), (3,3), (4,4), (5,5)$, constructed by joining armchair nanoribbons of FeTe₂ and NiTe₂ (with p and q formula units of constituents in their unit cells, respectively) commensurately. The results of these calculations are exemplified in Figures 3.29 and 3.30. Figure 3.29(a) displays the optimized atomic structure of A:(FeTe₂)₅/(NiTe₂)₅, where the bond-length strain distribution is indicated by coloring of the sticks representing the Fe-Te and Ni-Te bonds. The isosurfaces of spin densities and atomic magnetic moments of this heterostructure are shown in Figure 3.29(b), which reveal an inhomogeneous magnetic moment configuration owing to antiparallel (mostly parallel) arrangement of the Fe (Ni) and Te moments in the FeTe₂ (NiTe₂) stripe. The total magnetic moments of the FeTe₂ and NiTe₂ stripes are $+11.8\mu_{\text{B}}$ and $-1.8\mu_{\text{B}}$, respectively, indicating an antiparallel alignment of the magnetic moments of these

two constituent stripes. Remarkably, the total magnetic moment of $A:(\text{FeTe}_2)_5/(\text{NiTe}_2)_5$ have an integer value of $\mu_{\text{tot}} = 10\mu_B$, which is indicative for half-metallic behavior (cf. Refs. [169, 170]). The half metallicity of this heterostructure is also deduced from the total and local densities of states (LDOS) presented in Figure 3.29(c). Figure 3.29(d) shows the spatial variation of the band edge energies obtained from LDOS values. The transitions of the conduction and valence band edges occur rather sharp at the junction and hence from the electronics point of view the heterostructure character is realized. The band gap of the NiTe_2 side is significantly smaller than that of FeTe_2 side, showing that $A:(\text{FeTe}_2)_5/(\text{NiTe}_2)_5$ is a type-I, or straddling-gap, heterojunction. The occurrence of type-I band alignment can be traced to the close values of the work function ϕ for the bare FeTe_2 ($\phi = 4.12$ eV) and NiTe_2 ($\phi = 4.15$ eV) monolayers, which is attributable to the similar electronegativities of the Fe and Ni atoms [171]. This is supported by the fact that charge transfer at the interface between the FeTe_2 and NiTe_2 stripes, as well as change in the electronic charge ΔN throughout the heterostructure, remain small, as shown in Figure 3.29(e), which means that strong interface dipoles do not form.

In order to see if half-metallic behavior continues to exist when $p \neq q$, we also discuss our results for $A:(\text{FeTe}_2)_3/(\text{NiTe}_2)_1$, i.e. $(p,q) = (3,1)$, and $A:(\text{FeTe}_2)_1/(\text{NiTe}_2)_3$, i.e. $(p,q) = (1,3)$, heterostructures summarized in Figure 3.29. Owing to the fact that one of the constituents in the unit cell has very narrow width, these structures can be considered as the δ -doping of the wide constituent by the narrow one. For example, we can consider $A:(\text{FeTe}_2)_3/(\text{NiTe}_2)_1$ as if FeTe_2 monolayer is δ -doped by one formula unit, narrow stripe NiTe_2 in every other, three-formula unit wide FeTe_2 host. The band gap of spin-down electrons $E_g^\downarrow$ in $A:(\text{FeTe}_2)_3/(\text{NiTe}_2)_1$ and $A:(\text{FeTe}_2)_1/(\text{NiTe}_2)_3$ structures are 1.51 and 0.51 eV, respectively and hence exhibit dramatic change upon switching the values of p and q . However, it is noteworthy that the width of spin-down band gap $E_g^\downarrow$ is unaltered throughout the heterostructure. Accordingly, these heterostructures with $(p,q) = (3,1)$ and $(p,q) = (1,3)$ can be specified also as compounds, in which the metallic state of NiTe_2 undergoes a change and attains a half-metallic state owing to its proximity to FeTe_2 . In congruence with this, $A:(\text{FeTe}_2)_3/(\text{NiTe}_2)_1$ and $A:(\text{FeTe}_2)_1/(\text{NiTe}_2)_3$ structures have integer total magnetic moments, and inhomogeneous magnetic moment configurations characterized by parallel alignment of the Fe and Ni moments and antiparallel alignment of the Te moments.

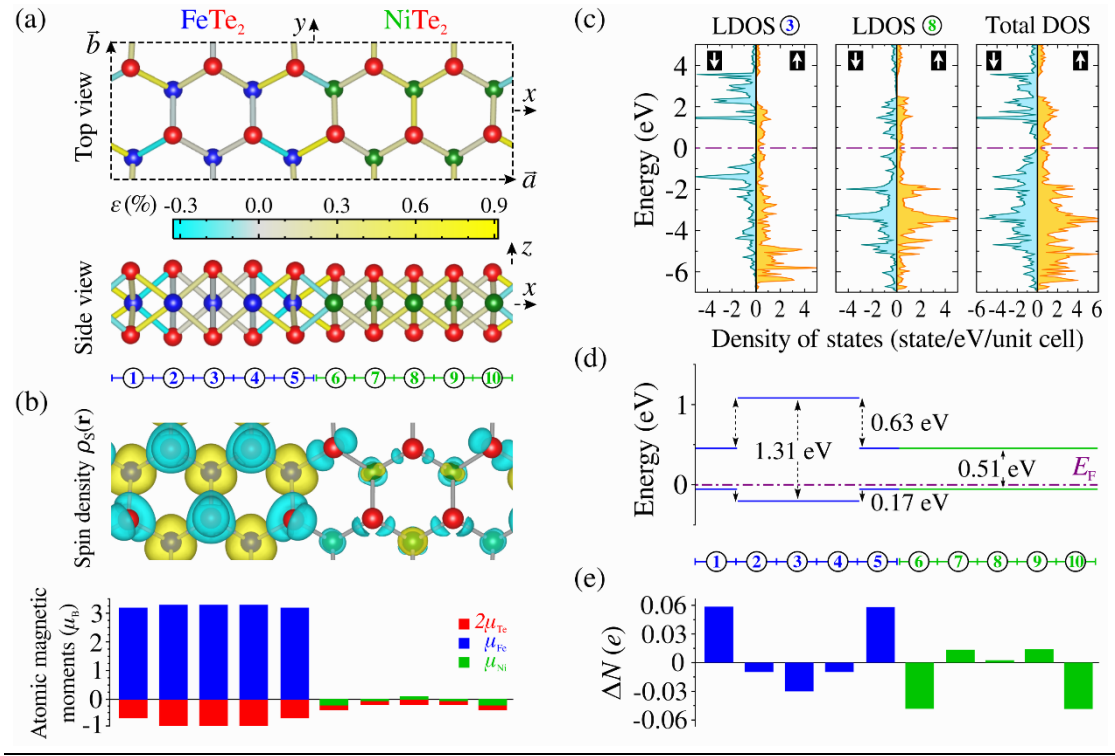


Figure 3.29: (a) Top and side views of the optimized atomic structure of lateral heterostructure A:(FeTe₂)₅/(NiTe₂)₅. The blue, green and red balls represent the Fe, Ni and Te atoms, respectively. The sticks representing the Fe–Te and Ni–Te bonds are colored to indicate the bond-length strain ε distribution, computed with respect to the bond lengths in the bare FeTe₂ and NiTe₂ monolayers. The subcells containing one formula unit in the FeTe₂ and NiTe₂ monolayers are specified by encircled numerals. (b) Isosurfaces of spin density $\rho_s(r)$ and atomic magnetic moments (in units of Bohr magneton). The algebraic sum of atomic magnetic moments in the FeTe₂ and NiTe₂ stripes are $+11.8\mu_B$ and $-1.8\mu_B$, respectively. (c) The spin-polarized local density of states (LDOS) for subcells ③ and ⑧ and total density of states (DOS). (d) Energy diagram showing the spatial variation of the spin-down conduction and valence band edge energies. The Fermi level is indicated by the dotted-dashed line. (e) The change in the electronic charge ΔN at each subcell with respect to the free-standing FeTe₂ and NiTe₂ monolayers.

