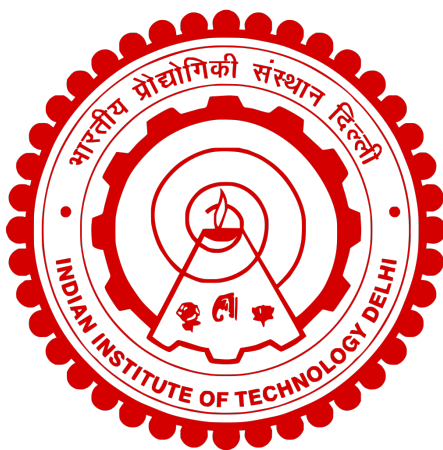


THEORETICAL INSIGHTS TO SYMMETRY-INDUCED SPIN SPLITTINGS AND TEXTURES IN (NON-)MAGNETIC MATERIALS

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2024

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by

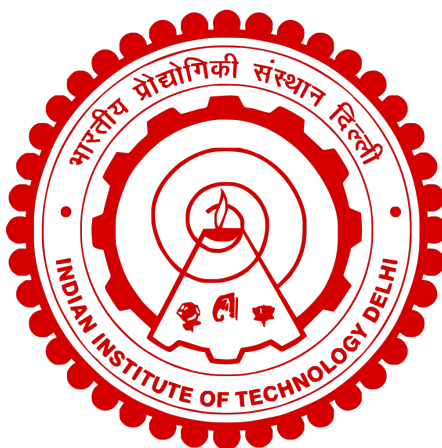
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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2024

Dedicated to my father

Certificate

This is to certify that the thesis entitled “**Theoretical Insights to Symmetry-Induced Spin Splittings and Textures in (Non-)Magnetic Materials**” being submitted by **Sajjan**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard. The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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Sajjan Sheoran

Abstract

Spin splittings and associated spin textures play a pivotal role in spintronics application (e.g., charge-to-spin conversion). The role of crystal symmetries in determining spin polarization through spin-orbit coupling (SOC) is established in pioneer works by Dresselhaus and Rashba. Nevertheless, the practical use of these materials in spin transport is constrained by the SOC-induced spin dephasing mechanisms. In addition, the toxicity, rarity, and instabilities of materials containing heavy atoms are also challenging. The materials with uniform spin configurations in the momentum space, termed as persistent spin texture (PST), provide nondephasing spin transport. However, PSTs observed in the regime of linear (in $\mathbf{k}$) splitting and exist locally in Brillouin zone (BZ).

Here, we report first-principles density functional theory simulation and symmetry-based $\mathbf{k}\cdot\mathbf{p}$ analysis to obtain novel spin-splitting mechanisms with nontrivial spin textures in magnetic and nonmagnetic crystalline materials. We demonstrate full-plane PSTs in the regime of purely cubic spin splitting protected by the in-plane mirror and threefold rotation symmetries. A large class of experimentally synthesized bulk materials shows cubic-ordered PSTs with D_{3h} and C_{3h} point group symmetries. Moreover, σ_h symmetry enforces the spin textures of two-dimensional (2D) materials to the out-of-plane direction in the entire BZ. Our calculations demonstrate that it is local site symmetries that determine the nature of spin splittings and PSTs.

Structural symmetry can be varied using external perturbations, i.e., electric and strain fields, to modulate the spin and valley physics in 2D materials. By performing DFT calculations on monolayer MSi_2N_4 (M=Mo, W), a prototypical septuple atomic layered two-dimensional material, we demonstrated that Rashba splitting can be induced by breaking the σ_h through an out-of-plane external electric field and chemical substitution of elements (*Janusization*). The low energy electron and hole valleys drift far off the K/K' point under uniaxial strains. The direction and strength of valley drift strongly depend on the nature of the charge carrier and uniaxial strain with a more substantial response along the zigzag path. The changing geometric

properties of Bloch states affect the Berry curvatures and circular dichroism. Specifically, Berry curvature dipole is significantly enhanced under the tensile strain along armchair and zigzag directions. Meanwhile, the particle-hole asymmetry arising from nonequivalent electron and hole valley drifts relaxes the selection rules, thus reducing the degree of circular polarization up to ~ 0.98 . Therefore, strain engineering of valley physics in the monolayer MSi_2N_4 is of prime importance for valleytronics.

Recently, antiferromagnetic (AFM) materials have emerged as viable substitutes for non-magnetic and ferromagnetic materials, benefiting from resilience towards stray fields, ultra-fast dynamics, magnetotransport effects, and lack of susceptibility to magnetic perturbations. Centrosymmetric antiferromagnetic semiconductors, although abundant in nature, appear less favorable in spintronics owing to the lack of inherent spin polarization and magnetization. We unveil hidden Zeeman-type nonrelativistic spin splitting (NRSS) in layered centrosymmetric antiferromagnets with asymmetric sublayer structures through first-principles simulations and symmetry analysis. In addition, we demonstrate a paradigm to harness NRSS by twisting the bilayer of centrosymmetric antiferromagnets with commensurate twist angles. We observe spin-momentum locking by first-principles simulations and symmetry analysis on prototypical MnPSe_3 and MnSe antiferromagnets. The strength of NRSS (up to $80 \text{ meV}\text{\AA}$) induced by twisting is comparable to SOC-induced linear Rashba-Dresselhaus effects. The results also demonstrate how applying biaxial strain and a vertical electric field tune the NRSS. The design principle to obtain Zeeman-type splitting in centrosymmetric antiferromagnets established here expands the range of materials to look for spintronics.

स्पिन स्प्लिटिंग और संबंधित स्पिन टेक्सचर्स, अर्थात मोमेंटम स्थान में स्पिन पॉलराइजेशन वेक्टर्स का वितरण, स्पिनट्रॉनिक्स अनुप्रयोग (उदा., चार्ज-टू-स्पिन कनवर्जन) में महत्वपूर्ण भूमिका निभाते हैं। क्रिस्टल सममितियों की भूमिका, जिनका संबंध स्पिन-ऑर्बिट कप्लिंग (SOC) के माध्यम से स्पिन पॉलराइजेशन का निर्धारण करने में है, इसे ड्रेसलरहांस और राशबा द्वारा किए गए प्रमुख कार्यों में स्थापित हो गई है। हालांकि, इन सामग्रियों का वाणिज्यिक उपयोग स्पिन परिवहन में स्पिन-ऑर्बिट कप्लिंग (SOC) के कारण होने वाले स्पिन डीफेजिंग प्रक्रियाओं से सीमित है, अर्थात एलियट-याफेट स्पिन रिलैक्सेशन और ड्याकोनोव-पेरेल स्पिन डीफेजिंग। इसके अलावा, भारी परमाणु अणुओं को शामिल करने वाली सामग्रियों की विषाक्तता, दुर्लभता, और अस्थिरताओं की चुनौतियाँ भी हैं। मोमेंटम स्थान में एक समरूप स्पिन विन्यास को बनाए रखने वाली सामग्रियाँ, जिसे स्थिर स्पिन टेक्सचर (PST) कहा जाता है, स्थिर स्पिन-हेलिक्स मैकेनिज्म के माध्यम से दीर्घकालीन कैरियर स्पिन जीवनकाल प्रदान करती हैं। हालांकि, अब तक अध्ययन की गई अधिकांश PSTs को k में रूपरेखा की गई स्प्लिटिंग का श्रेय दिया गया है और ये विशिष्ट उच्च-समरूपता बिंदुओं के आस-पास स्थानीय रूप से अस्तित्वहीन हो जाती हैं ब्रिल्वॉ क्षेत्र (BZ) के।

यहाँ, हम पहले-सिद्धांत सिमुलेशन और सिमेट्री-आधारित $k.p$ विश्लेषण का उपयोग करते हैं ताकि चुंबकीय और अचुंबकीय द्रव्यमानों में असामान्य स्पिन टेक्सचर्स के साथ नए स्पिन-स्प्लिटिंग मैकेनिज्म प्राप्त किए जा सकें। हम पूरी-तल PSTs की प्रकृति की रिपोर्ट करते हैं जो केवल क्यूबिक स्पिन स्प्लिटिंग क्षेत्र में पूरी तरह से बनाए जा रहे हैं, जिसे इन-प्लेन मिरर (σ_h) और तिनमुखी घूमन (C_3) द्वारा प्रबल किया जाता है। एक बड़े श्रेणी का प्रयोगशाला संश्लेषित बल्क सामग्रियों में D_{3h} और C_{3h} बिंदु समूह सममितियाँ दिखाती हैं। इसके अलावा, σ_h सममिति दो-आयामी (2D) सामग्रियों की स्पिन टेक्सचर्स को पूरी BZ में बाहरी-प्लेन दिशा में अनुबद्ध करती है। हमारी गणनाएँ दिखाती हैं कि यह स्थानीय स्थान सममितियाँ हैं जो स्पिन स्प्लिटिंग्स और PSTs की प्रकृति का निर्धारण करती हैं।

संरचनात्मक सममिति को विभिन्न कार्यात्मक प्रभावों का सामना करने के लिए बदला जा सकता है, उदाहरण के लिए, इलेक्ट्रिक और तनाव क्षेत्रों का उपयोग करके 2D सामग्रियों में स्पिन और वैली भौतिकी को सम्मोदित करने के लिए। मोनोलेयर MSi_2N_4 ($M=Mo, W$) पर घनत्व कार्यात्मक सिद्धांत (DFT) गणनाएँ करके, एक उदाहरणीय सप्तांश आणविक स्तर की 2D सामग्री, σ_h को ब्रेक करके बाहरी इलेक्ट्रिक फील्ड और तत्वों के रूप में उपयोग से राशबा स्प्लिटिंग प्रेरित किया जा सकता है। कम ऊर्जा इलेक्ट्रॉन और होल वैली टिरों केन्द्रित स्ट्रेन के तहत K/K' बिंदु के बहुआक्षरी दबाव के तहत दूर चला जाता है। वैली चलन की दिशा और ताकत का प्रतिकूल उत्तर चिरपथ के साथ अधिक स्थिर प्रतिक्रिया के साथ, आधारित है। हमारे फिंडिंग्स, सूक्ष्मक कक्षय योगदान और सममिति कमी की महत्वपूर्ण भूमिका को प्रदर्शित करते हैं। ब्लोच स्थितियों की बदलती रूपरेखा बेरी कर्वचर्स और सर्कुलर डाइक्रोइज्म को प्रभावित करती हैं। विशेष रूप से, आर्मचेयर और जिगजैग दिशाओं के साथ तनाव स्थिति के तहत बेरी कर्वचर डाइपोल सांग्राता को सुधारा जाता है। इसके बीच, गैरसमरूप इलेक्ट्रॉन और होल वैली चलन से उत्पन्न धारापूर्व असममिति नियमों को

धीरे-धीरे शांत करती है, जिससे चिरपथीकरण की दिशा में साइक्लर पोलराइजेशन की डिग्री को ~ 0.98 तक कम करती है। इसलिए, मोनोलेयर MSi_2N_4 में वैली भौतिकी के तनाव का इंजनियरिंग करना वैलीट्रॉनिक्स के लिए प्रधान महत्वपूर्ण है।

हाल ही में, एंटीफेरोमैग्नेटिक (AFM) सामग्रियाँ गैरचुंबकीय और फेरोमैग्नेटिक सामग्रियों के लिए व्यावसायिक विकल्प के रूप में प्रकट हो रही हैं, जो बिखरे क्षेत्रों, अल्ट्राफास्ट गतिविधि, मैग्नेटोट्रांसपोर्ट प्रभावों, और चुंबकीय उत्तेजनों के प्रति सहिष्णुता के लाभान्वित हो रही हैं। सेंट्रोसाइमेट्रिक एंटीफेरोमैग्नेटिक सेमीकंडक्टर्स, हालांकि प्राकृतिक रूप से प्रचुर हैं, स्वाभाविक रूप से स्पिन पोलराइजेशन और मैग्नेटाइजेशन की कमी के कारण स्पिनट्रॉनिक्स में कम पसंदीदा लगते हैं। हम लयरड सेंट्रोसाइमेट्रिक एंटीफेरोमैग्नेट्स में एसीमेट्रिक सबलेयर संरचनाओं के माध्यम से छिपे जीमेन-प्रकार के गैर सांवेधानिक स्पिन स्प्लिटिंग (NRSS) का खुलासा करते हैं, पहले-सिद्धांत सिमुलेशन और सिमेट्री विश्लेषण के माध्यम से। हाल ही में सिंथेसाइज़ किए गए मोनोलेयर MnSe के दो-तहती संरूप में, हम दिखाते हैं कि विशिष्ट k बिंदुओं के आस-पास समकक्ष उपतलों पर स्थानीय रूप से विभाजित अवस्थाएँ $\mathcal{PT}$ -सममित पैयर्स बनाती हैं। और अधिक महत्वपूर्ण है, हम $\mathcal{PT}$ -सममित एंटीफेरोमैग्नेट्स की दो-तहती को घुमाने के द्वारा NRSS का उपयोग करते हैं। प्रोटोटाइप MnSe और MnPSe_3 पर DFT सिमुलेशन करके, हम पूर्वानुमान करते हैं कि ब्रिल्युइन जोन के विशिष्ट पथों पर राशबा-ड्रेसेलहॉस और जीमेन-प्रकार NRSS उत्पन्न हो सकते हैं। घुमाने के द्वारा उत्पन्न राशबा-ड्रेसेलहॉस स्पिन स्प्लिटिंग की ताकत ($\sim 90 \text{ meV}\text{\AA}$) स्पिन-या-बाधित स्थिति की तुलना में है। परिणाम यह भी दिखाते हैं कि दो-सेंट्रिक तनाव और एक सीधी विद्युत क्षेत्र लागू करने से NRSS के मात्रा को स्वरूपित करने की संभावना है। यहाँ सेंट्रोसाइमेट्रिक एंटीफेरो मैग्नेट्स में जीमेन-प्रकार स्प्लिटिंग प्राप्त करने के लिए डिज़ाइन सिद्धांत विस्तार करता है और स्पिनट्रॉनिक्स के लिए सामग्रियों की खोज की सीमा को बढ़ाता है।

List of Publications

14. **Sajjan Sheoran*** and Saswata Bhattacharya*, “*Nonrelativistic spin splittings and antiferromagnetism in twisted bilayers of centrosymmetric antiferromagnets*”, Physical Review Materials (Letter) **8**, L051401 (2024).
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12. Ankita Phutela*, **Sajjan Sheoran**, Deepika Gill, and Saswata Bhattacharya*, “*Strain-driven topological quantum phase transition in the family of halide perovskites*”, Journal of Materials Chemistry C **12**, 2165 (2024).
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The Journal of Physical Chemistry Letters **14**, 10158 (2023).

6. Ashish Kumar, Manisha Sharma[†], **Sajjan Sheoran**[†], Shilpi Jaiswal[†], Abhijeet Patra*, Saswata Bhattacharya*, and Venkata Krishnan*, “*Tailoring defects in SrTiO₃ by one step nanoarchitectonics for realizing photocatalytic nitrogen fixation in pure water*”, Nanoscale **15**, 11667 (2023).
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3. Preeti Bhumla*, Manjari Jain, **Sajjan Sheoran**, and Saswata Bhattacharya*, “*Vacancy-ordered double perovskites Cs₂BI₆ (B = Pt, Pd, Te, Sn): An emerging class of thermoelectric materials*”, The Journal of Physical Chemistry Letters **13**, 11655 (2022).
2. Preeti Bhumla*, Deepika Gill, **Sajjan Sheoran**, and Saswata Bhattacharya*, “*Origin of Rashba spin splitting and strain tunability in ferroelectric bulk CsPbF₃*”, The Journal of Physical Chemistry Letters **12**, 9539 (2021).
1. Devendra Sharma, Priyanka Choudhary[†], **Sajjan Sheoran**[†], Sahil Kumar, Saswata Bhattacharya*, and Venkata Krishnan*, “*Synergistic coupling of nickel phosphide with graphitic carbon nitride for transfer hydrogenation of quinoline using formic acid as bio-renewable hydrogen source*”, (under review).