As exemplified in the preceding two paragraphs, the results obtained for various values of p and q indicate that all A:(FeTe₂) _{p} /(NiTe₂) _{q} structures considered in this study exhibit a half-metallic behavior associated with an integer total magnetic moment. It is interesting to note that for these A:(FeTe₂) _{p} /(NiTe₂) _{p} structures, the total magnetic moment is given by $\mu_{\text{tot}} = 2p\mu_B$. This indicates that the average magnetic moment $\mu = \mu_{\text{tot}}/p = 2\mu_B$ remains constant, i.e., independent of the width of the constituent nanoribbons.

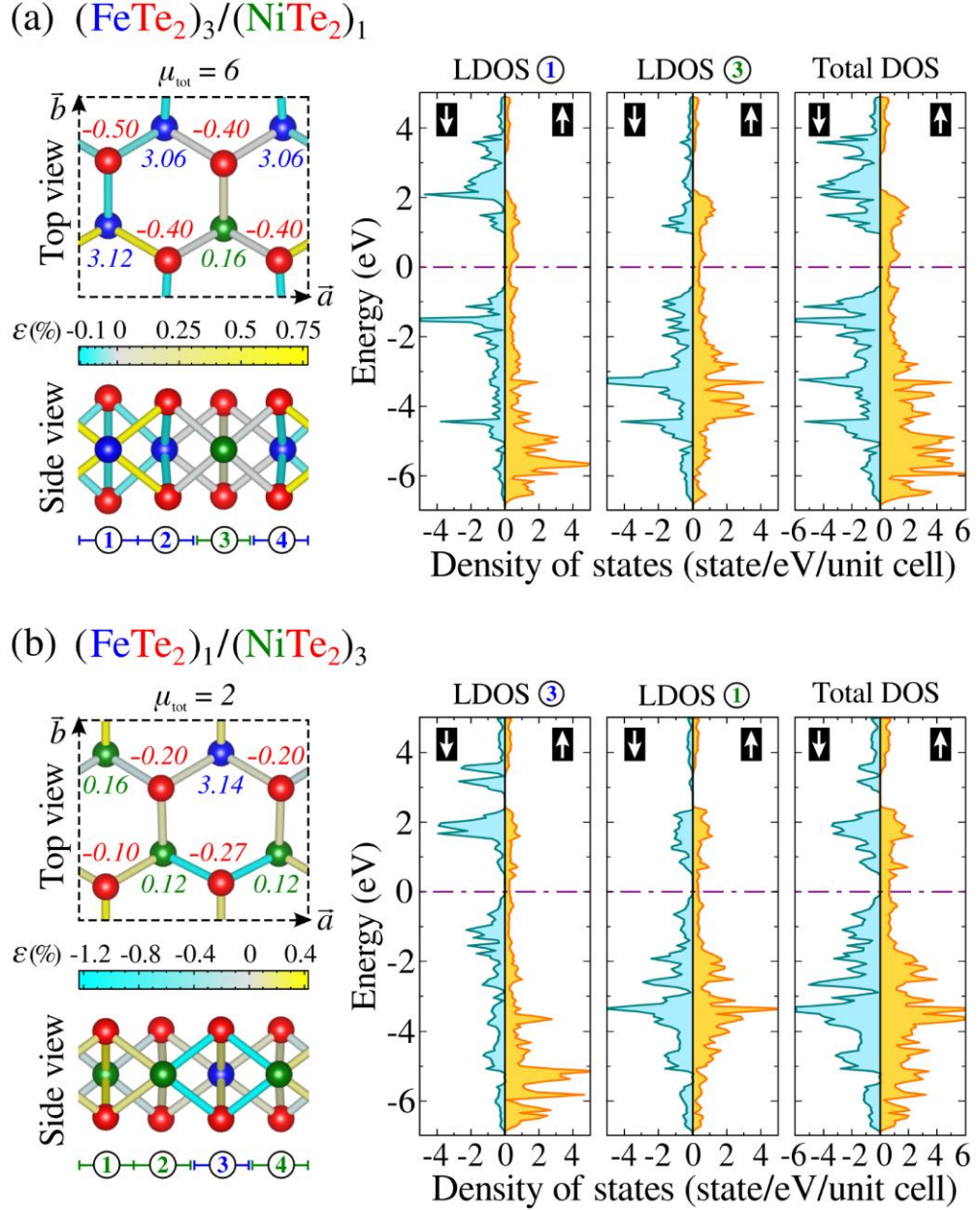


Figure 3.30: Atomic and electronic structures of (a) $A:(\text{FeTe}_2)_3/(\text{NiTe}_2)_1$, and (b) $A:(\text{FeTe}_2)_1/(\text{NiTe}_2)_3$ heterostructures (compounds). The spin-polarized total density of states (DOS) and local density of states (LDOS) for subcells ① and ③ are plotted. The blue, green and red balls represent the Fe, Ni and Te atoms, respectively, next to which the atomic magnetic moments (in units of Bohr magneton) are given as italic numbers. Note that $\mu_{\text{tot}} = p\mu_{\text{Fe}} + q\mu_{\text{Ni}} + 2(p+q)\mu_{\text{Te}}$ for $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$. The sticks representing the Fe–Te and Ni–Te bonds are colored to indicate the bond-length strain ε distribution, computed with respect to the bond lengths in the bare FeTe_2 and NiTe_2 monolayers. Since these heterostructures display a uniform band gap throughout the unit cell, they are specified also as compounds.

In Figure 3.30, the total and average magnetic moments of $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_p$, obtained from the LDA, PBE+D3 and HSE calculations are presented, in order to analyze how the predicted values of μ_{tot} and μ depend on the

treatment of the electron–electron interaction. It is seen that the predictions using LDA have an irregular trend for the variations of μ_{tot} and μ with p . While the structures with $p = 1, 3, 5, 8$ are nonmagnetic, those with $p = 2, 4, 6, 7, 9, 10$ have nonzero magnetic moments. It is also clear that the LDA and PBE+D3 calculations for the same structures result in quite different magnetic moments. In contrast, the PBE+D3 and HSE results exhibit quite similar trends. Nonetheless, the calculations using PBE+D3 predict *noninteger* magnetic moments, which is at odds with the HSE results. This latter disagreement between PBE+D3 and HSE calculations can be attributed to the erroneous closure of the spin–down band gap of the FeTe_2 monolayer in the PBE calculations, which originates from the improper description of strong correlations of localized d electrons with a semilocal exchange–correlation functional, leading to fractional magnetic moments [108]. The integer values of μ_{tot} and μ are obtained for the correct electronic ground state when the strong correlations are to some extent taken into account by either adding a Hubbard U term to the PBE functional or using a hybrid functional. In view of this analysis, we assess that the hybrid rather than semilocal DFT calculations is more reliable in predicting the ground state of the magnetic TMDC monolayers as well as their heterostructures.

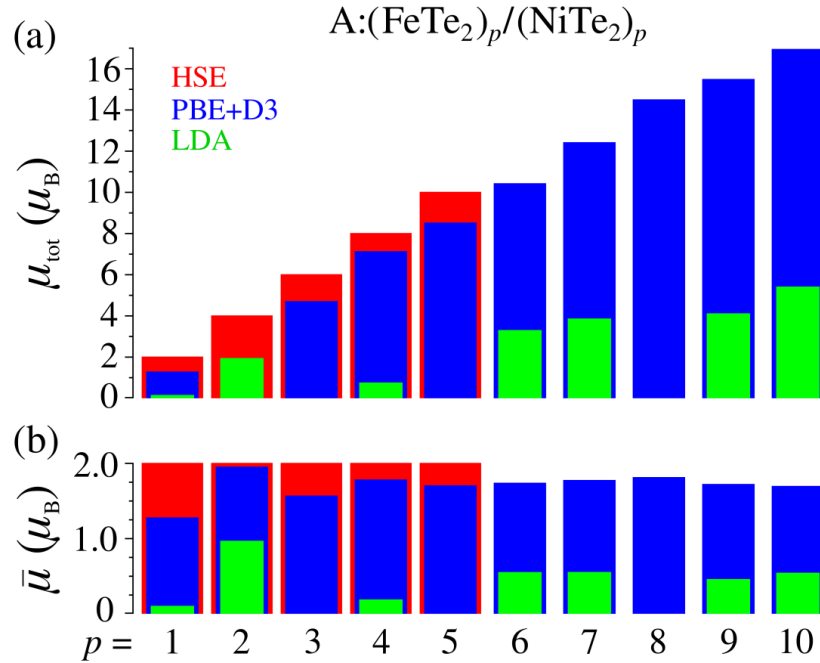


Figure 3.31: Variation of the (a) total magnetic moment μ_{tot} in units of Bohr magneton μ_B per cell, and (b) average magnetic moment $\mu = \mu_{\text{tot}}/p$ of the lateral $\text{A}:(\text{FeTe}_2)_p/(\text{NiTe}_2)_p$ structures, obtained from the LDA, PBE+D3, and HSE calculations.

The band edge energies for spin-down electrons in a variety of $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$ structures and the FeTe_2 monolayer (for comparison) are shown in Figure 3.32 where the Fermi level is taken as the zero of band energy. In this figure, the band offsets are indicated by the red double-sided arrows. The absence of band offsets for $p, q \leq 3$ is noteworthy. Electronically different domains in the heterostructure corresponding to the different constituent monolayers form only for $p = q \geq 4$, as signified by the formation of a type-I band offset. In view of this feature, we designate $A:(\text{FeTe}_2)_q/(\text{NiTe}_2)_q$ structures with $p, q \leq 3$ as compounds, as if a single material having the same repeating unit cell. On the other hand, the heterostructures with $p = q \geq 4$ can be viewed as semiconductor/semiconductor junction with a type-I band offset for spin-down electrons, but metal/metal junction for spin-up electrons.

It is seen in Figure 3.32 that the spin-down band gaps of the $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$ compounds are significantly smaller than that of the FeTe_2 monolayer. This band gap, i.e., $E_g^\downarrow$, varies with p and q : $E_g^\downarrow = 0.92$ eV for $p = q = 1$, which increases (decreases) to be 1.51 (0.51) eV when p (q) is increased to be 3 with $p = 1$ ($q = 1$). On the other hand, if p and q are both increased to be 2, the spin-down band gap becomes 1.06 eV. Further simultaneous increase of p and q to 3 increases the value of $E_g^\downarrow$ to 1.16 eV, which is still considerably smaller than the spin-down band gap of the bare FeTe_2 monolayer. It is also clear from Figure 3.32 that the spin-down band gap of the FeTe_2 side increases, while the NiTe_2 side decreases in the $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_p$ heterostructures as the constituent stripes get wider. Consequently, the difference between the band gaps of the FeTe_2 and NiTe_2 side increases as p gets larger, which is associated by an increase in both conduction and valence band off-sets.

In view of the above discussions, it is interesting to note that heterostructures with $p = q \geq 4$ can form periodic multiple quantum well structures. Excess spin down electrons through doping of FeTe_2 stripe can be confined at NiTe_2 stripe. They can form 1D or quasi 1D spin-down electron system, which can move in the quantum well along NiTe_2 stripes. This is an important outcome of these heterostructures that from 2D electrons of either monolayer one can realize/isolate 1D electrons with well-defined spin direction. Notably, in earlier bulk AlAs/GaAs heterostructures, 2D spin-unpolarized electrons were confined in the wells of GaAs [172].

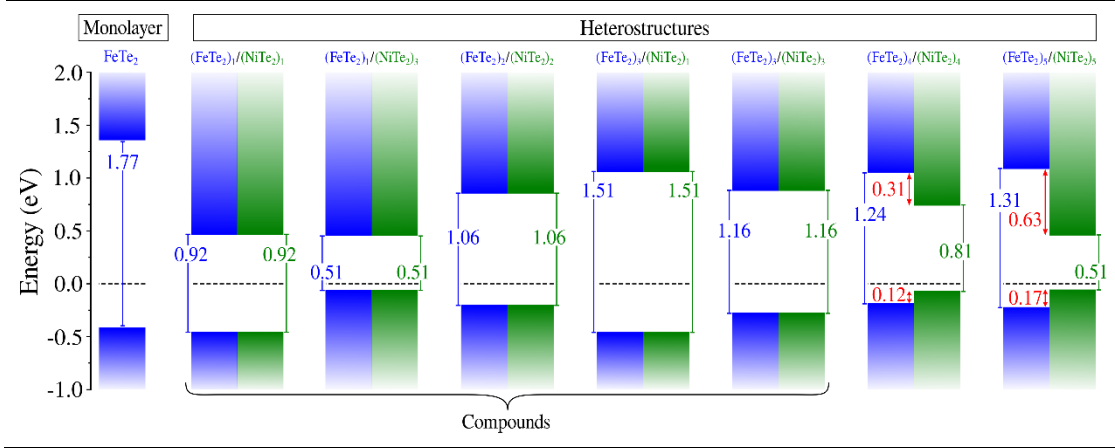


Figure 3.32: The band edge energies for spin-down electrons in the FeTe₂ monolayer and in a variety of A:(FeTe₂)_p/(NiTe₂)_q heterostructures. The Fermi level is indicated by the dashed line, which is taken as the zero of band energy. The spin-down band gap ($E_g^\downarrow$) values in the FeTe₂ (blue) and NiTe₂ (green) are given by blue and green arrows, respectively. Periodic heterostructures having the same $E_g^\downarrow$ value in both sides of the junction are designated as compounds. The band offsets for $p = q = 4$ and 5 are marked by the red double-sided arrows.