[†] Equal contribution

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Introduction

1.1 Materials

Shaping material properties to meet various requirements has been a fundamental aspect of human civilization, with the evolution of materials serving as a historical timeline for Earth [6]. For instance, the Stone-Age culture relied on locally available rocks, while the Bronze Age introduced the smelting and casting of metals, marking the inception of reshaping native metals for tools and weapons. The 4th millennium BC witnessed the first production of alloy bronze, contributing to the gradual evolution of the world as we know it today.

A significant milestone emerged with the advent of quantum mechanics, initially applied to understand atoms and later extended to comprehend crystalline compounds. This understanding of the electronic properties of solids directly led to the development of transistors in 1947. The subsequent introduction of junction transistors, replacing vacuum tubes, heralded the microchip revolution. In 1953, Morris Tanenbaum at Bell Laboratories successfully utilized Silicon as a transistor material, subsequently dominating the semiconductor industry and defining the current era as the Silicon Age.

In 1965, Gordon E. Moore, Intel's co-founder, predicted that the number of transistors in a dense integrated circuit would double approximately every two years—a foresight that held true for over 45 years and became known as "Moore's Law." However, Moore's Law is now encountering challenges [7]. As devices shrink in size, approaching the quantum regime, new issues such as tunneling effects need attention. Consequently, researchers and manufacturers are actively seeking novel materials to address these challenges and enhance device functionality.

1.2 Spintronics

Conventional electronics, which primarily rely on silicon-based integrated circuits, have been highly successful in powering modern technology. However, they do have some drawbacks like high power consumption due to Joule's heating, large size, speed limitations, vulnerability to external factors, and limited functionality integration. Electrons possess also spin degrees of freedom (DOF), but traditionally, charges and spins have been treated independently. In conventional electronics, electric fields manipulate charges while spins are disregarded. Spintronics constitutes a multidisciplinary field dedicated to actively controlling spin DOF in materials [8, 9]. In this context, "spin" refers to either the individual electron's spin (s), detectable through its magnetic moment or the net magnetization generated by the group of electrons. Manipulating spin involves controlling the population and phase of spin or performing spin operations on a single or a few-spin system. The overarching goal of spintronics is to comprehend the interplay between particle spin and crystal potential, ultimately leveraging this understanding to fabricate functional devices. Such a broader definition of spintronics leads to a wide array of subjects. On one end of the spectrum, researchers investigate the manipulation of individual localized spins found on singular atomic sites within crystals, such as NV centers in diamond or semiconductor quantum dots. These entities are recognized as spin qubits, offering potential for solid-state quantum computation. On the opposite end, researchers delve into the study of spin transport and dynamics in large-scale systems, exploring diverse connections between spin transport and spin dynamics.

The quest for effective methods to polarize a spin system is central to spintronics investigations. Spin current in nonmagnetic (NM) materials can be generated through numerous techniques, including spin injection through a ferromagnetic (FM) source, introduction to a magnetic field, electric field, and electromagnetic waves, Zeeman band splitting, spin motive force, thermal gradient, and mechanical rotation (see Figure 1.1). A widely employed approach involves spin injection from half-metallic and metallic FM materials through the ohmic contacts or tunneling the barriers. Electromagnetic waves, including circularly polarized light, can excite spin-polarized electrons in superconductors based on selection rules. Conversely, this phenomenon results in circularly polarized light emission with a spin-polarized electron current. Moreover, spin generation through electromagnetic waves, such as spin pumping and high-frequency spin induction, extends these capabilities. Additionally, a thermal gradient has

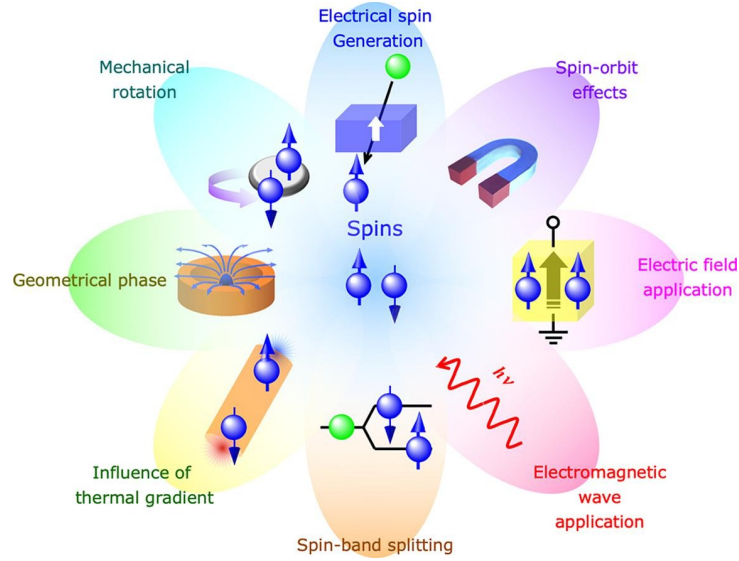


Figure 1.1: Graphical abstract for spins and related effects. This Figure is taken from Ref. [1].

been identified as a means to produce spin-polarized carrier flow through the spin Seebeck and Nernst effects, offering potential applications in energy harvesting.

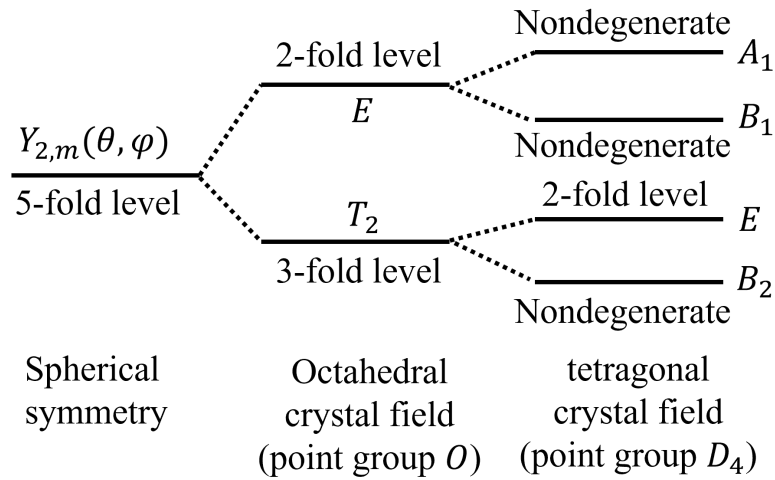


Figure 1.2: Splitting of d orbitals under octahedral and tetragonal crystal fields.

1.3 Symmetries in condensed matter

Symmetry operations play an crucial role in governing the splitting of atomic energy bands in crystals. This can be understood from the simplest case, i.e., an atom with angular momentum $l = 2$ in a crystalline field. Without any crystal field (under spherical symmetry), the d orbitals are five-fold degenerate [see Fig. 1.2]. If a atom is positioned in a cubic crystal (octa-

hedral symmetry), the five-fold degenerate levels split into two-fold degenerate and three-fold degenerate energy levels. If the symmetry is further reduced, i.e., by applying strain to reduce octahedral symmetry to tetragonal symmetry, the energy levels further split into three nondegenerate energy levels and a two-fold degenerate energy level. Thus, transformations of orbitals under symmetry operations play a crucial role in determining the energy degeneracy. Note that symmetry operations and group theory can only provide a qualitative picture of energy levels and energy degeneracy; however, it is insufficient in determining actual positions.

Periodic potentials exhibit translation symmetry, i.e., $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$, where $\mathbf{R}_n$ denotes an arbitrary lattice translation vector. Therefore, the electronic wavefunctions $\Psi_{\mathbf{k}}(\mathbf{r})$ (also known as Bloch functions) transform following the irreducible representation labeled by $\mathbf{k}$ in the translation group. $\Psi_{\mathbf{k}}(\mathbf{r})$ follows the transformation $\hat{T}_{\boldsymbol{\tau}}\Psi_{\mathbf{k}}(\mathbf{r}) = \Psi_{\mathbf{k}}(\mathbf{r} + \boldsymbol{\tau}) = e^{i\mathbf{k}\cdot\boldsymbol{\tau}}\Psi_{\mathbf{k}}$, where $\hat{T}_{\boldsymbol{\tau}}$ represents the translation in real space by the vector $\boldsymbol{\tau}$. Here, $\mathbf{k}$ denotes the crystal momentum, and the continuous energy eigenvalues $E_n(\mathbf{k})$ are generally referred to as the energy bands.

1.4 Spin splittings

The energy bands with momentum-dependent spin splitting are crucial for designing spintronics applications, specifically charge-to-spin conversion [10, 11]. While nonmagnetic solids, without a magnetic field, typically exhibit degenerate electron energy bands with up and down spins. Systems breaking spatial inversion symmetry introduce spin-orbit coupling (SOC). SOC generates spin-orbit field [$\Omega(\mathbf{k}) \propto \mathbf{E} \times \mathbf{k}$], where electric field ($\mathbf{E}$) is induced by the inversion asymmetry [12]. This SOF couples with the spin degree of freedom ($\boldsymbol{\sigma}$), leading to $\mathbf{k}$ -dependent spin splitting at generic $\mathbf{k}$, even without a magnetic field. Dresselhaus demonstrated that in acentric nonpolar crystals, SOC induces cubic (in k^3) spin-splitting [13], while Rashba elucidated terms linear in $\mathbf{k}$ in crystals with a polar axis [14] [see Figs. 1.3(a) and 1.3(b)]. Addressing a surface exposed to a vertical electric field $E = E_z\hat{z}$, the Rashba-SOC can be expressed as [15, 16]

$$H_R = \alpha_R(\boldsymbol{\sigma} \times \mathbf{k}) \cdot \hat{z} = \alpha_R(\sigma_x k_y - \sigma_y k_x). \quad (1.1)$$

Linear splitting in k can also be observed in nonpolar structures, belonging to gyrotropic point groups like D_{2d} , wherein the spin-momentum locking is described by the linear Dresselhaus

SOC [17] [see also Figs. 1.3(c)]

$$H_D = \alpha_D(\sigma_x k_x - \sigma_y k_y). \quad (1.2)$$

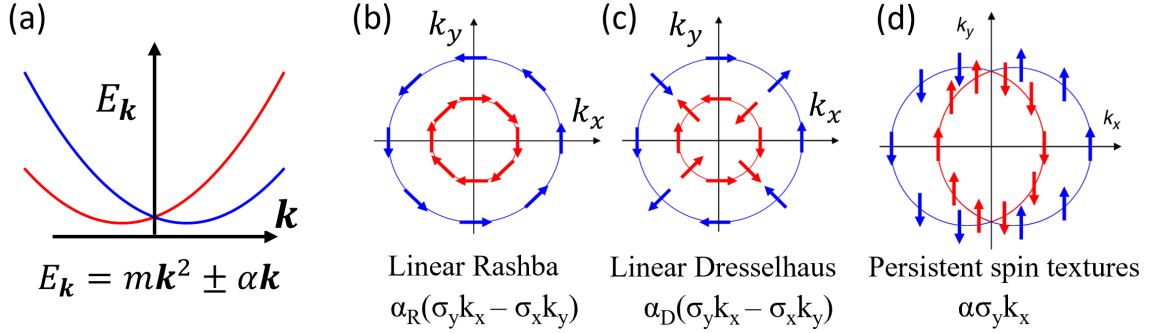


Figure 1.3: (a) Linearly dispersed bands and associated spin configurations in momentum space for (b) linear Rashba, (c) linear Dresselhaus, and (d) persistent spin texture cases.

The momentum-dependent spin splittings are well explained by linear Rashba (LR), linear Dresselhaus (LD) or some unique combination of LR and LD [18, 19, 20, 21, 22, 23]. In linear spin splitting including LR or LD, energy bands are dispersed with $\mathbf{k}$ having the relation $E_k = \alpha \mathbf{k}^2 \pm \tau \mathbf{k}$, where α and τ are the effective mass and linear splitting terms, respectively. However, SOF leads to Elliott-Yafet and Dyakonov-Perel spin-dephasing mechanism, limiting the experimental realization of spin currents. The persistent spin texture (PST), where spin configurations become independent of the crystal momentum ($\mathbf{k}$), overcome spin dephasing and provides dissipationless transport [21, 24, 25, 26, 27]. In the regime of linear splitting, PST can be obtained by tuning the strength of LR and LD effects, such that they compensate each other ($\alpha_R = \alpha_D$). In addition, PST with linear spin splitting can also be enforced by nonsymmorphic space group symmetry of the crystal and, therefore, not easily broken [21]. In recent times, cubic Rashba (CR) and cubic Dresselhaus (CD) effects have started to gain scrutiny owing to their unique benefits to spin transport like larger spin Hall conductivity as compared to linear spin splitting effects [28, 29, 30, 31, 32, 33, 34]. The purely cubic effects (CR or CD) can be distinguished from linear effects (LR or LD) by dispersion curve $E_k = \alpha \mathbf{k}^2 \pm \eta \mathbf{k}^3$. The CR and CD effects are described by the SOC Hamiltonians given by, $H_{CR} = (k_x - ik_y)^3(\sigma_x + i\sigma_y) - (k_x + ik_y)^3(\sigma_x - i\sigma_y)$ and $H_{CD} = (k_x k_z^2 - k_x k_y^2)\sigma_x + (k_y k_x^2 - k_y k_z^2)\sigma_y + (k_z k_y^2 - k_z k_x^2)\sigma_z$, respectively. The crucial experimental discoveries related to CR contain SrTiO₃(001) surface [29], asymmetric oxide heterostructure LaAlO₃/SrTiO₃/LaAlO₃ [32], strained-Ge/SiGe quantum well [28] and surfaces of antiferromagnets GdIr₂Si₂ and TbRh₂Si₂ [35, 36].

1.5 Spin-valley coupling

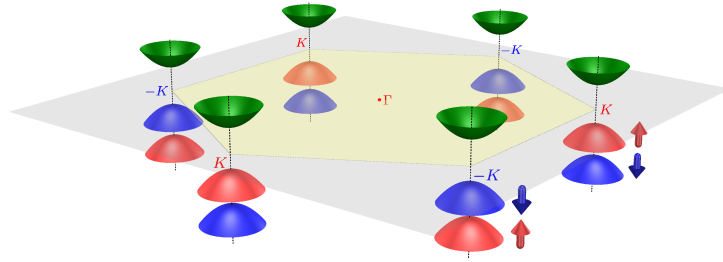


Figure 1.4: Schematic illustration of spin-valley coupling in 2D hexagonal materials. The spin polarization at the time-reversal conjugate points K and K' is opposite in nature.

The presence of well-separated multiple energy extremal points in momentum-space, generally referred to as valleys, constitutes a binary index for low energy carriers [37]. Valleytronics is an emerging field of study within condensed matter physics and electronics that explores the unique electronic properties associated with the manipulation of electron valleys in materials. In analogy to electron spintronics, which exploits the intrinsic spin of electrons, valleytronics harnesses the valley degree of freedom in materials with multiple equivalent energy valleys in their electronic band structure. Valley index is robust to the scattering by smooth deformations and long-wavelength phonons. One of the key features of valleytronics is to selectively populate or depopulate these valleys using external fields, such as electric or magnetic fields. This manipulation can be achieved through a variety of mechanisms, including the quantum-confined Stark effect and the valley Zeeman effect. Moreover, the valley index can serve as a binary information carrier, analogous to the spin in spintronics.

The 2D materials have potential for realizing physical properties desirable in spintronics and valleytronics [38, 39]. Inversion and TRS together force the double degeneracy throughout the Brillouin zone (BZ). The coupling of inversion symmetry breaking with SOC lifts the band degeneracy mainly through Rashba and Dresselhaus effects. However, if TRS breaks along with inversion symmetry breaking, the spin-valley effects are induced [see Fig. 1.4]. Therefore, it can be exploited for information processing and encoding. The lifting of band degeneracy results in non-trivial momentum-dependent spin textures, which are mainly governed by the type of splitting. Analogous to charge, utilizing the spin and valley DOF through the non-dissipative spin transport is a vital ingredient of spintronics and valleytronics.

Several intriguing phenomena are experimentally accomplished, such as the valley Hall

effect [40, 41, 42, 43], valley excitons [44, 45], valley Zeeman and AC Stark effects [46]. The valley effects are experimentally and theoretically observed in graphene and transition metal dichalcogenides. For a long period, monolayer MoS₂ has been regarded as a promising material for the valleytronic applications. However, the limited growth size and low carrier mobility of MoS₂ hinder their potential applications. Undoubtedly, centimeter-scale monolayer MoSi₂N₄ family of septuple layered materials is emerged as an alternative to monolayer MoS₂ owing to its advantages in practical applications. Monolayer MoSi₂N₄ have excellent ambient stability, large synthesis size (upto 15mm×15mm) [47]. The monolayer MoSi₂N₄ has pair of Dirac valleys at corners of the BZ connected through TRS and constitutes a binary index for low energy carriers [48, 49, 50, 51, 52, 53]. The breaking of inversion symmetry and high SOC leads to valley contrasting features in the spin splitting, berry curvatures, and optical circular dichroism [50]. Thus, valley polarization can be controlled by optical, transport, and magnetic interactions. Theoretical calculations predict the high electron/hole mobility up to 270/1200 cm²V⁻¹s⁻¹ for monolayer MoSi₂N₄, which is nearly six times larger than that of monolayer MoS₂ predicted [47]. The excellent stability, carrier mobility, suitable band gap, and protection of capped SiN layer from environmental disturbance promise an advantage over MoS₂ in valley transport properties, especially valley filtering, valley Hall effect, and valley-coupled spin Hall effect [47, 55].

The potential advantages of valleytronics lie in its ability to complement and enhance existing electronic technologies. Valleytronics may offer new avenues for faster and more energy-efficient information processing, as well as improved quantum computing capabilities. Ongoing research in this field focuses on understanding the fundamental physics of valley-dependent processes, exploring new materials, and developing practical valleytronic devices for future technological applications.

1.6 Nonrelativistic spin-moment coupling in antiferromagnets

SOC induced Rashba-Dresselhaus [13, 56, 15, 57] in nonmagnetic and Zeeman effects in ferromagnetic (FM) materials create spin splittings under certain crystalline (i.e., inversion [$\hat{P}$]) and TRS ($\hat{T}$) breaking [58], respectively. SOC-induced spin splitting and resulting spin polarization engender spin-orbit torques [59, 8]. However, the SOC effect introduces spin dephasing mech-

anisms, limiting the practical application. Four significant mechanisms identified in metals and semiconductors are Elliott-Yafet [60, 61], D'yakonov-Perel' [62], Bir-Aronov-Pikus [63], and hyperfine interaction mechanisms. In the Elliott-Yafet process, the spins undergo relaxation because the electron wavefunctions associated with a specific spin contain a mixture of opposite-spin states and SOC leads to spin relaxation by coupling spin-up and spin-down states. The D'yakonov-Perel' mechanism elucidates spin dephasing in materials lacking a center of symmetry. Spin dephasing results from an effective magnetic field experienced by electrons, arising from the absence of inversion symmetry and SOC, which changes direction randomly upon electron scattering to different momentum states. In addition, materials with heavy elements having significant SOC imparts additional challenges, including scarcity, toxicity, and instability. For example, SOC increases with increasing atomic number ($\sim Z^4$), however bond strength decreases with increasing atomic number resulting into instabilities. Therefore, SOC-independent spin splitting is an important avenue to pursue.

In 1964, Pekar and Rashba proposed a phenomenological theory regarding magnetic spin splitting [64]. Their proposal suggested that the existence of a spatially varying intrinsic magnetic field, denoted as $\mathbf{h}(\mathbf{r})$, which exhibits periodicity corresponding to the crystal period in magnetic compounds, couples with $\boldsymbol{\sigma}$. This leads to the SOC-like coupling with nonrelativistic origin [$H \sim \boldsymbol{\sigma} \cdot \mathbf{h}(\mathbf{r})$]. Consequently, this coupling could give rise to a magnetically-driven $\mathbf{k}$ -dependent spin splitting even without SOC. Therefore, SOC-independent spin splittings can be seen in the ferromagnetic and antiferromagnetic materials. Ferromagnetic materials have undergone extensive investigation and have been extensively utilized in the field of spintronics for many years [65, 66, 67, 68]. These materials possess inherent capabilities to facilitate spin-polarized currents through controllable spin splittings, which are essential for various transport phenomena like giant magnetoresistance (GMR) [69] and spin-transfer torque (STT) [70] in magnetic tunnel junctions. These phenomena play an important part in the electrical writing and reading of magnetic state. [68].

Antiferromagnets have recently emerged as a viable substitute for nonmagnetic and ferromagnetic materials in spintronic applications [71, 72, 2, 73, 74]. Because of their resilience against magnetic disruptions, absence of stray fields, and ability to exhibit exceptionally rapid spin dynamics, antiferromagnets possess the potential to outperform ferromagnets. Recent research focused on investigating spin splittings within various magnetic space groups, encompassing antiferromagnets [75, 76]. $\hat{P}\hat{T}$ and $\hat{U}$ symmetries combined with $\hat{\tau}$ may trans-

Magnetic structure	Spin splitting prototype (SST)	Main feature	Symmetry conditions			Consequences of symmetry conditions on SS at generic k	
			Is θIT in MSG?	MSG type	Is the crystal CS or NCS?	When SOC is off	When SOC is on
AFM	SST-1	AFM, No spin splitting	Yes	III	CS	No	No
	SST-2	AFM, No spin splitting	Yes	IV	CS	No	No
	SST-3A	SOC-induced (AFM as background)	No	IV	CS	No	Yes
	SST-3B		No	IV	NCS		
	SST-4A	AFM-induced	No	I/III	CS	Yes	Yes
	SST-4B		No	I/III	NCS		
FM	SST-5	Zeeman effect	No	I/III	Either	Yes	Yes
NM	SST-6	NM, No spin splitting	Yes	II	CS	No	No
	SST-7	Rashba and Dresselhaus effect	No	II	NCS	No	Yes

Figure 1.5: This Figure is taken from Ref. [2] © Copyright 2021 American Physical Society. Classification of spin splittings prototypes (SSTs) based on the magnetic ordering and present symmetries. Here, θ , I , and T represent time-reversal, inversion and translation operation, respectively. Note that the notation we followed may differ from the one used in this Figure and will be specified whenever required.

form spin-up eigenstate to spin-down eigenstate, enforcing spin degeneracy throughout the BZ. Therefore, numerous efforts have been undertaken to investigate spin splittings in AFM materials by breaking combined $\hat{P}\hat{T}\hat{\tau}$ and/or $\hat{U}\hat{\tau}$ symmetries, where $\hat{U}$ and $\hat{\tau}$ are spinor and translation symmetry, respectively [77, 78, 79, 2, 80, 81, 75]. L. D. Yuan *et al.* [2] classified the spin splittings in different prototypes depending on the magnetic order, presents symmetries within, spin splittings will be present with or without SOC [see Fig. 1.5]. Centrosymmetric (in four-dimensional spacetime) antiferromagnetic (AFM) semiconductors [SST-1 and SST-2 in Fig. 1.5], which lack polarization and magnetization, pose challenges in generating substantial and controllable spin splitting using magnetic or electric fields [82, 83, 84]. As a result, despite their abundance in nature, centrosymmetric AFM semiconductors do not appear promising for practical applications in spintronics.

1.7 Motivation of this thesis

This thesis mainly consists of understanding spin splitting and, consequently, their spin polarization. We have thoroughly studied the role of symmetries, i.e., point group and space group symmetry, in perovskite and perovskite-inspired materials. First, within the framework of state-of-the-art density functional theory and symmetry analysis, we have studied the stability of various perovskites with different space groups. All the calculations are validated in the best possible way, ensuring that the findings are not just an artifact of the choice of functional. After that, we analyzed the electronic structure regarding spin splitting and textures. Following this, we qualitatively verified the strength and nature of spin splittings using a symmetry-adapted model Hamiltonian. After that, we obtained the mechanism to tune spin splitting in perovskites using biaxial strain. Finally, we have shown that these spin textures can be reversed by changing the polarization direction.

On the other hand, spin splittings of higher order are promising for spin transport. In addition, persistent spin textures associated with spin splittings provide a route to nondephasing spin transport. Therefore, based on the symmetry operation, we have performed high-throughput screening of hexagonal materials with persistent spin textures with cubic order. Symmetry-enforced PSTs sustain over a larger part of the BZ, i.e., the full plane in bulk materials and the full BZ in 2D materials. We find a large class of experimentally synthesized bulk materials having D_{3h} and C_{3h} point symmetries hosting full-plane persistent spin textures. Furthermore, we have shown that it is actually local site symmetries (not global symmetry) that determine the spin polarization associated with the states segregated on these specific sites. Furthermore, we have understood the coupling of spin DOF with other DOF associated with the electron, i.e., valley, orbital, layer, and sublattice. We have understood the role reduced symmetry plays in coupled spin-valley physics in septuple-layered 2D materials, including MoSi_2N_4 and WSi_2N_4 . We have applied an external electrical field and uniaxial strain to modulate the spin-valley physics.

In addition, we have also introduced SOC-independent spin-splitting in $\hat{P}\hat{T}$ -symmetric AFM 2D materials by following two ways: (i) a global $\hat{P}\hat{T}$ -symmetric layer with asymmetric site symmetries and (ii) two layers with a relative twist in between. Mechanisms introduced here generated Zeeman-type and Rashba-Dresselhaus-type spin splittings even without SOC. These AFM-induced spin splittings support nondephasing spin transport in materials, even with

low-Z elements.

1.8 Organization of this thesis

The organization of proposed thesis in the form of different chapters is discussed below:

Chapter 2: In this chapter, we discuss the methods used to obtain electronic structures of materials. A brief overview of first-principles-based DFT and first-order $k.p$ perturbation theory is presented here. Readers are encouraged to Refer [115, 5, 223] for more detailed discussion.

Chapter 3: In this chapter, we have explored the Rashba and Dresselhaus effects in perovskites and perovskites-inspired materials. We have discussed R3m and R3c phases of FE oxide KIO_3 and $Cmc2_1$ and $Cmcm$ phases of $\text{Sn}_2\text{SbX}_2\text{I}_3$ ($X = \text{S, Se}$) for potential spintronics applications. Firstly, we have determined the FE polarization in both phases. Subsequently, the crucial contribution of SOC has been shown in the band structures. The Rashba spin splitting energy and offset momentum have been determined from the splitting at the VBM and CBM. Furthermore, plotting the spin texture has characterized the splitting type. The Rashba and Dresselhaus parameters are determined after fitting the $k.p$ model Hamiltonian to the DFT band structure. Finally, the effect of polarization on the parameters mentioned above has been investigated. The Chapter 3 is adapted from the published work of the author in Refs. [85, 86].

Chapter 4: In this chapter, using DFT calculations, duly supplemented with the effective model Hamiltonian obtained from the symmetry invariants method, we reveal the PCS in a large family of materials with D_{3h} point-group symmetry. The in-plane mirror and threefold rotation symmetry lead to the PCS around Γ and A points in the BZ. In addition, the PSTs are observed in a larger region and preserved in whole Γ -M-K plane. More importantly, $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ manifests large spin splitting of conduction bands around the Γ , M, and A points. The spin splitting can be further tuned with the application of uniaxial strain preserving the full-plane PST. Additionally, we have also shown that the 2D materials with D_{3h} point group exhibit persistent spin textures in the full BZ. By taking the example of WSi_2N_4 2D materials, we observe full-zone persistent spin texture (FZPST) protected by in-plane mirror symmetry. In addition to spin-valley locked splitting at the corners of BZ, we observe cubic splitting around the center of the BZ. Significant splitting around the M point is linear in k , which is found to be comple-

mentary to the linear Rashba and Dresselhaus effects. It is a well-known fact that SIS hinders the conventional linear Rashba spin splitting, which is later observed under the application of an vertical electric field. The $\mathbf{k}\cdot\mathbf{p}$ analysis shows that persistent spin textures along the M-K path are robust to external electric fields. It is generally expected that the inversion symmetry in the bulk WSi_2N_4 causes the spin splitting and polarization to vanish. However, our calculations show 100% spin polarization of doubly degenerate bands in centrosymmetric bulk and even layered WSi_2N_4 , which are spatially segregated. We demonstrate that such hidden spin polarization arises from the inversion-asymmetric site point group of the W atom. Thus, the WA_2Z_4 family broadens the horizons of materials in the fields of spintronics and valleytronics. The Chapter 4 discusses the results reported in Refs. [87, 54].

Chapter 5: This chapter demonstrates strain-induced electron and hole valley drifts and their effects in monolayer MoSi_2N_4 . We theoretically apply in-plane lattice deformation up to 10% along three crystallographic nonequivalent directions, i.e., armchair (AC), intermediate (IM), and zigzag (ZZ). The energy valley drifts are responsive to the strain directions. For example, drifts are more pronounced for the strain along ZZ direction than IM and AC directions. Additionally, electron valleys are more sensitive to the deformation when compared to the hole valleys. The group theoretical perspective and microscopic orbital contribution explain the underlying mechanism behind the asymmetric nature of valley drifts. Afterward, we provide the effect of asymmetric valley drifts on Berry curvature distribution and optical circular dichroism.

Additionally, we have investigated the effect of stacking of layers to modulate the electronic properties, focusing on their spintronics and valleytronics aspects. We have taken the unexplored Janus WSiGeZ_4 as an example to study these effects. The valleys show contrasting physics, i.e., spin polarization, optical circular dichroism and Berry curvature. The broken surface inversion symmetry induces Rashba effect at the center of the BZ. The findings imply that symmetry control enhances Berry curvature by more than 300%. Furthermore, Rashba splitting increases significantly by modifying the out-of-plane asymmetry. The underlying mechanism behind the unconventional enhancement is duly investigated through microscopic orbital contribution and macroscopic charge transfer. This method is more effective compared to the strain and electric field, in modulating the Berry curvature and Rashba effect. The high carrier mobilities and tunable electronic properties suggest their great potential in spintronics and valleytronics. This Chapter summarizes the results from published works [88, 89].

Chapter 6: This chapter examines the hidden Zeeman-type spin splitting (HZSS) in $\hat{P}\hat{T}$ -symmetric AFM 2D materials originating from specific local sites asymmetries. We perform symmetry analysis and DFT simulations on prototypical layered MnSe to show that doubly degenerate states with opposite spin polarization are segregated on different sublayers connected through $\hat{P}\hat{T}$ symmetry. The specific states from a single layer are locally Zeeman-split, exhibiting a unique spin-sublayer locking effect. In addition, the mirror plane ($\hat{M}_x$) enforces the spins to be $\mathbf{k}$ -independent. Strikingly, a tiny electric field splits the otherwise doubly degenerate bands, preserving the spin configurations. Switching the electric field can reverse the electronic spin magnetization connected to the energy level splitting.

Additionally, we aim to generate nonrelativistic spin splitting (NRSS) from $\hat{P}\hat{T}$ -symmetric AFM monolayers vdW stacked with a twist angle between the layers. We extensively performed first-principles DFT simulations on twisted bilayer (tb-) MnPSe₃ and MnSe as prototypical candidates. Further calculation demonstrated that Rashba-Dresselhaus (RD) and Zeeman-like momentum-dependent spin splittings arise along certain crystallographic $\mathbf{k}$ -paths. Based on the symmetry analysis, we find that the strengths of RD and Zeeman-like spin splittings are comparable to the conventional SOC-induced counterparts. Moreover, external perturbations (i.e., electric and strain fields) provide exceptional tunability to NRSS in tb-MnPSe₃ and tb-MnSe. The Chapter 6 is based on the published work [90] and the preprint [91].

Chapter 7: This chapter sums up the important conclusions of the present thesis. The future scope of the present work is also suggested in this chapter.

Modeling electronic structure: Density functional and $k.p$ perturbation theory

2.1 Background

Electrons, the elementary subatomic particles, act as “quantum glue” responsible for binding atomic nuclei within matter. A comprehensive comprehension of material behavior hinges significantly on understanding its electronic configuration. Frequently, the initial step in gaining insights into a material’s electronic characteristics involves the computation of its band structure. This task crucially relies on efficiently determining the energy levels of each band in reciprocal space, invariably accomplished through the solution of a ‘Schrödinger-like equation.’ The method and complexity of this process may vary depending on the specific material properties of interest and scalability. In this chapter, we will briefly discuss density functional theory (DFT), a widely utilized and adaptable tool designed for this purpose. At its core, DFT’s fundamental concept involves considering the total particle density as the primary parameter from which various system properties can be computed. The domain of density functional theory is vast and thoroughly established. The ensuing discourse provides only a concise glimpse into the foundational principles of this methodology. For a more comprehensive exploration, I recommend referring to standard textbooks [92, 93].