Even though we were unable to carry out HSE calculations for larger $p = q$, it appears that the band gap of spin-down electrons, which attributes a half-metallic character to whole heterostructure, ceases at the NiTe₂ side for higher values of q . Under these circumstances, one expects that the heterostructures considered here can change to a half-metal/metal junction for large q . This behavior as well as the band gaps of δ -doped heterostructures suggest that the metallic character of NiTe₂ constituent can dominate the electronic structure gradually with the increasing width of its stripe.

Here, it is demonstrated that for $3 < p = q \leq 5$ both sides of junctions are half-metallic with different band gaps. Now, in this prediction, an interesting question worth addressing is how half-metallic behavior is maintained throughout whole heterostructure despite the fact that one of their constituents, NiTe₂, is a metal when free-standing. We believe that strong Fe-Te-Ni bonds at the sharp armchair boundary between adjacent FeTe₂ and NiTe₂ stripes facilitate the spread of half-metallicity into NiTe₂ stripes of narrow widths. This feature can be utilized to design spintronic devices with tunable band gap corresponding to a given spin direction.

3.4.3. Vertical Heterostructures of FeTe₂/NiTe₂

The vertical heterostructures are constructed by the vertical stacking of FeTe₂ and NiTe₂ monolayers, which are kept by the weak van der Waals (vdW) attraction. In an earlier study, [108] we have demonstrated that the half-metallic behavior of FeTe₂ monolayer continues to occur in its bilayer; but it is destroyed in trilayers (TL) and thicker multilayers (ML). Therefore, we consider periodically repeating V:(FeTe₂)_p/(NiTe₂)_q vertical heterostructures for $p = q = 1, 2$. Optimized atomic structures, atomic magnetic moments, LDOS at selected layers and total DOS, obtained from the HSE calculations, are presented in Figure 3.33.

The minimum energy stacking sequence, where metal atoms (Fe or Ni) resides on top of chalcogen atoms to form hexagons in the top view, is determined by structure optimization. The average binding energy per constituent layer is found to be $\bar{E}_b = 86$ meV per layer per formula unit. Because of weak vdW coupling the interlayer distance is large and prevents constituent layers from strong coupling. As a result, in the vertical heterostructure the constituent layers in the stack retain their electronic and magnetic properties to a large extent. In this respect, while the FeTe₂ layers in the vertical heterostructures with $p = q \leq 2$ remain half-metal with semiconducting spin-down electrons and metallic spin-up electrons, the NiTe₂ layers are metallic for both spin directions. The TMDC monolayers at either side of the junctions (1/1) and (2/2) are found to have antiparallel magnetic moments at different constituent atoms; the total magnetic moments per unit cell are calculated to be 2.35 and 4.70 μ_B , respectively. Accordingly, both heterostructures consist of periodic semiconductor/metal junction for spin-down electrons and metal/metal junction for spin-up electrons. The band gap at the semiconducting FeTe₂ layer is deduced from LDOS calculations to be $E_g^\downarrow = 1.27$ eV for $p = q = 2$. Even though the width of this semiconducting side is thin, we nevertheless estimate the Schottky barrier energy for the spin up electrons to be $E_s = 1.09$ eV.

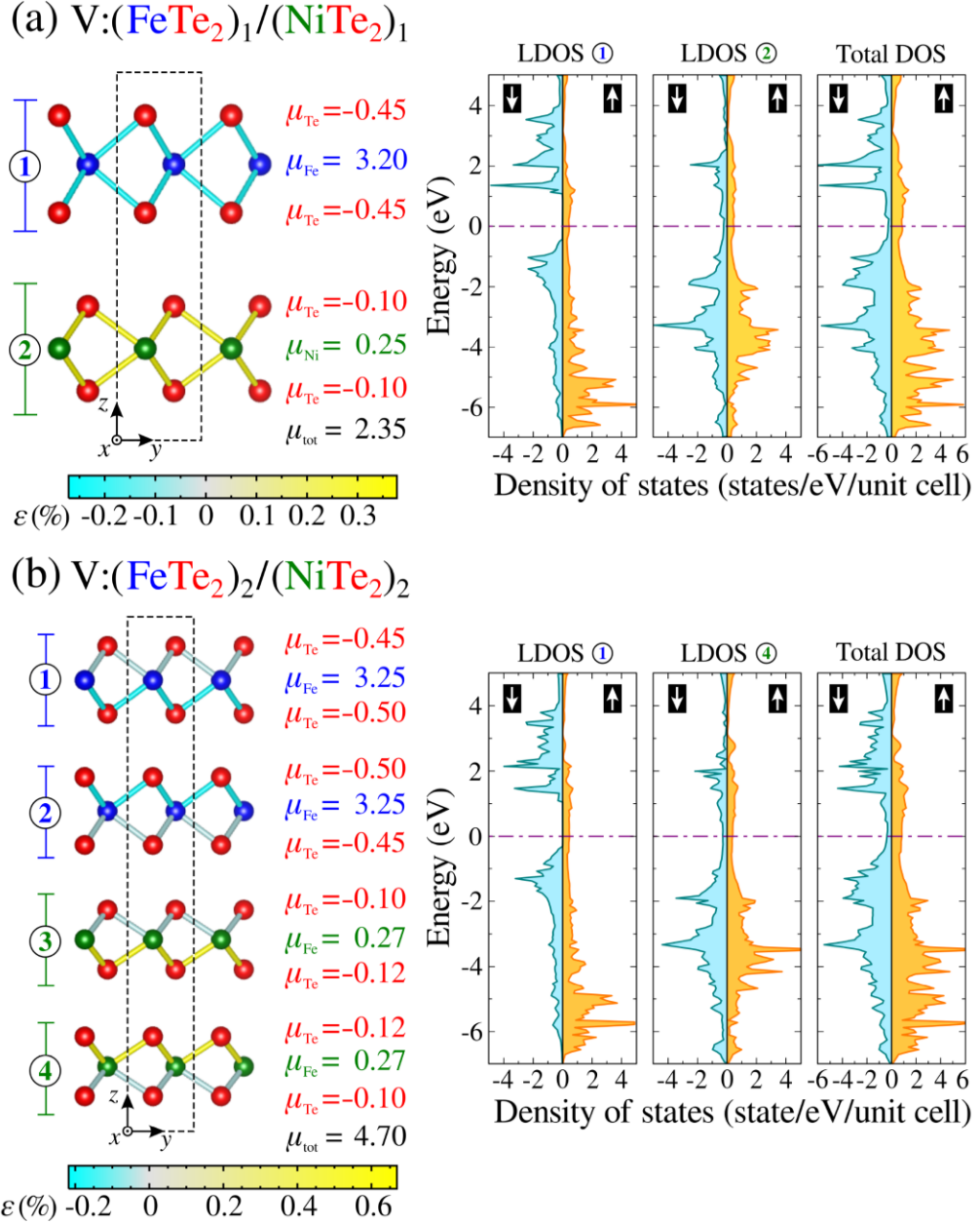


Figure 3.33: Atomic and electronic structures of vertical heterostructures (a) $V:(\text{FeTe}_2)_1/(\text{NiTe}_2)_1$, and (b) $V:(\text{FeTe}_2)_2/(\text{NiTe}_2)_2$. Left: Side views of atomic structures. The blue, green and red balls represent the Fe, Ni and Te atoms, respectively. The sticks representing the Fe–Te and Ni–Te bonds are colored to indicate the bond-length strain ε distribution, computed with respect to the bond lengths in the bare FeTe_2 and NiTe_2 monolayers. Numerals in circles identify the layers. Middle: The atomic (μ_{Fe} , μ_{Ni} , μ_{Te}) magnetic moments in units of Bohr magneton. The magnetic moments at transition-metal and chalcogen atoms are aligned antiparallel as long as μ_{Fe} , $\mu_{\text{Ni}} > 0$ and $\mu_{\text{Te}} < 0$. Right: Density of states projected to the specific layers indicated by numerals (LDOS) and total density of states (TDOS).