2.2 Many-body physics: A theoretical framework

The initial step is computing the energies of multi-electron systems subject to various external potentials involves the time-independent Schrödinger equation, which represents the eigenvalue equation for the energy operator. In case of electrons within a solid, the Schrödinger equation are formulated in terms of the many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)$

as

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M), \quad (2.1)$$

where E represents the system's energy and $\hat{H}$ signifies the system's Hamiltonian. The Hamiltonian comprises five distinct components:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}, \quad (2.2)$$

the kinetic energy of the nuclei ($\hat{T}_N$) and the electrons ($\hat{T}_e$), the internal repulsive potential energy among the electrons ($\hat{V}_{ee}$), the potential energy stemming from the electrons' interaction with the nuclei ($\hat{V}_{eN}$), and the potential energy arising from the interaction between nuclei ($\hat{V}_{NN}$). These individual terms can be explicitly expressed as follows:

$$\hat{T}_N = -\sum_{j=1}^N \frac{\hbar^2}{2M_j} \nabla_{\mathbf{R}_j}^2 \quad (2.3)$$

$$\hat{T}_e = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_i}^2 \quad (2.4)$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j \neq i}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.5)$$

$$\hat{V}_{eN} = -\frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1}^N \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} \quad (2.6)$$

$$\hat{V}_{NN} = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (2.7)$$

Here, $\nabla_{\mathbf{R}_i}^2$ represents the Laplacian operator applied to the i^{th} nucleus positioned at $\mathbf{R}_i$, with a mass of M_i and a nuclear charge of Z_i . N corresponds to the overall count of nuclei, while N_e denotes the total number of electrons. Additionally, $\nabla_{\mathbf{r}_i}^2$ stands for the Laplacian operator pertaining to the i^{th} electron located at $\mathbf{r}_i$. Due to the large difference in mass between the nucleus and the electron ($M_z \gg M_e$), we can make the approximation that the nucleus remains stationary when addressing the electronic movement, known as the Born-Oppenheimer approximation. Hence, the wavefunctions for both electrons and nuclei can be separated and represented as follows:

$$\begin{aligned} \Psi_{total} &= \psi_{electronic} \times \psi_{nuclear} \\ \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) &= \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \times \psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \end{aligned} \quad (2.8)$$

The energy components associated with the nuclei, such as the kinetic energy of nuclei and the repulsion energy between nuclei, can be incorporated later, subsequent to solving for the electron-related aspects. Thus, the nuclear and electronic motions can be treated independently, leading to the Hamiltonian for electronic structure theory:

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{V}_{int} \quad (2.9)$$

In atomic units, the kinetic energy operator for electrons ($\hat{T}$) can be expressed as:

$$\hat{T} = - \sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 \quad (2.10)$$

The $\hat{V}_{ext}$ is interaction between electrons and nuclei, and is given by:

$$\hat{V}_{ext} = \sum_{i=1}^{N_e} \sum_{I=1}^N V_I(|\mathbf{r}_i - \mathbf{R}_I|) \quad (2.11)$$

Additionally, the electron-electron interaction, $\hat{V}_{int}$, is defined as:

$$\hat{V}_{int} = \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j \neq i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.12)$$

Even with the Born-Oppenheimer approximation in place, solving the Schrödinger equation with the electronic Hamiltonian remains a challenging task for $3N_e$ variables. Therefore, further approximations are necessary to tackle the Schrödinger equation. Hartree's initial assumption posits that we can represent the many-electron wavefunction in the following manner:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \dots \phi_N(\mathbf{r}_N) \quad (2.13)$$

In this equation, each $\mathbf{r}_i$ encompasses both the spatial coordinates and a spin coordinate for the i^{th} electron, while $\phi_i(\mathbf{r}_j)$ signifies the single-electron spin-orbital. Equation 2.13 implies that the electrons are considered as if they are uncorrelated, behaving independently and interacting solely with the average electron density. This assumption serves as a fundamental basis for subsequent advancements in the methodologies employed to address many-electron systems.

Nonetheless, it's crucial to recognize a significant shortcoming of the Hartree approximation: it does not meet the inherent antisymmetry requirement in electronic wavefunctions. This failure to satisfy the antisymmetry constraint leads to a violation of the Pauli exclusion principle, resulting in an incomplete description of the electronic component. This is precisely where the Hartree-Fock (HF) approximation becomes essential. In the HF, the variational wavefunction assumes the form of a Slater determinant, ensuring strict adherence to the antisymmetry

condition. As a direct consequence, the Pauli exclusion principle is upheld, establishing that two fermions cannot simultaneously occupy the same orbital.

The Slater determinant for N_e orbitals is expressed as follows:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_{N_e}(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_{N_e}(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_{N_e}) & \phi_2(\mathbf{r}_{N_e}) & \cdots & \phi_{N_e}(\mathbf{r}_{N_e}) \end{vmatrix} \quad (2.14)$$

In this representation, $\mathbf{r}_i$ contains both the spatial coordinates and a spin coordinate for the i^{th} electron, while $\phi_i(\mathbf{r}_j)$ denotes the i^{th} single-electron spin orbital. Hartree-Fock takes care of the exact exchange, but it lacks electronic correlation, which is pivotal in processes like bond breaking and formation. Furthermore, there exist many wavefunctions that satisfy the antisymmetric nature but cannot be described by the single Slater determinant form, making them unattainable within the Hartree-Fock approximation. To account for these correlation effects, one must turn to correlated methods that deal with multi-determinant wavefunctions. However, these post-Hartree-Fock methods are computationally intensive, and their demands escalate with the system's size.

Alternatively, density functional theory (DFT) offers a conceptually straightforward and computationally feasible strategy that encompasses both exchange and correlation effects.

2.3 Density functional theory

Within the framework of DFT, the primary focus is on the electron density, a scalar function dependent on position. This approach diverges from the conventional wavefunction approach utilized for solving the Schrödinger equation. The electron density $n(\mathbf{r})$ can be written as

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} \langle \psi | \delta(\mathbf{r} - \mathbf{r}_i) | \psi \rangle = N_e \iint \dots \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})|^2 \delta(\mathbf{r} - \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_{N_e}, \quad (2.15)$$

The $n(\mathbf{r})$ is three-dimensional, i.e., it does not change the dimension on increasing the number of electrons. This facilitates the DFT to be used for a large number of atoms with reasonable computational cost. Therefore, DFT is widely used to tackle the many-electron systems, specifically, atoms, molecules and solids. Therefore, one would like to express energy in term of electron density $n(\mathbf{r})$. Initially models for energy and $n(\mathbf{r})$ relationship were made by

Thomas, Fermi, and Dirac in 1927 to 1930, known as *Thomas-Fermi-Dirac approximation*. This model is insufficient for accurately predicting the electronic structure since it relies on crude approximations and lacks the fundamental physics, specifically the effects of electron correlation. That leads to the foundation of modern density functional theory based on the theorems proposed by the Hohenberg and Kohn in 1964 [94].

2.3.1 Hohenberg-Kohn formalism

Theorem I: “For any system of interacting electrons in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, apart from a trivial additive constant, by the electronic ground-state density $n(\mathbf{r})$.”

Proof: Assuming the existence of two distinct potentials, denoted as $V_{ext}(\mathbf{r})$ and $V'_{ext}(\mathbf{r})$, which yield the same ground-state electron density $n(\mathbf{r})$, and two distinct Hamiltonians, H and H' . Solving the Schrödinger equation yields distinct wavefunctions, Ψ and Ψ' , corresponding to these Hamiltonians. Consequently, the ground-state energies for Ψ and Ψ' are determined as $E = \langle \Psi | H | \Psi \rangle$ and $E' = \langle \Psi' | H' | \Psi' \rangle$. Applying the variational principle to estimate E and E'

$$E < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle = E' + \int n(\mathbf{r}) [V_{ext}(\mathbf{r}) - V'_{ext}(\mathbf{r})] d\mathbf{r} \quad (2.16)$$

$$E' < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H | \Psi \rangle + \langle \Psi | H' - H | \Psi \rangle = E + \int n(\mathbf{r}) [V'_{ext}(\mathbf{r}) - V_{ext}(\mathbf{r})] d\mathbf{r} \quad (2.17)$$

Summing up Equations 2.16 and 2.17 leads to:

$$E + E' < E + E' \quad (2.18)$$

This inequality is self-contradictory, thereby disproving our initial assumption, and establishing that the ground-state density uniquely determines the potential.

This analysis primarily considers the non-degenerate case, but the proof of the Hohenberg-Kohn (HK) theorem can be extended to the degenerate case as well (Martin, 2004).

Theorem II: “A universal energy functional $E[n]$ using density $n(\mathbf{r})$ can be defined, valid for any number of particles and any external potential $V_{ext}(\mathbf{r})$. For a given potential $V_{ext}(\mathbf{r})$, the $E[n]$ equals the correct ground-state energy of the system which is the global minimum value for the correct ground-state density $n(\mathbf{r})$.”

Proof: We confine the space of admissible densities to those that can be represented by a potential, referred to as V-representable. Notably, it is possible to establish these principles

without this constraint, as detailed in Ref [95]. Since any physical properties of a many-electron system are derivable from the $n(\mathbf{r})$, we can express the energy functional as follows:

$$E_{HK}[n] = T[n] + E_{int}[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} = F_{HK}[n] + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (2.19)$$

Here, $F_{HK}[n]$ incorporates the kinetic energy of electrons and electron-electron interaction energy, making it the universal functional of $n(\mathbf{r})$. Given that $V_{ext}(\mathbf{r})$ is contingent on nuclear coordinates, its contribution is system-specific. Now, let's consider the ground-state density of a system as $n_1(\mathbf{r})$, corresponding to potential $V_{ext}^1(\mathbf{r})$. The energy is then computed as the expectation value of the Hamiltonian

$$E_1 = E_{HK}[n_1] = \langle \Psi_1 | H | \Psi_1 \rangle \quad (2.20)$$

Where Ψ_1 being the ground state wavefunction. Let us assume an alternative wavefunction Ψ_2 with different density $n_2(\mathbf{r})$, the variational principle tells us:

$$E_1 = E_{HK}[n_1] = \langle \Psi_1 | H | \Psi_1 \rangle < \langle \Psi_2 | H | \Psi_2 \rangle = E_{HK}[n_2] = E_2 \quad (2.21)$$

Hence, the HK functional, derived from the true ground-state density, yields the lowest energy when compared to any other arbitrary density. This implies that if we know the functional of the density, we can determine the energy and density of ground state through minimizing it concerning variations in the density. Importantly, this functional exclusively provides access to the ground state, offering no insight into excited states.

While these theorems establish the existence of a universal functional $F_{HK}[n]$, they do not specify how to ascertain it. The Kohn-Sham (KS) equations, however, offer a practical framework for solving many-electron systems.

2.3.2 Kohn-Sham ansatz

Minimizing the energy functional can be challenging in actual systems. Kohn and Sham [96] introduced an efficient DFT calculation method, mapping the interacting real system to a fictitious non-interacting system where electrons respond to an effective single-particle potential, $V_{KS}(\mathbf{r})$. A schematic illustration of the same is shown in Figure 2.1. The auxiliary Hamiltonian consists of standard kinetic energy operator and a localized potential, $V_{eff}^\sigma(\mathbf{r})$, acting on the electron with spin σ at position $\mathbf{r}$:

$$\hat{H}_{aux}^\sigma = -\frac{1}{2}\nabla^2 + V_{eff}^\sigma(\mathbf{r}) \quad (2.22)$$

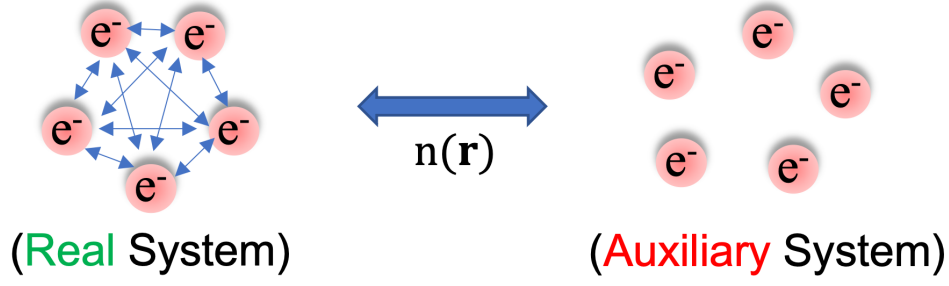


Figure 2.1: The mapping of interacting system's to a auxiliary non-interacting system with the same ground-state electron density.

Here, $\psi_i^\sigma(\mathbf{r})$ represents the eigenstates (known as KS orbitals) with the lowest eigenvalues ε_i^σ derived from this Hamiltonian. The density of this fictitious system is expressed as:

$$n(\mathbf{r}) = \sum_{\sigma} n(\mathbf{r}, \sigma) = \sum_{\sigma} \sum_{i=1}^{N\sigma} |\psi_i^\sigma(\mathbf{r})|^2 \quad (2.23)$$

The kinetic energy, denoted as T_s , for this independent-electron auxiliary system, is given as a functional of the KS orbitals:

$$T_s = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N\sigma} \int |\nabla \psi_i^\sigma(\mathbf{r})|^2 d\mathbf{r} \quad (2.24)$$

The classical Coulomb interaction energy of the electron density $n(\mathbf{r})$ interacting with itself is represented as:

$$E_{Hartree}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2.25)$$

Consequently, the total energy in the KS formulation is

$$E_{KS}[n] = T_s[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{Hartree}[n] + E_{xc}[n] \quad (2.26)$$

In this equation, all many-body interactions related are encapsulated within the E_{xc} , which is expressed as

$$E_{xc}[n] = F_{HK}[n] - (T_s[n] + E_{Hartree}[n]) \quad (2.27)$$

Or

$$E_{xc}[n] = \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{int} \rangle - E_{Hartree}[n]. \quad (2.28)$$

Here, $\langle \hat{T} \rangle$ is the kinetic energy, and $\langle \hat{V}_{int} \rangle$ is the internal interaction energy of the original many-body interacting system. $E_{xc}[n]$ is responsible for the binding of atoms into molecules and solids. Consequently, the KS equations can be formulated as:

$$H_{KS}^\sigma \psi_i^\sigma(\mathbf{r}) = \varepsilon_i^\sigma \psi_i^\sigma(\mathbf{r}) \quad (2.29)$$

Where

$$H_{KS}^{\sigma}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{KS}^{\sigma}(\mathbf{r}) \quad (2.30)$$

And

$$V_{KS}^{\sigma}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^{\sigma}(\mathbf{r}) \quad (2.31)$$

These equations are solved self-consistently, as depicted in Figure 2.2. However, the precise functional dependence of $E_{xc}[n]$ on the density n remains unknown and certain approximations are utilized.

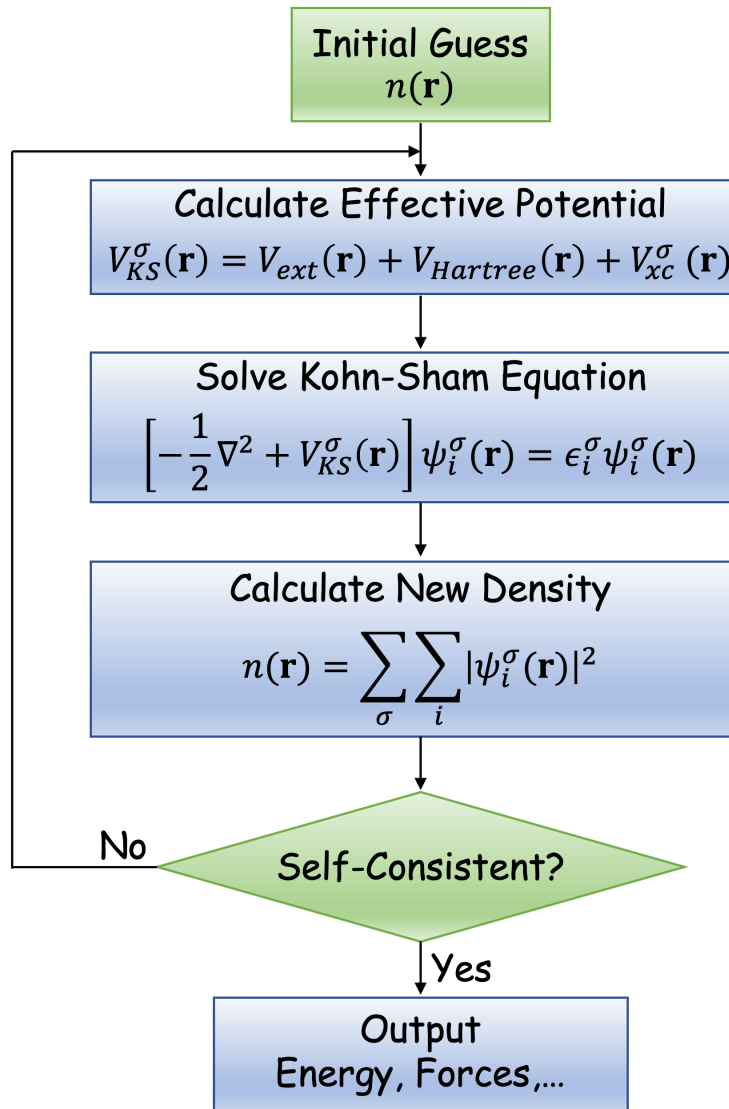


Figure 2.2: Self-consistent scheme to solve the KS equations.

2.3.3 Exchange and correlation Energy

Since the precise form of $E_{xc}[n]$ remains unknown, approximations are necessary for practical calculations. As exchange and correlation energy, $E_{xc}[n]$, is inherently non-local, we introduce $\varepsilon_{xc}([n], \mathbf{r})$ as the E_{xc} per electron, assuming a degree of locality. The most commonly used approximation in this context is the local-density approximation (LDA) [97]. Within the LDA, $E_{xc}[n]$ can be written as

$$E_{xc}^{LDA}[n] = \int d\mathbf{r} \varepsilon_{xc}^{LDA}(n(\mathbf{r}))n(\mathbf{r}) \quad (2.32)$$

We can further break down the $\varepsilon_{xc}[n]$ into distinct exchange and correlation energies, denoted as $\varepsilon_x[n]$ and $\varepsilon_c[n]$, respectively

$$\varepsilon_{xc}[n] = \varepsilon_x^{LDA}[n] + \varepsilon_c^{LDA}[n] \quad (2.33)$$

Within the LDA, the exchange part is analytically known, as we treat KS electrons as free electrons in a uniform positive background. It can be derived as follows:

$$\varepsilon_x^{LDA}[n] = -e^2 \left(\frac{3n(\mathbf{r})}{\pi} \right)^{1/3} \quad (2.34)$$

While the correlation part lacks an exact known form, precise Quantum Monte Carlo calculations conducted by Ceperley and Alder have been parameterized by multiple researchers and are now integrated into the majority of DFT software packages.

Alternative approximations for the $E_{xc}[n]$ could be better suited for different materials and type of information. One such used approximation is the Generalized Gradient Approximation (GGA) [98]. GGA posits that the $E_{xc}([n], \mathbf{r})$ is influenced gradient of electronic density $\nabla n(\mathbf{r})$ in addition to $n(\mathbf{r})$. Analytically, we can say that

$$E_{xc}^{GGA}[n] = \int d\mathbf{r} \varepsilon_{xc}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)n(\mathbf{r}) \quad (2.35)$$

In 1968, Ma and Bruekner introduced the gradient expansion (GE) [99]

$$E_{xc}^{GE}[n] = \int n(\mathbf{r}) \varepsilon_{xc}^{unif}(n(\mathbf{r}))d\mathbf{r} + \int B_{xc}[n] \frac{|\nabla n|^2}{n^{4/3}} d\mathbf{r}. \quad (2.36)$$

In this expression, the coefficient $B_{xc}[n]$ is determined through an approximate calculation. $B_{xc}[n]$ consists of an exchange component that is independent of the electron density n and a correlation component that has a weak dependence on n . While the GE is exact for slowly changing electron densities up to order $|\nabla n|^2$, it exhibits significant inaccuracies when applied

to real systems composed of atoms. This is primarily due to the substantial errors in the correlation part for real systems. Consequently, the gradient expansion needs to be applied more cautiously while preserving all relevant contributions to the desired order and adhering to the essential constraints dictated by exchange and correlation holes.

To address these limitations, modified versions of the gradient expansion, known as generalized gradient approximations (GGAs), have been developed. One notable GGA, introduced by Perdew, Burke, and Ernzerhof (PBE) in 1996 [100], is particularly well-regarded. In the PBE GGA, all parameters are derived from fundamental constants and it has gained widespread acceptance. Binding energies and bond lengths of atoms are improved by GGA over LDA. Also, the bond lengths are improved. The GGA has certain limitations in the accuracy because non-local effect of exchange term is not taken into account completely, and self-interaction error is not fully recovered.

The concept of hybrid functionals was introduced by Becke in 1993 [101]. It involves blending a fraction of exact exchange (Hartree-Fock exchange, denoted as HF exchange) with exchange and correlation from generalized gradient approximation (GGA). The hybrid functional's mathematical representation is as follows:

$$E_{xc}^{hyb} = \alpha E_x^{HF} + (1 - \alpha) E_x^{GGA} + E_c^{GGA}, \quad (2.37)$$

where the coefficient α can either be empirically determined or theoretically estimated. Hybrid functionals are known for their high level of accuracy and their ability to account for non-local effects. However, computationally evaluating the HF exchange, particularly for extended systems, can be a challenging task.

2.3.4 Spin-Polarized DFT

Although the preceding discussion of DFT is applicable to nonmagnetic systems, an expansion of the approach is necessary to accommodate complex magnetic structures. In this regard, the magnetization density is represented by $\mathbf{m}(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$, where $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$ denote the electron densities for different spin components. The $\mathbf{m}(\mathbf{r})$ is the addition variable other than $n(\mathbf{r})$ to be obtained using the self-consistent method using HK theorem [102]. Consequently, the variational method can be generalized to the spin-polarized scenario as follows:

$$E[n(\mathbf{r}), \mathbf{m}(\mathbf{r})] \geq E[n_0(\mathbf{r}), \mathbf{m}_0(\mathbf{r})] \quad (2.38)$$

The KS orbitals now adopt the structure of two-component Pauli spinors to the spin-polarized scenario as follows:

$$\psi_i(\mathbf{r}) = \begin{pmatrix} \psi_i^\uparrow(\mathbf{r}) \\ \psi_i^\downarrow(\mathbf{r}) \end{pmatrix} \quad (2.39)$$

The electron and magnetization density are expressed as

$$n(\mathbf{r}) = \sum_i^{N_e} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \quad (2.40)$$

$$\mathbf{m}(\mathbf{r}) = \sum_i^{N_e} \psi_i^*(\mathbf{r}) \boldsymbol{\sigma} \psi_i(\mathbf{r}) \quad (2.41)$$

with $\boldsymbol{\sigma}$ being the Pauli matrices vector. Similar to the nonmagnetic scenario, the application of the variational principle leads to KS equations, which now take the form of Schrödinger-Pauli equations as follows:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_i(\mathbf{r}) + V_{KS}(\mathbf{r}) \psi_i(\mathbf{r}) + \boldsymbol{\sigma} \cdot \mathbf{B}_{KS}(\mathbf{r}) \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}). \quad (2.42)$$

Here, $V_{KS}(\mathbf{r})$ is the effective potential, which includes the already familiar term from Equation 2.29, and an additional effective magnetic field comprising two components appears as:

$$\mathbf{B}_{KS}(\mathbf{r}) = \mathbf{B}_{ext}(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r}). \quad (2.43)$$

The first component represents magnetic field from external source, while the second component is the variation of exchange-correlation energy concerning magnetization density:

$$\mathbf{B}_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r}), \mathbf{m}(\mathbf{r})]}{\delta \mathbf{m}(\mathbf{r})}. \quad (2.44)$$

An alternative yet entirely equivalent approach to describe spin-polarized systems within Density Functional Theory involves the density matrix, which is particularly useful for handling non-collinear magnetism. The density matrix is defined as:

$$\underline{n}(\mathbf{r}) = \frac{1}{2} n(\mathbf{r}) I_2 + \boldsymbol{\sigma} \cdot \mathbf{m}(\mathbf{r}), \quad (2.45)$$

where I_2 represents the (2×2) identity matrix. Similarly, potential are represented as:

$$\underline{V}(\mathbf{r}) = V(\mathbf{r}) I_2 + \mu_B \boldsymbol{\sigma} \cdot \mathbf{B}(\mathbf{r}) \quad (2.46)$$

In the case of collinear magnetism, such as ferromagnetic or antiferromagnetic alignment, the magnetization is oriented along a specific direction, typically chosen as the z -axis without any loss of generality. Consequently, the off-diagonal terms of the potential matrix (as described

in Equation 2.46) become zero, decoupling the two parts in Equation 2.39. This allows the spin-up and spin-down problems to be addressed independently, much like the nonmagnetic scenario, using the potentials $V_{\uparrow} = V + \mu_B B_z$ and $V_{\downarrow} = V - \mu_B B_z$. This approach offers the advantage of significantly reduced computational requirements compared to dealing with non-collinear magnetic configurations.

2.3.5 SOC in DFT

Electrons that move in the proximity of atomic nuclei experience a significant impact due to the steep potential gradient, leading to a high speed. This requires the consideration of relativistic effects to accurately describe their electron's behavior. In the context of relativistic DFT, the KS one-particle Hamiltonian, under the influence of an electromagnetic field, is expressed as follows [103]:

$$H_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - I_4) mc^2 + \frac{e\hbar}{2mc}\boldsymbol{\beta} \cdot \boldsymbol{\Sigma} \cdot \mathbf{B} - eVI_4. \quad (2.47)$$

Here, V signifies the effective Coulomb potential experienced by the electron due to its interactions with both the atomic nuclei and other electrons. The symbols $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ represent the Dirac matrices, defined as:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \boldsymbol{\beta} = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad \boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} \quad (2.48)$$

with $\boldsymbol{\sigma}$ being the Pauli spin matrices. These matrices act on the wavefunction represented by four-component Dirac bispinor

$$\psi_i(\mathbf{r}) = \begin{pmatrix} \phi_i(\mathbf{r}) \\ \chi_i(\mathbf{r}) \end{pmatrix}, \quad (2.49)$$

which consists of both a large and a small component, denoted as $\phi_i(\mathbf{r})$ and $\chi_i(\mathbf{r})$, respectively. $\mathbf{B}$ characterizes an effective magnetic field arising from the exchange interaction among electrons and any potential external fields. e represents the absolute value of the electric charge, $\mathbf{p}$ stands for the momentum operator, and I_2 and I_4 represent the (2×2) and (4×4) identity matrices, respectively. Due to the coupling between the large and small components of the spinor, as indicated in Equation 2.49, solving the relativistic KS equations proves to be significantly more complex compared to the non-relativistic case. However, in situations where the velocity of valence electrons (v) is much smaller than the speed of light (c), i.e., $\frac{v^2}{c^2} \ll 1$, the Dirac operator (as described in Equation 2.47) are expressed into a power series based on $\frac{v^2}{c^2}$. This

results into Pauli operator acting on the larger component of the bispinor and takes the form as

$$\mathcal{H}_{\text{Pauli}} = \frac{\mathbf{p}^2}{2m} - eV + \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \mathbf{B} - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{e\hbar}{8m^2c^2}\boldsymbol{\nabla} \cdot \mathbf{E} + \frac{e\hbar^2}{4m^2c^2}\boldsymbol{\sigma} \cdot (\mathbf{E} \times \mathbf{p}). \quad (2.50)$$

The first two nonrelativistic terms describe kinetic and electrostatic potential energies, respectively. The third term represents the interaction of magnetic moment,

$$\mu = -\frac{e\hbar}{2mc}\boldsymbol{\sigma} = -g\mu_B\mathbf{S}, \quad (2.51)$$

with the effective magnetic field. The fourth and fifth spin-independent terms are scalar-relativistic approximation [104]. Particularly, the fourth term in Equation 2.50 serves as a relativistic correction stemming from kinematic mass enhancement. The fifth term is the Darwin term, coming from the rapid oscillatory motions of the electron on the order of the Compton wavelength ($\lambda_C = \frac{\hbar}{mc}$). As a result, the position operator does not have well-defined eigenfunctions; rather, the electron extends over a length of λ_C and thus exhibits heightened sensitivity to electric fields.

The last term within the Pauli Hamiltonian in Equation 2.50 describes the SOC, H_{SOC} . This term describes the coupling between the electronic spin and the Lorentz-transformed magnetic field (also known as spin-orbit field) induced by the circular orbital motion of the electron. Since this orbital motion is linked to the crystal lattice through the electric potential of the ions, it results in a coupling between the spin space and the crystal lattice, giving rise to magnetocrystalline anisotropy. The contribution of SOC becomes pronounced in the vicinity of the nuclei, where electron's kinetic energy and potential gradient are most significant. When approximating the potential as spherical, $V(\mathbf{r}) \approx V(r)$, the corresponding electric field is expressed as:

$$\mathbf{E}(\mathbf{r}) = -\boldsymbol{\nabla}V(r) = -\frac{dV(r)}{dr}\frac{\mathbf{r}}{r}. \quad (2.52)$$

Incorporating this relationship into the SOC Hamiltonian, specifically the last term of Equation 2.50, results in the following:

$$H_{\text{SOC}} = -\frac{e\hbar^2}{4m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\boldsymbol{\sigma} \cdot (\mathbf{r} \times \mathbf{p}) = \xi(r)\mathbf{L} \cdot \mathbf{S}. \quad (2.53)$$

In this equation, $\mathbf{L}$ signifies the angular momentum operator, while $\xi(r)$ represents the SOC constant as a function of the radial distance (r) from the nucleus's position. In many models, an effective or averaged coupling strength (ξ) suffices. In the context of electron eigenfunctions within a spherical region surrounding the nucleus, the anticipation of the SOC operator's

expected value can be dissected into two components: a matrix element pertaining to position and a (2×2) spin space element. The radial aspect of the position space matrix element, which characterizes the intensity of the SOC, can be approximated based on scalar-relativistic considerations. Assuming a Coulomb potential of the form $V(\mathbf{r}) = -\frac{Ze}{r}$ and non-relativistic radial functions $R_{nl}(\mathbf{r}) \propto r^l$, with l representing the angular momentum quantum number, the SOC constant can be expressed as:

$$\xi_{nl} \propto \frac{Z^3}{a_B n^3 l^2}, \quad (2.54)$$

where a_B is the Bohr radius, Z is the atomic number, and n is the principal quantum number. It is evident that the strength of the SOC exhibits a fourth-order dependence on the atomic number Z . In the case of 3d transition metals (TM) like Mn and Fe, which have relatively low atomic numbers, the SOC constant (ξ_{nl}) typically falls in the range of ~ 50 meV [105].

2.3.6 Basis set

The previous section provided an overview of fundamental concepts in Density Functional Theory (DFT), with a specific focus on the KS equations. These equations serve to simplify the intricate many-body problem by modeling the behavior of non-interacting electrons in an effective potential, thereby transforming it into a more manageable single-particle problem. Here, we will delve into computational approaches for solving these KS equations. Particularly, we will explore the fundamental principles of the projector augmented wave method, which serves as the core of the VASP code. For more comprehensive information regarding these methods and the general solution of KS equations, you can refer to Refs. [106, 107, 108, 109].