4. CONCLUSIONS

In this thesis, we first present that single-layer, in-plane junctions of MoTe_2 , and NiTe_2 stripes along zigzag or armchair edges can construct periodically repeating or finite-size commensurate composite structures. We showed that they can constitute a new class of materials with a very wide range of features and functionalities, such as 2D metallic or narrow band gap semiconducting compounds, narrow 1D metallic interconnects or nanowires in a wide 2D semiconductor sheet, tunneling barriers and resonant tunneling double barrier structures, nanocapacitor, and single and periodic metal-semiconductor junctions forming Schottky barrier. These features can be controlled by the type and width of the stripes of single layer transition-metal dichalcogenides and can be exploited in various device applications.

Fundamental features revealed in these composites, such as metal-insulator transitions, nonmagnetic-magnetic metal phase separation, formation of strictly 1D states in a 2D system, are interesting and able to initiate further research. In-plane heterostructures constructed by nearly lattice matched semiconducting stripes of different band gaps such as MoTe_2 can form multiple quantum well structures.

The calculations reveal that periodic lateral and vertical heterostructures formed by semiconducting SL MoTe_2 and metallic SL NiTe_2 constitute two different class of composite materials exhibiting diverse electronic properties depending on the composition (extension) of the constituents.

In armchair edged, lateral heterostructures of $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ the coupling between different constituents is strong because of covalent+ionic Mo-Te and Ni-Te bonds crossing the boundaries. For narrow stripes of constituents, the heterostructure is a composite metal. Upon widening of stripes, $p \geq 5$, a band gap is opened in the MoTe_2 side. Electrons of metallic NiTe_2 having energies coinciding with the band gap decay into the semiconducting side and pin the Fermi level. This way the metallic region penetrates the semiconductor and charge can transfer across the boundaries between two constituents. The boundaries have finite width, but are symmetric. The average electronic potential energy, which is rather flat and horizontal in the stripes, changes linearly across the boundary; no sawtooth-like tilting occurs. For finite size semiconducting stripes, the band edges can conveniently be retrieved from the density of states projected to the chalcogen-metal-chalcogen

units in the unit cell. This way, confinement effects are taken into account. For wide stripes, one can attain the fundamental band gap of 2D SL MoTe₂. Energies of band edges relative to the average potential of SL 2D MoTe₂ should coincide with those obtained directly from the LDOS at the center of the wide stripe. Our calculations indicate that the band gap is not uniform, but it is closed in the vicinity of the boundary. According to earlier methods developed initially for 3D heterostructures, Schottky barrier energy would be determined as the energy from the Fermi level to the edge of the conduction band, which follows the electronic potential energy $\bar{V}(z)$ and bends. However, we found that band edges traced this way in the direct space deviate near the boundary from the ones determined directly using LDOS. This situation constitutes the dramatic effect of dimensionality.

Vertical heterostructures of $V:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ obtained by the periodic stacking of constituent 2D MoTe₂ and NiTe₂ layers behave rather differently from the armchair edged lateral heterostructure. The van der Waals interaction, albeit weak, is the main cause of the differences. The vertical heterostructure with $p = q = 1$ exhibits semimetallic character along the z -direction with minute state density at the Te–Mo–Te unit, which is a good metal in the xy -plane. For $p = q \geq 2$ semiconducting and metallic phases are separated and metal–semiconductor junction is formed. The interface is sharp and planar; band bending is negligible for undoped MoTe₂ stacks. The plane averaged electronic potential, $\bar{V}(z)$, is relatively high between two adjacent layers, which may limit the conductivity along the z -direction. The Schottky barrier is calculated as the energy from the Fermi level to the conduction band edge. The fundamental band gap at the semiconductor side is narrower as compared to lateral heterostructure, since the band gap of MoTe₂ decreases and changes from direct to indirect by going from monolayer to bilayer and multilayers.

The δ -doping is even more interesting in vertical structures. We predict that, by replacing one sheet of NiTe₂ multilayer slab with MoTe₂ monolayer, the structure acquires directional features: Along the z -direction it is a semimetal with the conduction band of MoTe₂ touching the Fermi level and hence has poor perpendicular conductivity, $\sigma_{\perp}$, but it is a good metal and has good lateral conductivity $\sigma_{\parallel}$ in the NiTe₂ slab. Conversely, by replacing one sheet of the MoTe₂ slab by NiTe₂ monolayer, one can attain a strictly 2D metallic sheet within a

semiconductor. Staircase-like densities of states and quantized conductance and also other features related to the dimensionality can be attained and exploited in 2D device applications.

2D sheets of semiconducting and metallic TMDCs stacked vertically and held by van der Waals interaction form vertical heterostructures that display features at variance with the lateral heterostructures constructed from the stripes of the same TMDCs joined commensurately along their armchair edges. However, a Schottky barrier develops in both types of heterostructures when electrons become confined in different TMDCs having sufficient size, i.e., width or thickness. It is demonstrated that by varying the size of constituents one can control the electronic structure and attain diverse properties. While the present study considered periodic arrangements of two constituents, finite arrangements or conformers with diverse size and orders of constituents can also result in crucial electronic devices.

We also performed extensive first-principles analysis in order to reveal the true magnetic ground state of three transition-metal dichalcogenide monolayers, viz., FeTe₂, VS₂, and NiTe₂. Our investigation demonstrates that semilocal DFT calculations fail in predicting the ground state of magnetic MX₂ monolayers; the results of DFT+*U* and hybrid DFT calculations agree on the correct magnetic ground state and magnetic properties of FeTe₂ and VS₂ monolayers. Remarkably, both *H*- and *T*-phases of the foregoing MX₂ monolayers have magnetic ground states with antiparallel alignment of local magnetic moments at *M* and *X* atoms owing to the spin polarization of the chalcogen atoms via *p*-*d* hybridization. It is clarified that the exchange coupling between the *M* and *X* atoms is negative, which may facilitate the use of MX₂ monolayers in spin transfer applications.

Our results indicate that the FeTe₂ monolayer in its lowest-energy structure is a half-metal, the half metallicity of which can prevail under both compressive and tensile strains. Half metallicity occurs also in FeTe₂ bilayers. These properties make FeTe₂ monolayers and bilayers promising nanomaterials for spintronic devices such as two-dimensional magnetic tunnel junctions. The VS₂ monolayer is a magnetic semiconductor with two different band gaps of different character and widths for spin-up and spin-down states, which can offer critical functionalities in spintronic applications. The NiTe₂ monolayer, which used to be known as a nonmagnetic metal, is a magnetic metal with a small magnetic moment. Since chalcogen atoms display similar characters in compounds, we expect other Fe, V, and Ni dichalcogenide

monolayers have a similar magnetic ground state. Further studies on ultrathin lateral and vertical composite structures or heterostructures constructed from these magnetic monolayers with intriguing electronic properties and proximity effects can offer interesting research directions.