In the realm of DFT-based electronic structure methods, categorization is based on how the density, potential, and, most crucially, the KS orbitals are represented. It's essential to make an appropriate choice to strike a balance between computational efficiency and accuracy. Mostly, the KS equations are solved using basis set expansion of single-particle orbitals. These orbitals are expressed as a linear combination:

$$\psi_i(\mathbf{r}) = \sum_{\alpha} c_{i\alpha} \phi_{\alpha}(\mathbf{r}), \quad (2.55)$$

where $\psi_i(\mathbf{r})$ are KS orbitals, $\phi_i(\mathbf{r})$ represents the respective basis functions, and $c_{i\alpha}$ are the expansion coefficients. Once the basis set is selected, the task primarily involves determining these coefficients for the occupied orbitals in a manner that minimizes the total energy. By inserting Equation 2.55 into the eigenvalue problem described in Equation 2.22, we derive a

matrix eigenvalue equation:

$$(\mathbf{H} - e_i \mathbf{S}) \mathbf{c}_i = 0, \quad (2.56)$$

where the matrix $\mathbf{H}$ encapsulates the KS Hamiltonian within the chosen basis, and $\mathbf{S}$ represents the overlap matrix, arising due to the non-orthogonality of basis functions from different atoms. Equation 2.56 serves as a generalized eigenvalue problem, necessitating the solution of the KS equations through diagonalization of the matrix $[\mathbf{H} - e_i \mathbf{S}]$.

Bloch theorem

The Bloch's theorem states that the eigenstates of single-particle Schrödinger equation in a periodic crystal $V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r})$, expressed in terms of plane waves, can be written as:

$$\psi(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k} \cdot \mathbf{T}} \psi(\mathbf{r}) \quad (2.57)$$

for every translation $\mathbf{T}$ in the Bravais lattice. Here, $\mathbf{k}$ is the wave vector. The values of $\mathbf{k}$ are typically confined to the reciprocal unit cell, conventionally chosen as the first Brillouin zone (BZ). For a given $\mathbf{k}$, different independent eigenstates exist, which can be labeled with a band index n .

An alternative statement of Bloch's theorem specifies that all eigenfunctions $\psi_{n\mathbf{k}}$ of the single-particle Schrödinger equation with a periodic potential can be represented as a plane wave multiplied by a function $u_{n\mathbf{k}}$ with the periodicity of the Bravais lattice [110]:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (2.58)$$

where

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{n\mathbf{k}}(\mathbf{r}) \quad (2.59)$$

for all $\mathbf{T}$ in the Bravais lattice.

This allows calculations of eigenfunctions to be confined within one unit cell, with eigenfunctions in other unit cells determined using Equation 2.58. It is convenient to normalize the eigenfunctions with respect to a single unit cell:

$$\int_{\Omega_c} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{r} = 1 \quad (2.60)$$

Choice of suitable basis set

Since the functions $u_{n\mathbf{k}}(\mathbf{r})$ are periodic, they can be expanded as a set of plane waves. Therefore, Equation 2.58 can be expressed as:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.61)$$

where $c_{n\mathbf{k}}(\mathbf{G})$ are the Fourier coefficients. The KS equations, in the notation of Bloch states, can be written as:

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right) \psi_{j\mathbf{k}}(\mathbf{r}) = \epsilon_{j\mathbf{k}} \psi_{j\mathbf{k}}(\mathbf{r}) \quad (2.62)$$

where

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}[n] + V_{xc}[n] \quad (2.63)$$

and

$$n(\mathbf{r}) = 2 \frac{\Omega_c}{(2\pi)^3} \sum_j \int_{\text{BZ}} |\psi_{j\mathbf{k}}(\mathbf{r})|^2 \Theta(E_F - \epsilon_{j\mathbf{k}}) d\mathbf{k} \quad (2.64)$$

Here, to differentiate between electron density and band index, we use n for electron density and j for the band index. The factor of two in Equation 2.64 accounts for electron spin. Θ is the step function, which is one for positive arguments and zero for negative arguments. E_F represents the Fermi energy up to which the single-particle states need to be occupied.

BZ Sampling

Applying Bloch's theorem allows one to determine a finite number of eigenstates for wave vectors $\mathbf{k}$ within the first BZ, instead of calculating an infinite number of electronic states extended over the entire solid. While this may seem like a minor improvement, fine sampling of the BZ is required for accurate calculations. However, since the lattice-periodic part $u_{n\mathbf{k}}(\mathbf{r})$ depends weakly on $\mathbf{k}$, a relatively small number of $\mathbf{k}$ -points is sufficient to sample the BZ [111]. Therefore, the integral over the BZ can be replaced by a discrete sum over a chosen $\mathbf{k}$ -point mesh of N_{kpt} $\mathbf{k}$ -points:

$$\frac{\Omega_c}{(2\pi)^3} \int_{\text{BZ}} \dots \Theta(E_F - \epsilon_{j\mathbf{k}}) d\mathbf{k} \rightarrow \frac{1}{N_{\text{kpt}}} \sum_{\mathbf{k}} f_{j\mathbf{k}} \dots \quad (2.65)$$

where $f_{j\mathbf{k}}$ are occupation numbers, either one or zero. Various methods have been proposed in the literature to construct $\mathbf{k}$ -point meshes [112, 113, 114]. In this thesis work, the Monkhorst-Pack scheme is used to sample the BZ. The error due to replacing the integral with a finite sum over $\mathbf{k}$ -points can be reduced by using a denser $\mathbf{k}$ -point mesh. For larger supercells,

a coarser $\mathbf{k}$ -point mesh is needed to obtain converged results, as the BZ of the supercell is smaller. Additionally, insulators typically require a coarser $\mathbf{k}$ -point mesh, while metals require a denser one to accurately sample the Fermi surface.

Fourier representation of the Kohn-Sham equation

The Fourier representation of the KS equation simplifies the form when the wavefunction is expanded in plane waves. Upon substituting Equation 2.61 into Equation 2.62 and performing some mathematical manipulations, the resulting matrix eigenvalue equation is obtained [115]:

$$\sum_{\mathbf{G}} \left(\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}'\mathbf{G}} + V_{eff}(\mathbf{G}' - \mathbf{G}) \right) c_{\mathbf{G}}^{jk} = \epsilon_{jk} c_{\mathbf{G}'}^{jk} \quad (2.66)$$

Practically, the Fourier expansion of the wavefunction given by Equation 2.61 is truncated by considering only plane waves with kinetic energy lower than a given cutoff value E_{cut} :

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{cut} \quad (2.67)$$

Consequently, convergence of the relevant quantity is achieved by systematically increasing the value of E_{cut} .

The Fourier representation of electron density is expressed as:

$$n(\mathbf{G}) = \frac{2}{N_{kpt}} \sum_{j\mathbf{k}} f_{j\mathbf{k}} \sum_{\mathbf{G}'} \left(c_{\mathbf{G}'-\mathbf{G}}^{jk} \right)^* c_{\mathbf{G}'}^{jk} \quad (2.68)$$

As electron density $n \propto |\psi|^2$, Fourier components extending twice in each direction compared to those needed for the ψ .

Calculating all Fourier components using Equation 2.68 involves a double sum scaling as N_G^2 , where N_G is the number of required $\mathbf{G}$ vectors. This becomes computationally expensive for large systems. Alternatively, if Bloch states are identified at a grid comprising N_R points within real space, computing the electron density becomes feasible through N_R operations. Employing the fast Fourier transform (FFT) enables the transition between spaces in $N \ln N$ operations, where $N = N_R = N_G$ [115]. Consequently, working with plane waves is advantageous as expressions can be efficiently evaluated using FFT.

2.3.7 Pseudopotentials

The solution of the KS equations poses computational challenges, requiring determination of wavefunctions for N electrons. Additionally, a large number of plane waves is needed to

expand tightly bound core orbitals and capture rapid oscillations of valence electron wavefunctions in the core region [116]. The pseudopotential approach addresses this by allowing the expansion of electronic wavefunctions with a smaller number of plane waves.

Valence electrons significantly influence material properties, prompting the pseudopotential approximation to replace core electrons and the strong ionic potential with a weaker pseudopotential acting on pseudo wavefunctions. This approach is illustrated in Figure 2.3. Pseudopotentials are constructed to match valence wavefunctions with those from all-electron calculations outside a cutoff radius r_c . Pseudopotentials with larger r_c are softer but less transferable, while smaller r_c yields harder pseudopotentials that require more plane waves for convergence. The use of pseudopotentials also allows the inclusion of relativistic effects on valence electrons treated non-relativistically.

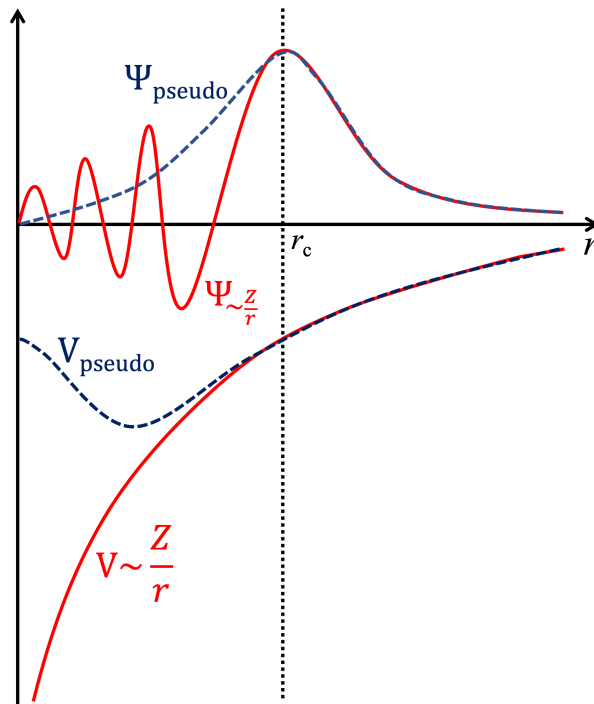


Figure 2.3: Schematic illustration of pseudopotential approach. The all-electron wavefunction associated with Coulomb potential is shown by red lines. The pseudo wavefunction consistent with pseudopotential is shown by blue dashes.

Norm-conserving pseudopotentials

Hamann, Schlüter, and Chiang [115, 117] introduced energy-independent norm-conserving pseudopotentials in 1979. These pseudopotentials satisfy four criteria:

1. Equality of all-electron (AE) and pseudo (PS) valence eigenvalues for a given atomic configuration.

$$\epsilon_{nl}^{\text{AE}} = \epsilon_{nl}^{\text{PS}} \quad (2.69)$$

2. Equality of AE and PS valence wavefunctions beyond a chosen core radius r_c .

$$\psi_{nl}^{\text{AE}}(r) = \psi_{nl}^{\text{PS}}(r) \quad \text{for } r \geq r_c \quad (2.70)$$

3. Norm conservation: equality of integrals of charge densities inside the core region.

$$\int_0^{r_c} |\phi_{nl}^{\text{AE}}|^2 r^2 dr = \int_0^{r_c} |\phi_{nl}^{\text{PS}}|^2 r^2 dr \quad (2.71)$$

4. Equality of logarithmic derivatives and the first energy derivative of the logarithmic derivatives of AE and PS wavefunctions at r_c .

$$\left[\left(r \phi_{nl}^{\text{AE}}(r) \right)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \phi_{nl}^{\text{AE}}(r) \right]_{r_c} = \left[\left(r \phi_{nl}^{\text{PS}}(r) \right)^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \phi_{nl}^{\text{PS}}(r) \right]_{r_c} \quad (2.72)$$

Norm-conserving pseudopotentials are advantageous for electronic structure calculations, offering accuracy, transferability, and computational efficiency.

Ultrasoft pseudopotentials

The effectiveness of norm-conserving pseudopotentials is constrained when applied to systems featuring highly localized valence orbitals like $2p$ and $3d$. This limitation arises from the challenge of accurately representing the pseudo wavefunction within a plane wave basis set. Ultrasoft pseudopotentials address this limitation by relaxing the norm-conserving constraint, resulting in a reduced requirement for plane waves. These ultrasoft pseudopotentials are inherently fully nonlocal but transition to a local nature outside the core region [118]. The nonlocal character of ultrasoft pseudopotentials depends self-consistently on the charge density, enhancing their transferability. Optimization of the smoothness of the pseudo wavefunction occurs as the norm-conserving condition is lifted. The pseudo wavefunction is partitioned into two components: (i) the ultrasoft valence wavefunction, which does not adhere to the norm conservation constraint, and (ii) the core augmentation charge, representing the charge deficit in the core region. The reduction in the plane wave energy cutoff is significant due to the former feature. However, the latter aspect introduces additional terms in the KS formalism, adding complexity and necessitating a greater number of operations per computational cycle. Despite the increased computational efforts, the overall reduction in computational cost achieved by lowering the plane wave energy cutoff predominates in many cases.

2.3.8 Projector augmented-wave method

In 1994, Blöchl [119] introduced the projector augmented-wave (PAW) method, a synthesis of concepts from both the pseudopotential approach and the linearized augmented plane wave (LAPW) method [120, 121]. The core idea is to correlate the KS all-electron wavefunction $|\phi_s^0\rangle$ for state s with a smooth pseudo wavefunction $|\tilde{\phi}_s^0\rangle$ and associated correction terms to restore oscillatory behavior in the core region.

The mapping of $|\phi_s^0\rangle$ is achieved through a linear transformation $\hat{T}$:

$$|\phi_s^0\rangle = \hat{T}|\tilde{\phi}_s^0\rangle \quad (2.73)$$

Considering the oscillatory nature of $|\phi_s^0\rangle$ near the core region and its smoothness beyond a certain distance, the LAPW method categorizes space into two regions: (i) the augmentation region around the nuclei Ω_a , where a is an atom index, and (ii) an interstitial region Ω_i [122]. The Ω_a region is defined by a cutoff radius r_c^a to prevent overlap of augmentation spheres. Since the pseudo wavefunction should align with the all-electron wavefunction outside Ω_a , the linear transformation $\hat{T}$ modifies $|\phi_s^0\rangle$ solely in the augmentation region. Consequently, $\hat{T}$ is expressed as:

$$\hat{T} = 1 + \sum_a \hat{T}^a \quad (2.74)$$

Here, the atom-centered contribution $\hat{T}^a$ transforms $|\phi_s^0\rangle$ within Ω_a , enclosing the atom. The transformation operator is derived by defining the all-electron partial waves φ_j^a and pseudo partial waves $\tilde{\varphi}_j^a$ inside the augmentation region:

$$\hat{T} = 1 + \sum_a \sum_j \left(|\varphi_j^a\rangle - |\tilde{\varphi}_j^a\rangle \right) \langle \tilde{p}_j^a | \quad (2.75)$$

Here, $|\tilde{p}_j^a\rangle$ represents smooth projector functions. Within the augmentation sphere, these projector functions are orthonormal to the pseudo partial waves. Applying this to the all-electron wavefunction equation 2.73, one obtains the following expression:

$$|\phi_s^0\rangle = |\tilde{\phi}_s^0\rangle + \sum_a \sum_j \left(|\varphi_j^a\rangle - |\tilde{\varphi}_j^a\rangle \right) \langle \tilde{p}_j^a | \tilde{\phi}_s^0 \rangle \quad (2.76)$$

The following conditions hold inside the augmentation region, i.e., for $\mathbf{r} \in \Omega_a$:

$$\phi_s^0(\mathbf{r}) = \phi_s^a(\mathbf{r}) \quad \tilde{\phi}_s^0(\mathbf{r}) = \tilde{\phi}_s^a(\mathbf{r}) \quad (2.77)$$

And outside the augmentation region, i.e., for $\mathbf{r} \in \Omega_i$:

$$\phi_s^0(\mathbf{r}) = \tilde{\phi}_s^0(\mathbf{r}) \quad \phi_s^a(\mathbf{r}) = \tilde{\phi}_s^a(\mathbf{r}) \quad (2.78)$$

Here, $\phi_s^a(\mathbf{r})$ and $\tilde{\phi}_s^a(\mathbf{r})$ are expanded as follows:

$$\phi_s^a(\mathbf{r}) = \sum_j \varphi_j^a(\mathbf{r}) \langle \tilde{p}_j^a | \tilde{\phi}_s^0 \rangle \quad \tilde{\phi}_s^a(\mathbf{r}) = \sum_j \tilde{\varphi}_j^a(\mathbf{r}) \langle \tilde{p}_j^a | \tilde{\phi}_s^0 \rangle \quad (2.79)$$

The pseudo wavefunctions are expanded in a plane waves basis set, with a lower energy cutoff due to smoothness. The partial waves and the projectors are calculated as radial functions multiplied by spherical harmonics. The PAW method proves computationally efficient in electronic structure calculations.