Finally, we discuss the crucial and novel features of magnetic heterostructures with underlying physics. It is demonstrated that the proper treatment of electron correlation is essential in determining the correct magnetic order in the lateral heterostructures. In particular, if the band gap of a constituent or compound structures were underestimated to be a metallic state for one of the sides, the corresponding half-metallic states usually could have been skipped. Thus, this shortcoming prevents us from the prediction of the correct magnetic state of the heterostructure. The results demonstrate that HSE method is suitable for this purpose.

Another critical feature unveiled in this thesis is the hybridization between p - d orbitals of chalcogen and transition metal atoms in TMDC heterostructure and resulting non-uniform/antiparallel distribution of magnetic moments in $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$, which has been skipped in earlier studies. Furthermore, small but antiparallel magnetic moments on chalcogen atoms are decisive for the correct description of the magnetic ground state of the heterostructure.

The energy band gap and band offset variations with width of the strips involve interesting physical phenomena and herald potential applications thereof. Even though an in-plane heterostructure is constituted from two TMDC stripes, one being half-metal and the other metal like $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$, it can attain half-metallic ground state all the way across the device. Close proximity maintained by strong Fe-Te-Ni bonds at the boundary between two constituents is the cause of the transfer or spread of half-metallic state from FeTe_2 side to the otherwise metallic NiTe_2 side. A noteworthy situation is that the band gaps of spin-down electrons are uniform across the unit cell for p and $q \leq 3$ (but strongly dependent on their values) as if a single crystal, but differ abruptly when $p = q > 3$. Accordingly, a non-uniform band diagram in direct space with a sharp, normal band alignment occurs at junctions. This is the manifestation of the formation of electronically different zones at both sides of the junction. It should be noted that, in contrast to in-plane, lateral heterostructures, the spread of half-metallic character from FeTe_2 side to NiTe_2 side cannot be realized in the absence of strong Fe-Te-Ni bonds between layers at the junction.

The band gap of NiTe₂ side being smaller than that of FeTe₂ side and also further decreasing with increasing q , constitutes a 1D multiple quantum well structure. The depth of this well or the energy barrier to FeTe₂ side increases with increasing q . Upon the modulation doping of FeTe₂ side, the excess spin down electrons flowing into 1D quantum well and occupying well defined quantum well states can become confined. The formation of the confined states and their level splitting can be deduced from the effective mass theory. This way 2D itinerant electrons of in-plane heterostructure undergo a $2D \rightarrow 1D$ change in dimensionality, and they become confined to NiTe₂ side. These electrons can transport spin and charge only along armchair edge in NiTe₂ in well-defined conduction channels. Owing to the modulation doping in FeTe₂ side, the impurity scattering in NiTe₂ side is minimized and the phase breaking length is maximized. The energy level splitting of these channels change with the band offset or the energy barrier (height) between the conduction band edges of FeTe₂ and NiTe₂ and hence with q . Accordingly, the barrier height provides a means of tunability for 1D quantum conduction.

One can deduce interesting devices from the normal band line up. For example, (FeTe₂) _{p} /(NiTe₂) _{q} /(FeTe₂) _{p} structure with p and $q > 3$, commensurately joined to two wide stripes of NiTe₂ from both (FeTe₂) _{p} ends can form a double barrier resonant tunneling (DBRT) device. While both wide NiTe₂ stripes capping (FeTe₂) _{p} from their free ends are metallic, (NiTe₂) _{q} in between is half-metallic, narrow band semiconductor and form localized (confined) states for spin-down electrons. The metallic electron in the wide NiTe₂ side at the left can tunnel through these confined states to the other wide NiTe₂ side at the right when energies are matched. The confined states at the middle part of the device act as spin-filter. It is known that the tunneling across two FeTe₂ barriers through these confined states occur in very short time when the energies are matched. The operation parameters of this device can be monitored by the width of NiTe₂ between FeTe₂ barriers.

Heterostructures can be constructed not only from very long stripes of constituents as in the present study but also from finite size stripes or from nanoribbons. The width (parallel to boundary) and length (perpendicular to the boundary) of nanoribbons and the type of edge termination are available parameters to monitor the physical properties of the device. Carriers in heterostructures formed from nanoribbons are quasi-1D along the axis of the nanoribbon. The quantum well

formation and resulting confinement in one of the constituents lead to the change of dimensionality from 1D to 0D (namely, quantum dots).

The antiparallel alignment of local magnetic moments at constituent elements constructed through the spin polarization at chalcogen atoms as a result of p - d orbital hybridization and hence the negative exchange coupling between transition metal and chalcogen atoms may facilitate the spin transfer in these heterostructures.

In conclusion, we considered lateral and vertical heterostructures composed of FeTe_2 and NiTe_2 monolayers using HSE method, which allowed us to predict the correct magnetic ground state for these stand-alone monolayers. The armchair edged heterostructures with $p = q = 1-5$, as well as δ -doping realized thereof are found to be half-metallic with integer magnetic moment per cell. Namely, all these structures were semiconductor for spin-down electrons, but metallic for spin-up electrons. Due to different band gaps occurred in different and wide TMDC stripes, normal band-line ups are deduced. Additionally, the indirect band gap of these half-metallic structures exhibit an excellent tunability with the width of the constituent stripes. Strong variations of the band gap can be attained by δ -doping. The appearance of half-metallic behavior in the whole material for a limited range of alternation of constituents is found to be a rare. The spread of half-metallicity from one (FeTe_2) to the other (NiTe_2) side, which is metallic when stand-alone, is attributed to the strong Fe-Te-Ni bonds at the sharp boundary. While the electrons in the periodic $A:(\text{FeTe}_2)_p/(\text{NiTe}_2)_q$ with $p, q \leq 3$ is two dimensional (2D), excess spin-down electrons in heterostructures with $p = q > 3$ may change their dimensionality from 2D to 1D through the quantum confinement in the quantum wells at NiTe_2 stripe. The quantization (that is different from 2D) and the quantum conductance of these 1D, spin-down electrons can be of fundamental and technological interest, and should be experimentally observable.

In contrast to lateral heterostructures, the half-metallic character can be retained only in FeTe_2 side in the thin, vertical heterostructures. While the FeTe_2 side has a band gap for spin-down electrons, the NiTe_2 side is metallic for the same spin direction. However, both sides are metallic for the spin up electrons. Accordingly, the vertical heterostructure forms a semiconductor/metal junction with a Schottky barrier for one spin direction, but metal/metal junction for the opposite spin direction. Hence, such a system shall function as diode for one spin direction and conductor for the opposite spin direction. In the present study, we estimated the

Schottky barrier energy for a single spin direction. Interestingly, the inhomogeneous magnetic order with antiparallel magnetic moments at constituent atoms are also retained for thin alternation of constituents. This functionality is rather rare in vertical, van der Waals heterostructures and can promise crucial spintronic applications.

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APPENDICES

Appendix A: Cohesive and Formation Energy Formulations

The cohesive energy $E_C(\text{MX}_2)$ per formula unit is given by

$$E_C(\text{MX}_2) = E_{\text{atom}}(\text{M}) + 2E_{\text{atom}}(\text{X}) - E_T(\text{MX}_2) \quad (\text{A1.1})$$

where $E_{\text{atom}}(\text{M})$ and $E_{\text{atom}}(\text{X})$, denote the total energies of M and X atoms, respectively, and $E_T(\text{MX}_2)$ is the total energy of MX_2 .