2.3.9 Computational methods

In this thesis work, we have employed the relativistic first-principles simulations based on DFT as implemented in Vienna *ab initio* Simulation Package (VASP) [123]. The simulations are done using plane-wave basis set and projector augmented wave method [124]. We have used the Perdew-Burke-Ernzerhof (PBE) as the exchange-correlation (ϵ_{xc}) functional [125] and set plane-wave cut off energy to 1.5 times the cutoff energy. To get a more accurate band gap, calculations are also benchmarked using non-local Heyd-Scuseria-Ernzerhof (HSE06) ϵ_{xc} functional [126]. Initially, experimental lattice parameters and atomic positions are taken as a starting point. In structural optimization, the change in total energy between two electronic steps is set to 10^{-6} eV and are converged until Hellmann-Feynman forces are smaller than $1 \text{ meV}\text{\AA}^{-1}$ without including spin-orbit coupling. The Brillouin zone was sampled in $\mathbf{k}$ -space with Monkhorst-Pack [127] scheme with a $\mathbf{k}$ -mesh of spacing less than $0.02\text{\AA}^{-1}$. After the structure optimization, we have also confirmed the dynamical stability using density functional perturbation theory (DFPT) as implemented in PHONOPY code [128]. The spin textures from DFT are calculated using a dense $\mathbf{k}$ -mesh of 31×31 around high-symmetry-point in $k_x - k_y$ plane. The model band structures and spin textures are calculated by parameterizing the models using minimization of the summation

$$S = \sum_{i=1}^2 \sum_{\mathbf{k}} f(\mathbf{k}) |Det[H(\mathbf{k}) - E^i(\mathbf{k})I]|^2 \quad (2.80)$$

over i^{th} energy eigenvalues ($E^i(\mathbf{k})$) as training sets, where $f(\mathbf{k})$ is the weight attached to $\mathbf{k}$ -point. Here, H , "Det" and I represent model Hamiltonian, determinant and identity matrix, respectively. We have used normal distribution for $f(\mathbf{k})$ to get a better fit near high-symmetry-point as used in Ref[129]. We have conducted symmetry analysis using Bilbao crystallographic server [130, 131], SEEK-PATH software [132] and FINDSYM [133]. The Mathematica [134]

and PyProcar [135] are used to plot spin textures, band structures and parameterize the models. In case of nonmagnetic materials, the final spin configurations are obtained from the electronic self-consistent loop without initializing spin configurations. Tight-binding models and Berry curvatures are obtained from the maximally localized Wannier functions as implemented in the Wannier90 [136]. The Wannier representations were obtained by projecting the Bloch states from first principles calculations on orbitals contributing to the low energy states [137]. FE properties are calculated within the framework of berry phase theory for polarization [138, 139, 140]. The few other DFT packages, such as Quantum ESPRESSO [141] and FHI-aims [142], are also used with similar settings and are greatly acknowledged.

2.4 $k.p$ perturbation theory with SOC

The symmetry properties of a specific crystal can draw significant conclusions about the form of energy bands. The group of wave vector demonstrates the fundamental questions like band “degeneracy” and “connectivity” can be addressed solely through group theory. There is no imperative need to explicitly solve Schrödinger’s equation to determine “degeneracies” and “connectivity” relations for electronic band $E_n(\mathbf{k})$. Utilizing interpolation/extrapolation techniques using the crystal symmetries can yield the functional form of $E_n(\mathbf{k})$ without the need for directly solving Schrödinger’s equation. This approach serves as a valuable interpolation method for experimental data and facilitates band calculations, conducted meticulously at a few $\mathbf{k}$ -points in the BZ. The $k.p$ perturbation theory finds straightforward application in the two-band model, representing one of its simplest uses. These models prove effective in characterizing the electronic band dispersion $E_n(\mathbf{k})$ around a specific point ($\mathbf{k}_0$). These bands exhibit strong coupling between each other while maintaining weak connections to all other bands. The set characterized by strong coupling is termed the nearly degenerate set (NDS). Following the resolution of the strongly interacting bands, the weakly coupled bands can be conveniently addressed using perturbation theory if necessary. The two-band model can be extended to easily adapted scenarios involving three strongly coupled bands, such as the valence band in semiconductors like silicon and germanium [143]. Moreover, the model can be further extended to address situations involving four strongly coupled bands, as observed in materials like graphite [144].

The method considered in this thesis is first-order degenerate $k.p$ perturbation theory and

two-band model. An electron subjected to a periodic potential including SOC follows the one-electron Hamiltonian:

$$\left\{ \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar}{4m^2c^2} (\nabla V \times \mathbf{p}) \cdot \boldsymbol{\sigma} \right\} \psi_{n,\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k}) \psi_{n,\mathbf{k}}(\mathbf{r}) \quad (2.81)$$

$\boldsymbol{\sigma}$ represents the spin operator [$\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$]. The first two terms in Eq. 2.81 represent the kinetic energy and periodic potential of the one-electron Hamiltonian reflecting the crystal symmetry. The third term signifies the SOC. The incorporation of the spin operator $\boldsymbol{\sigma}$ in the spin-orbit term H_{SO} requires the use of spin-dependent wavefunctions with double-group symmetry designations for energy bands. Given that the strength of the SOC effect is comparable to band gaps in many materials, it becomes essential in such cases to explicitly consider the SOC when considering electronic bands. Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$ become two-component spinors $\psi_{n\mathbf{k}\uparrow}(\mathbf{r})$ and $\psi_{n\mathbf{k}\downarrow}(\mathbf{r})$. These spinor basis functions can be expressed as

$$\psi_{n\mathbf{k}\uparrow}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \phi_{n\mathbf{k}\uparrow}(\mathbf{r}) \quad (2.82)$$

$$\psi_{n\mathbf{k}\downarrow}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \phi_{n\mathbf{k}\downarrow}(\mathbf{r}) \quad (2.83)$$

The arrow in the subscript of $\psi_{n\mathbf{k}\uparrow}(\mathbf{r})$ indicates that the state is generally spin up, or the expectation value of σ_z in this state is positive. Conversely, the down arrow implies a negative expectation value for σ_z , so that

$$\langle \psi_{n\mathbf{k}\uparrow} | \sigma_z | \psi_{n\mathbf{k}\uparrow} \rangle > 0 \quad (2.84)$$

$$\langle \psi_{n\mathbf{k}\downarrow} | \sigma_z | \psi_{n\mathbf{k}\downarrow} \rangle < 0 \quad (2.85)$$

The Bloch states are purely spin-up or spin-down in the limiting case when SOC is zero or weak (as in altermagnets). Note that here $\mathbf{k}$ is measured from high-symmetry point $\mathbf{k}_0$. Therefore, $\phi_{n\mathbf{k}}(\mathbf{r})$ should satisfy boundary condition $\phi_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}_0 \cdot \mathbf{T}} \phi_{n\mathbf{k}}(\mathbf{r})$, where $\mathbf{T}$ being the lattice translation. The substitution of $\psi_{n\mathbf{k}}(\mathbf{r})$ into Schrödinger's equation results into eigenvalue equation for the periodic function $\phi_{n\mathbf{k}}(\mathbf{r})$:

$$\hat{H}_0 + \hat{H}'_{\mathbf{k},\mathbf{p}} \phi_{n\mathbf{k}}(\mathbf{r}) = \mathcal{E}_n(\mathbf{k}) \phi_{n\mathbf{k}}(\mathbf{r}). \quad (2.86)$$

Here unperturbed Hamiltonian H_0 and perturbed Hamiltonian $H'_{\mathbf{k},\mathbf{p}}$ are

$$\hat{H}_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar}{4m^2c^2} (\nabla V \times \mathbf{p}) \cdot \boldsymbol{\sigma} \quad (2.87)$$

and

$$\hat{H}'_{\mathbf{k},\mathbf{p}} = \frac{\hbar \mathbf{k}}{m} \cdot \left(\mathbf{p} + \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma} \times \nabla V \right) \quad (2.88)$$

where $\mathcal{E}_n(\mathbf{k}) = E_n(\mathbf{k}) - \frac{\hbar^2 \mathbf{k}^2}{2m}$. In accordance with the $\mathbf{k.p}$ method, it is assumed that $E_n(\mathbf{k})$ is known at a specific point $\mathbf{k} = \mathbf{k}_0$, either from experimental data or through the direct solution of Schrödinger's equation for some model potential $V(\mathbf{r})$. Initially, we observe that due to the independence of the spin in H_0 , the solutions of Equation 2.87 maintain degeneracy in spin space. The presence of time reversal symmetry $\hat{T}\hat{H}_0(\mathbf{k})\hat{T}^{-1} = \hat{H}_0(-\mathbf{k})$ with $\hat{T}\psi = \psi^*$ immediately implies that $\mathcal{E}_0(-\mathbf{k}) = \mathcal{E}_0(\mathbf{k})$ and $\phi_{-\mathbf{k}}^0 = \phi_{\mathbf{k}}^{0*}$, where the phase of $\phi_{\mathbf{k}}^0$ has been arbitrarily fixed. It is evident that a polynomial representation of $\mathcal{E}_0(\mathbf{k})$ only includes even powers, with the first nontrivial (second-order) terms being related to the effective masses. Further relationships can be established through point-group symmetry. Let $G_{\mathbf{k}_0}$ be the small group of $\mathbf{k}_0$, denoted by $g\mathbf{k}_0 = \mathbf{k}_0 + \mathbf{K}$ for any $g \in G_{\mathbf{k}_0}$, where $\mathbf{K}$ represents an appropriate reciprocal-lattice vector. Using the standard definition for the action of a symmetry operation $(g \circ f)(\mathbf{r}) = f(g^{-1}\mathbf{r})$ and the symmetry of the Hamilton operator $g \circ H_0(\mathbf{k}) = H_0(g\mathbf{k})$, it can be derived that $\mathcal{E}_0(g\mathbf{k}) = \mathcal{E}_0(\mathbf{k})$ and $g \circ \phi_{\mathbf{k}_0} = \phi_{g\mathbf{k}}$.

2.4.1 Method of invariants

Taking $\hat{H}'_{\mathbf{k}.p}$ as a perturbation and $\phi_{\mathbf{k}_0}\chi_s$ with χ_s being spin eigenfunctions ($s = \pm\frac{1}{2}$) as unperturbed wavefunctions, first-order degenerate perturbation theory is applied. The SOC Hamiltonian $\hat{H}_{SO}(\mathbf{k})$ is defined as the corresponding 2×2 matrix,

$$\hat{H}_{SO}(\mathbf{k}) = \boldsymbol{\alpha}(\mathbf{k}) \cdot \boldsymbol{\sigma},$$

where general functional form of the n th-order polynomial $\alpha_i(\mathbf{k})$ can be written $\alpha_i(k_x, k_y, k_z) = \sum_{l=1}^n c_{ilm} k_x^l k_y^{n-l} k_z^{n-l-m}$ (for $i = x, y, z$). Here, non-zero coefficients c_{ilm} can be determined using symmetry invariance conditions. The matrix elements of the perturbed Hamiltonian are $H'_{ij} = \langle \phi_i | \hat{H}'_{\mathbf{k}.p} | \phi_j \rangle$. Note that the Hamiltonian $\hat{H}'_{\mathbf{k}.p}$ transforms like vector, since it is directly proportional to the vector $\mathbf{k}$, representing the electronic system. The parameter $\mathbf{k}$ is treated as an external variable unrelated to the system. In context of $\mathbf{k.p}$ perturbation theory, the vector $\mathbf{k}_0$ dictates the point group symmetry employed for the classification of wavefunctions and eigenvalues associated with $\hat{H}'_{\mathbf{k}.p}$. $\langle \phi_i | \hat{H}'_{\mathbf{k}.p} | \phi_j \rangle$ is allowed by symmetry of it transform like fully symmetric representation according to the group of wave vector of $G_{\mathbf{k}_0}$.

First, let's consider the simplest case, i.e., the space group $P1$ with the point group C_1 . The point group C_1 has only the symmetry element identity operation (E). Additionally, the time-reversal operation ($\hat{T}$) is also an operation ($\hat{T}\mathbf{k}_0 = -\mathbf{k}_0 + \mathbf{K}$). Therefore, all coefficients

Table 2.1: The transformations of the $\mathbf{k}$ and $(\boldsymbol{\sigma})$ Pauli matrices under the operations belonging to C_{2v} point group. The symbol K represents complex conjugation.

Operation	(k_x, k_y, k_z)	$(\sigma_x, \sigma_y, \sigma_z)$	Symmetry Invariants
$\hat{T} = i\sigma_y K$	$(-k_x, -k_y, -k_z)$	$(-\sigma_x, -\sigma_y, -\sigma_z)$	$k_i \sigma_i \quad (i, j = x, y, z)$
$\hat{C}_{2z} = i\sigma_z$	$(-k_x, -k_y, k_z)$	$(-\sigma_x, -\sigma_y, \sigma_z)$	$k_z \sigma_z, k_x \sigma_x, k_x \sigma_y, k_y \sigma_x, k_y \sigma_y$
$\hat{M}_{xz} = i\sigma_y$	$(k_x, -k_y, k_z)$	$(-\sigma_x, \sigma_y, -\sigma_z)$	$k_x \sigma_y, k_z \sigma_y, k_y \sigma_x, k_y \sigma_z$
$\hat{M}_{yz} = i\sigma_x$	$(-k_x, k_y, k_z)$	$(\sigma_x, -\sigma_y, -\sigma_z)$	$k_x \sigma_y, k_x \sigma_z, k_y \sigma_x, k_z \sigma_x$

c_{ilm} are allowed using symmetry. Consequently, the H_{SO} Hamiltonian can be expressed as

$$\hat{H}_{C_1} = \sum_{\alpha, \beta, \gamma=x,y,z} k_\gamma^i k_\alpha \sigma_\beta \quad (i = 0, 2, 4, \dots).$$

Suppose the point group has an inversion operation ($\hat{I}$) in addition to $\hat{T}$, where $\hat{I}$ transforms $\mathbf{k}$ and $\boldsymbol{\sigma}$ as follows: $(k_x, k_y, k_z) \rightarrow (-k_x, -k_y, -k_z)$ and $(\sigma_x, \sigma_y, \sigma_z) \rightarrow (\sigma_x, \sigma_y, \sigma_z)$. In this case, all the coefficients c_{ilm} are forbidden by symmetry. In summary, we can assert that $\alpha(\mathbf{k})$ should contain only odd terms if $\hat{T}$ is the only operation and contain only even terms if $\hat{I}$ is the only operation. When both $\hat{T}$ and $\hat{I}$ symmetries exist, it imposes a condition on

$$\hat{T}\hat{I}\phi_{n\mathbf{k}\uparrow} = \hat{T}\phi_{-\mathbf{k}\uparrow} = \phi_{\mathbf{k}\downarrow}$$

transforming the spin-up eigenstate to a spin-down eigenstate at arbitrary $\mathbf{k}$, leading to spin-degeneracy throughout the BZ. Therefore, among $\hat{T}$ and $\hat{I}$, one symmetry should be broken to eliminate spin-degeneracy. For example, nonmagnetic materials with noncentrosymmetric point groups lack $\hat{I}$ symmetry. Therefore, Rashba and Dresselhaus-like effects arise around time-reversal-invariant momenta. On the other hand, when $\hat{T}$ symmetry is broken, as in ferromagnetic cases, spin-degeneracy is broken even in centrosymmetric (in real space) materials.

Now, let's consider the case of the most common point group in materials, C_{2v} , which includes the symmetry operations $\hat{E}$, $\hat{C}_{2z}$, $\hat{M}_{xz}$, and $\hat{M}_{yz}$. Here, $\hat{C}_{2z}$ represents a two-fold rotation around the z -axis, and $\hat{M}_{ij}$ denotes the mirror plane in the $i-j$ plane. The transformation rules for (k_x, k_y, k_z) and $(\sigma_x, \sigma_y, \sigma_z)$ for symmetry operations belonging to C_{2v} and the time-reversal operation ($\hat{T}$) are provided in Table 2.1. By collecting all the invariant terms, the corresponding SOC Hamiltonian can be expressed as

$$\hat{H}_{C_{2v}} = \alpha k_x \sigma_y + \beta k_y \sigma_x.$$

Here, α and β are the splitting coefficients determining the strength of spin splitting. It is important to note that symmetry operations provide qualitative insights into the splitting, not quantitative values. Therefore, α and β can be determined by fitting the band dispersion obtained from Density Functional Theory (DFT) or angle-resolved photoemission spectroscopy (ARPES) measurements.