The formation energy $E_f(\text{MX}_2)$ per formula unit is given by

$$E_f(\text{MX}_2) = E_C(\text{MX}_2) + E_{\text{bulk}}(\text{M}) - E_{\text{bulk}}(\text{X}) \quad (\text{A1.2})$$

where $E_{\text{bulk}}(\text{M})$ and $E_{\text{bulk}}(\text{X})$, denote the cohesive energies of constituent elements M and X in their equilibrium bulk phases, respectively, and $E_C(\text{MX}_2)$ is the cohesive energy of MX_2 .

The formation energy $E'_f(\text{MX}_2)$ per formula unit relative to the parent 3D crystals given by

$$E'_f(\text{MX}_2) = E_C(3\text{D MX}_2) - E_C(2\text{D MX}_2) \quad (\text{A1.3})$$

where $E_C(3\text{D MX}_2)$ denotes cohesive energy of parent 3D crystal and $E_C(2\text{D MX}_2)$ is cohesive energy of the 2D SL, 2L or 3L of MX_2 .

The average cohesive energies $\bar{E}_C(p/q)$ per formula unit of 2D lateral A:(p/q) and 3D vertical V:(p/q) heterostructures is given by

$$\bar{E}_C(p/q) = [pE_{\text{atom}}(\text{Mo}) + qE_{\text{atom}}(\text{Ni}) + 2(p+q)E_{\text{atom}}(\text{Te}) - E(p/q)]/(p+q) \quad (\text{A1.4})$$

where $E_{\text{atom}}(\text{Mo})$, $E_{\text{atom}}(\text{Ni})$ and $E_{\text{atom}}(\text{Te})$ denote the total energies of Mo, Ni and Te atoms, respectively, and $E(p/q)$ is the total energy of $(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ lateral or vertical heterostructure.

The average formation energy $\bar{E}_f(p/q)$ per formula unit of 2D lateral A:(p/q) and 3D vertical V:(p/q) heterostructures is given by

$$\bar{E}_f(p/q) = \bar{E}_C(p/q) - [pE_C(3\text{D MoTe}_2) + qE_C(3\text{D NiTe}_2)]/(p+q) \quad (\text{A1.5})$$

where $E_C(3\text{D MoTe}_2)$ and $E_C(3\text{D NiTe}_2)$ denote the cohesive energies of 3D bulk MoTe_2 and NiTe_2 crystals, respectively, and $\bar{E}_C(p/q)$ is the average cohesive energy of the composite structure.

Appendix B: Cohesive and Formation Energies and Crystallographic Data Tables

Table B1.1: Energetic, electronic and geometric parameters of 2D [singlelayer (SL), bilayer (2L), trilayer (3L)] and 3D crystals. Cohesive energy E_C , formation energy E_f , formation energy relative to the parent 3D crystals E'_f , direct (d) or indirect (i) bandgaps E_g , lattice constants $a = b$ and c (Å), Mo–Te and Ni–Te bond lengths d_{M-X} , layer thickness Δ , interlayer spacing Δ_{int} (Å).

Structure	Method	E_C (eV/f.u.)	E_f (eV/f.u.)	E'_f (eV/f.u.)	E_g (eV)	$a = b$ (Å)	C (Å)	d_{M-X} (Å)	Δ (Å)	Δ_{int} (Å)
3D MoTe ₂	(LDA)	15.882	0.917		0.884 ^{<i>i</i>}	3.469	13.738	2.692	3.597	3.272
3D MoTe ₂	(PBE)	13.117	1.770		0.751 ^{<i>i</i>}	3.515	14.076	2.718	3.617	3.421
3L MoTe ₂	(PBE)	13.003	1.656	0.114	0.834 ^{<i>i</i>}	3.516		2.720	3.620	3.367
2L MoTe ₂	(PBE)	12.947	1.599	0.171	0.943 ^{<i>i</i>}	3.519		2.720	3.617	3.367
2D MoTe ₂	(LDA)	15.661	0.756	0.160	1.253 ^{<i>d</i>}	3.466		2.688	3.589	
2D MoTe ₂	(PBE)	12.789	1.442	0.328	1.145 ^{<i>d</i>}	3.519		2.722	3.623	
3D NiTe ₂	(LDA)	13.152	0.483			3.619	11.608	2.551	2.928	2.876
3D NiTe ₂	(PBE)	11.009	1.243			3.686	11.703	2.592	2.960	2.892
2D NiTe ₂	(LDA)	12.295	0.125	0.357		3.589		2.535	2.918	
2D NiTe ₂	(PBE)	10.510	0.744	0.499		3.672		2.585	2.959	

Table B1.2: Structural values of lateral heterostructures, $A:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ for $1 \leq p = q \leq 10$. The optimized values of semiconducting (S) MoTe_2 and metallic (M) NiTe_2 stripes' layer thicknesses Δ_S and Δ_M ; Mo–Te and Ni–Te bond lengths, $d_{\text{Mo–Te}}$ and $d_{\text{Ni–Te}}$, in interface (i) and bulk region (b). All values are given in Å.

Composite	Δ_S	Δ_M	$d_{\text{Mo–Te}}$	$d_{\text{Ni–Te}}$
$A:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$	3.751	3.187	2.653	2.595
$A:(\text{MoTe}_2)_2/(\text{NiTe}_2)_2$	3.644	2.906	2.701	2.548
$A:(\text{MoTe}_2)_3/(\text{NiTe}_2)_3$	3.329 ⁱ	3.098 ⁱ	2.713	2.534
	4.140 ^b	2.807 ^b		
$A:(\text{MoTe}_2)_4/(\text{NiTe}_2)_4$	3.039 ⁱ	3.134 ⁱ	2.724 ⁱ	2.536 ⁱ
	3.906 ^b	2.864 ^b	2.707 ^b	2.542 ^b
$A:(\text{MoTe}_2)_5/(\text{NiTe}_2)_5$	3.427 ⁱ	3.119 ⁱ	2.704 ⁱ	2.522 ⁱ
	3.624 ^b	2.948 ^b	2.714 ^b	2.555 ^b
$A:(\text{MoTe}_2)_6/(\text{NiTe}_2)_6$	3.310 ⁱ	3.071 ⁱ	2.707 ⁱ	2.533 ⁱ
	3.668 ^b	2.923 ^b	2.705 ^b	2.541 ^b
$A:(\text{MoTe}_2)_7/(\text{NiTe}_2)_7$	3.113 ⁱ	3.176 ⁱ	2.715 ⁱ	2.508 ⁱ
	3.620 ^b	2.976 ^b	2.683 ^b	2.534 ^b
$A:(\text{MoTe}_2)_8/(\text{NiTe}_2)_8$	3.396 ⁱ	3.135 ⁱ	2.701 ⁱ	2.496 ⁱ
	3.631 ^b	3.025 ^b	2.692 ^b	2.515 ^b
$A:(\text{MoTe}_2)_9/(\text{NiTe}_2)_9$	3.323 ⁱ	3.132 ⁱ	2.705 ⁱ	2.511 ⁱ
	3.620 ^b	3.022 ^b	2.687 ^b	2.527 ^b
$A:(\text{MoTe}_2)_{10}/(\text{NiTe}_2)_{10}$	3.344 ⁱ	3.153 ⁱ	2.704 ⁱ	2.492 ⁱ
	3.607 ^b	3.024 ^b	2.693 ^b	2.518 ^b

Table B1.3: Structural values of vertical heterostructures, $V:(\text{MoTe}_2)_p/(\text{NiTe}_2)_q$ for $1 \leq p = q \leq 5$. Optimized values of semiconducting (S) MoTe_2 and metallic (M) NiTe_2 layer thicknesses Δ_S and Δ_M ; Mo–Te and Ni–Te bond lengths $d_{\text{Mo-Te}}$ and $d_{\text{Ni-Te}}$; MoTe_2 – NiTe_2 , MoTe_2 – MoTe_2 and NiTe_2 – NiTe_2 interlayer spacing Δ_{S-M} , Δ_{S-S} , and Δ_{M-M} , respectively, in interface (i) or bulk region (b). All values are given in Å.

Composite	Δ_S	Δ_M	$d_{\text{Mo-Te}}$	$d_{\text{Ni-Te}}$	Δ_{S-M}	Δ_{M-M}	Δ_{M-M}
$V:(\text{MoTe}_2)_1/(\text{NiTe}_2)_1$	3.561	3.019	2.732	2.563	3.108		
$V:(\text{MoTe}_2)_2/(\text{NiTe}_2)_2$	3.568	3.052	2.731	2.565	3.227	3.337	2.880
$V:(\text{MoTe}_2)_3/(\text{NiTe}_2)_3$	3.568 ⁱ	3.051 ⁱ	2.730 ⁱ	2.575 ⁱ	3.271	3.292	2.940
	3.564 ^b	3.077 ^b	2.729 ^b	2.576 ^b			
$V:(\text{MoTe}_2)_4/(\text{NiTe}_2)_4$	3.567 ⁱ	3.037 ⁱ	2.732 ⁱ	2.570 ⁱ	3.203	3.347 ⁱ	2.909 ⁱ
	3.565 ^b	3.059 ^b	2.731 ^b	2.574 ^b		3.339 ^b	2.949 ^b
$V:(\text{MoTe}_2)_5/(\text{NiTe}_2)_1$	3.611 ⁱ	3.112	2.722 ⁱ	2.563	3.306	3.380 ⁱ	
	3.608 ^b		2.721 ^b			3.330 ^b	
$V:(\text{MoTe}_2)_1/(\text{NiTe}_2)_5$	3.516	2.969 ⁱ	2.745	2.578 ⁱ	3.105		2.883 ⁱ
		2.993 ^b		2.587 ^b			2.915 ^b

Table B1.4: The predicted values of Curie temperature T_C for VS_2 and FeTe_2 monolayers.

Monolayer	T_C (K)	
FeTe_2	166	Ref. [156] Curie temperature from Monte Carlo simulations Exchange constant from $J = (E_{\text{AFM}} - E_{\text{FM}})/(8 \times 2S^2)$ Energy difference $E_{\text{AFM}} - E_{\text{FM}}$ from the PBE calculations
VS_2	90	Ref. [154] Curie temperature from $T_C = 0.89J/k_B$ Exchange constant from $\Delta E_{\text{mag}} = 8J$ Energy difference ΔE_{mag} between the FM and AFM states obtained from the LDA+ U calculations
	138	Ref. [155] Curie temperature from $T_{C_1} = J_1/k_B$ Exchange constant from $S^2 J_1 = (E_{\text{F1}} - E_{\text{A1}})/2$
	292	Ref. [155] Curie temperature from Monte Carlo simulations
	309	Ref. [168] Curie temperature from $k_B T_C = (2/3)E_{\text{ex}}$ $E_{\text{ex}} = (E_{\text{AFM}} - E_{\text{FM}})/N$ from the PBE calculations
	369	Ref. [155] Curie temperature from $T_{C_2} = (2/3k_B)(E_{\text{AFM}} - E_{\text{FM}})/N$

Appendix C: Publications *within* the Scope of the Thesis Study

- [C1] Aras M., Kılıç Ç., Ciraci S., (2020), “Magnetic Heterostructures of Transition Metal Dichalcogenides: Antiparallel Magnetic Moments of Half-metallic State”, The Journal of Physical Chemistry C, 124 (42), 23353–23360.
- [C2] Aras M., Kılıç Ç., Ciraci S., (2020), “Magnetic Ground State in FeTe₂, VS₂, and NiTe₂ Monolayers: Antiparallel Magnetic Moments at Chalcogen Atoms”, Physical Review B, 101 (5), 054429.
- [C3] Aras M., Kılıç Ç., Ciraci S., (2018), “Lateral and Vertical Heterostructures of Transition Metal Dichalcogenides”, The Journal of Physical Chemistry C, 122 (3), 1547–1555.
- [C4] Aras M., Kılıç Ç., Ciraci S., (2017), “Planar Heterostructures of Single-layer Transition Metal Dichalcogenides: Composite Structures, Schottky Junctions, Tunneling Barriers, and Half Metals”, Physical Review B, 95 (7), 075434.

Appendix D: Publications *not* within the Scope of the Thesis Study

- [D1] Aras M., Güler-Kılıç S., Kılıç Ç., (2022), “Enhancement of the Magnetic Anisotropy in Single Semiconductor Nanowires via Surface Doping and Adatom Deposition”, Nanotechnology, 33 (20), 205202.
- [D2] Aras M., Güler-Kılıç S., Kılıç Ç., (2020), “Segregation Tendencies of Transition-metal Dopants in Wide Band Gap Semiconductor Nanowires”, Physical Chemistry Chemical Physics, 22 (48), 27987–27998.
- [D3] Aras M., Kılıç Ç., (2019), “Surface Doping of ZnO Nanowires with Bi: Density-functional Supercell Calculations of Defect Energetics”, Physical Review B, 99 (4), 045412.
- [D4] Aras M., Kılıç Ç., (2018), “Electrical Tuning of Spin Splitting in Bi-doped ZnO Nanowires”, Physical Review B, 97 (3), 035405.
- [D5] Güler-Kılıç S., Aras M., (2017), “Magnetic Functionalization of Bismuth-adsorbing Zinc Oxide Nanowires”, Sakarya University Journal of Science, 21 (6), 304190.
- [D6] Aras M., Güler-Kılıç S., Kılıç Ç., (2017) “Doping-induced Spin-orbit Splitting in Bi-doped ZnO Nanowires”, Physical Review B, 95 (15), 155404.
- [D7] Kılıç Ç., Aras M., Güler-Kılıç S. (2016), “Computational Studies of Bismuth-doped Zinc Oxide Nanowires” in Low Dimensional and Nanostructured Materials and Devices, Editors, Ünlü H., Horing N. J. M., Dabrowski J., Springer International Publishing.

- [D8] (Oral Presentation) Aras M., Güler-Kılıç S., Kılıç Ç., (2016), “Doping-induced Spin Splitting in ZnO Nanowires: A Density Functional Theory Study”, The 2016 E-MRS Fall Meeting and Exhibit, Warsaw University of Technology, Warsaw, Poland, 19–22 September.
- [D9] (Poster Presentation) Aras M., Güler-Kılıç S., Kılıç Ç., (2016), “Doping of Zinc Oxide Nanowires with Bismuth: A DFT+*U* Study”, The 2016 E-MRS Spring Meeting and Exhibit, Lille Grand Palais, Lille, France, 2–6 May.