It is worth emphasizing that a similar procedure can be extended to magnetic structures where the concept of a magnetic point group becomes important (see Chapter 6). In magnetic point groups, in addition to the positions of atoms, the direction of magnetic moments also plays a crucial role. For magnetic point groups, consideration of the time-reversal operation ($\hat{T}$) is essential in addition to spatial operations.

Linear Rashba-Dresselhaus effects in perovskite oxides and chalcogenides

3.1 Introduction

Ferroelectric Rashba semiconductors (FERSC) have recently created a huge sensation in the field of spintronics owing to their robust spontaneous electrical polarization [145, 146, 147, 148, 149, 150]. These materials find applications in spin field effect transistors, ferroelectric tunnel junctions, storage and memory devices [151, 152, 153, 154, 155, 156]. The long-range order dipoles aligned in same direction induce polarization in ferroelectric materials, leading to inversion asymmetry. Ferroelectric Rashba semiconductors interlink the phenomena of Rashba-type splitting and ferroelectricity, enabling the electric control of electron's spin. In ferroelectric Rashba semiconductors, Rashba parameters can be enhanced with the application of ferroelectric (FE) polarization.

Ferroelectric materials, because of their robust spontaneous electrical polarization, are widely used in various applications. Interestingly, the spins can be reversed by inverting the direction of electric polarization using external electric field [22]. Electrical control of spins makes them suitable for spintronic devices. Some well known examples of ferroelectric Rashba semiconductors are KTaO_3 [157], BiAlO_3 [22], LiZnSb [158] and FASnI_3 (FA=Formamidinium) [159]. GeTe was the first ferroelectric material, in which Rashba effect was predicted theoretically [20] and observed experimentally [160]. However, it has a tendency to form Ge vacancy [161], which leads to p -type semiconducting behavior. This in turn poses a challenge to electric control of the spin as it leads to a p -degenerate semiconducting behavior. This means that GeTe has a high concentration of holes (positive charge carriers) due to the missing germanium atoms. The excess carriers increase the conductivity of the material, making it difficult to control the

ferroelectric state through an applied electric field. The switching of the ferroelectric state is crucial for controlling the spin texture in FERSCs, and the high conductivity of GeTe due to Ge vacancies hinders this process. Additionally, GeTe has a small band gap of around 0.5 eV. A small band gap implies that electrons can easily be excited from the valence band to the conduction band, even at room temperature. This can lead to leakage currents when an electric field is applied, further complicating the experimental realization of spin texture control in GeTe. In this context, ferroelectric oxide perovskites such as KIO_3 (KIO) show excellent piezoelectric, pyroelectric and non-linear optical properties [162, 163]. KIO, in particular, is experimentally synthesized at high temperature in non-centrosymmetric rhombohedral phase with $R3m$ space group symmetry [164]. A thermodynamically favorable rhombohedral $R3c$ phase was also theoretically predicted [165, 163, 166]. In both phases, distortion of octahedra centered at I-atom induces spontaneous FE polarization. Furthermore, the presence of heavy element (I), contributing to significant SOC and inversion asymmetric nature may induce interesting Rashba- and Dresselhaus-type band splitting.

Note that SOC and broken inversion symmetry play a pivotal role for the materials to exhibit Rashba and Dresselhaus (RD) effect [156, 151, 167, 168]. In crystals, lacking inversion symmetry, a relativistically moving electron experiences a Lorentz-transformed magnetic field due to a finite potential gradient. This results in spin-based splitting of degenerate bands at non-time-reversal-invariant k -points, which lifts the Kramer's degeneracy leading to RD splitting. The spin-orientation is determined by the momentum dependent spin-orbit field. For acentric non-polar crystals, Dresselhaus was the first to show band splitting, which has a cubic dependence on momentum space for zincblende-type crystal structures [169]. For gyrotropic point group symmetries, linear Dresselhaus-type spin splitting can also be realized. In polar crystals and 2D electron gas, linear splitting terms are allowed as shown by Rashba and Bychkov [170, 171]. The SOC Hamiltonian $H_{SO} = \mathbf{\Omega}(\mathbf{k}) \cdot \boldsymbol{\sigma}$ describes these effects, where $\boldsymbol{\sigma}$ is Pauli matrices vector and $\mathbf{\Omega}(\mathbf{k})$ is spin-orbit field. The latter is odd in momentum space (i.e. $\mathbf{\Omega}(-\mathbf{k}) = -\mathbf{\Omega}(\mathbf{k})$) to preserve the time-reversal symmetry of H_{SO} . $\mathbf{\Omega}(\mathbf{k})$ depends on the spatial symmetry of the system. For simplest case, C_{2v} point group symmetry, $\mathbf{\Omega}(\mathbf{k})$ can be written as vector sum of linear Rashba ($\mathbf{\Omega}_R = \alpha_R(k_y, -k_x, 0)$) and Dresselhaus ($\mathbf{\Omega}_D = \alpha_D(k_y, k_x, 0)$) spin-orbit fields [10]. Here, α_R and α_D are the RD coefficients, respectively. Energy eigenvalues corresponding to linear Rashba Hamiltonian are given by $E_{\pm}(k) = \hbar^2 k^2 / 2m \pm \alpha_R k$. RD effects lead to the same type of band splitting. However, type of splitting can be character-

ized by projecting spin-orientation in Fourier space, usually referred as spin texture [17]. The strength of the spin-orbit coupling (SOC) is determined by the atomic masses of the constituent elements in the material. Heavier elements generally exhibit stronger SOC due to the larger nuclear charge and the resulting stronger electric field experienced by the electrons. The symmetry of the crystal also plays a crucial role in determining the specific form of the spin-orbit coupling. For instance presence of inversion symmetry leads to the vanishing spin splitting. Different crystal symmetries breaking allow for different types of spin-orbit interactions, such as the Rashba (breaking mirror symmetry) and Dresselhaus effects (breaking inversion symmetry). Therefore, magnitude of spin splitting coefficients effects are controlled by the strength of SOC and crystal symmetry [19].

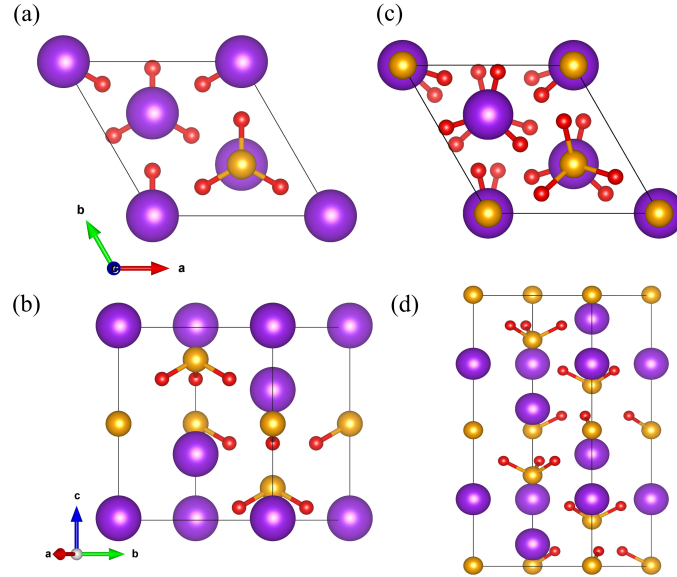


Figure 3.1: Crystal structure of KIO_3 in the (a)-(b) $R3m$ phase and (c)-(d) $R3c$ phase. The violet, orange and red balls denote the K, I and O ions, respectively.

3.2 Rashba spin splitting in bulk perovskite KIO_3

In this section, we have studied the RD effects in $R3m$ and $R3c$ phases of FE oxide KIO using state-of-the-art DFT and symmetry adapted two-band $\mathbf{k}\cdot\mathbf{p}$ model Hamiltonian. Firstly, we have determined the FE polarization in both the phases. Subsequently, the crucial effect of SOC has been shown in the band structures. The Rashba spin splitting energy and offset momentum have been determined from the splitting at the CBM and VBM. Furthermore, the type of splitting has been characterized by plotting the spin texture. The RD parameters are determined after

fitting the $k \cdot p$ model Hamiltonian to the DFT band structure. Finally, the effect of polarization on the aforementioned parameters has been investigated.

3.2.1 Structural and ferroelectric properties

KIO mainly exists in $Pm\bar{3}m$, $R3m$ and $R3c$ space group symmetries. The $Pm\bar{3}m$ phase is centrosymmetric that contains an inversion center and therefore, does not show the Rashba-type splitting. Hence, we have studied the non-centrosymmetric rhombohedral phases $R3m$ and $R3c$ in detail for RD properties. The $R3m$ phase is symmorphic as all generating symmetry operations leave one common point fixed, apart from the lattice translations. On the contrary, $R3c$ phase is non-symmorphic containing the glide planes. Figure 3.1 shows the conventional hexagonal unit cells of $R3m$ and $R3c$ phase of KIO. The lattice parameters of both phases are given in Table 3.1. The atomic positions were optimized without including spin-orbit coupling (SOC), but test calculations showed no significant changes when SOC was considered. This suggests that the effect of SOC on the forces acting on the atoms during relaxation is negligible. The reason for this is that SOC primarily affects the electronic structure, leading to energy shifts and spin splitting of the bands. However, the overall potential energy landscape experienced by the ions is mainly determined by the electrostatic interactions between the nuclei and the electron charge density, which are not significantly altered by SOC. The lattice parameters of the $R3m$ phase of KIO_3 were computed with and without SOC. The parameters agree to within $\pm 1\%$. The calculated lattice parameters of $R3m$ phase are in well agreement with experimental values ($a = 6.34 \text{ \AA}$, $c = 7.94 \text{ \AA}$) [164]. The lattice parameters of $R3c$ phase coincide with crystal structure already reported using DFT ($a = 6.37 \text{ \AA}$, $c = 15.92 \text{ \AA}$) [165]. At equilibrium (without considering the strain), the formation energy of the $R3c$ phase is lowest. Our calculated formation energy of the $R3c$ phase is 18 meV/f.u. lower than that for the $R3m$ phase. For $R3m$ phase, we have calculated change in ferroelectric polarization i.e., dipole moment per unit volume ($\frac{P}{V}$) with respect to centrosymmetric structure, of $41 \mu\text{C}/\text{cm}^2$ along the [0001] direction in hexagonal setting (along the [111] direction in rhombohedral setting). However, in $R3c$ phase, we have found slightly smaller polarization of $29 \mu\text{C}/\text{cm}^2$ along the [0001] direction in hexagonal setting. In previous studies on BiFeO_3 thin films, it has been shown that FE polarization can be enhanced to as large as $150 \mu\text{C}/\text{cm}^2$ using the strain [172, 173, 174]. In view of this, we have also verified the enhancement in FE polarization of KIO on the application of strain. The FE polarization increases (decreases) under the application

Table 3.1: Lattice parameters and polarization for rhombohedral phases of KIO calculated using PBE ϵ_{xc} functional.

Space group	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	$P(\mu\text{C}/\text{cm}^2)$
$R3c$	6.37	15.91	558.6	29
$R3m$	6.29	8.11	278.1	41

of tensile (compressive) strain and direction remains the same. The FE polarization has varied from 21 to 35 $\mu\text{C}/\text{cm}^2$ and 29 to 50 $\mu\text{C}/\text{cm}^2$ in $R3m$ and $R3c$ phases, respectively, on applying strain in the range of -5% to $+5\%$.

3.2.2 Electronic properties and spin splitting effects

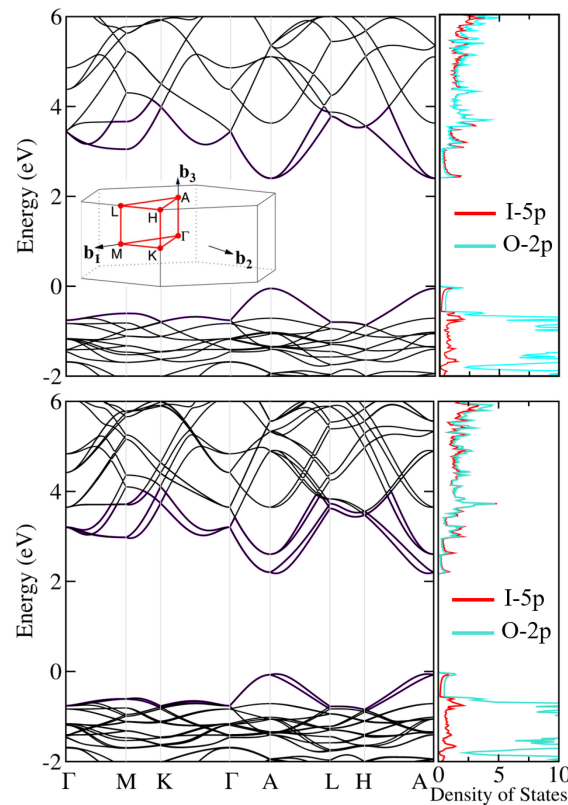


Figure 3.2: Band structure and PDOS for $R3m$ phase calculated using PBE (a) without SOC and (b) with SOC. Here, inset shows the first BZ for the hexagonal phase.

Figure 3.2(a) shows the simulated electronic structure of the $R3m$ phase without SOC along the HSP in the first BZ[see Fig. 3.2(a) inset for HSP]. A direct band gap of 2.51 eV is observed

at k -point A. Since the PBE [175] exchange-correlation (ϵ_{xc}) functional is known to underestimate the band gap, it is also calculated using non-local HSE06 [176] ϵ_{xc} functional. A larger direct band gap of 3.50 eV is observed at the k -point A. The uppermost valence band (VB) has a width of about 2.5 eV and the electronic states are mainly derived from O-2p orbitals [see partial density of states (PDOS) in Fig. 3.2]. The lowest conduction band (CB) has a width of nearly 4 eV and the electronic states are mainly derived from equal contribution of I-5p and O-2p orbitals. Figure 3.2(b) shows the calculated band structure and PDOS with inclusion of SOC. The VBM and CBM shift from k -point A towards L, which is known as the offset momentum (δk). The energy difference between the k -point A and extremum is known as the Rashba spin splitting energy (δE). A slightly indirect band gap of 2.24 and 3.27 eV is observed using PBE+SOC and HSE06+SOC, respectively. Despite the underestimation of the band gap by PBE, the band dispersion around the HSP is known to be similar to HSE06 [20]. We have compared the band structures obtained using PBE+SOC and HSE06+SOC and found that they are resulting in similar Rashba parameters. Therefore, all the calculations are performed using PBE, since it is more cost effective. The presence of large SOC is attributed to the heavy elements like I. A dominant spin splitting can be seen in the plane $k_z = \frac{\pi}{c}$, which is perpendicular to the polarization axis [see Figs. 3.3(a) and 3.3(b)]. In contrast, splitting is completely absent in direction Γ -A, which is parallel to the polarization axis [0001]. It is consistent with the Rashba model, where splitting occurs in direction perpendicular to the polarization axis. The δE for CB and VB is 27.3 and 18.1 meV, respectively. The δk for CB and VB is 0.047 and 0.054 $\text{\AA}^{-1}$, respectively. Within the linear approximation, these values lead to α_R ($\frac{2\delta E}{\delta k}$) of 1.16 and 0.67 eV $\text{\AA}$, respectively. We have observed comparatively larger Rashba splitting at the CBM than VBM due to the higher contribution of I-5p orbitals at the CBM (see Fig. 3.2).

In order to have better understanding of the spin splitting nature, spin texture is plotted near the VBM and CBM around k -point A. The 2D spin texture is calculated by projecting expectation values of σ_x , σ_y and σ_z in Fourier plane (k_x - k_y). Figures 3.3[(c)-(d)] and 3.3[(e)-(f)] show the calculated x -, y - and z -component of spin texture near the VBM and CBM, respectively. The spin textures obtained using PBE and HSE06 are in close agreement. Thus, we have further used PBE for computing spin textures. The in-plane spin components (S_x , S_y) show helical nature with inner and outer bands having opposite orientation. This confirms the existence of Rashba-type splitting. A significant S_z component can also be seen for the CBM, which is absent for the VBM. The S_z has three-fold symmetry, which is in agreement with the three-fold

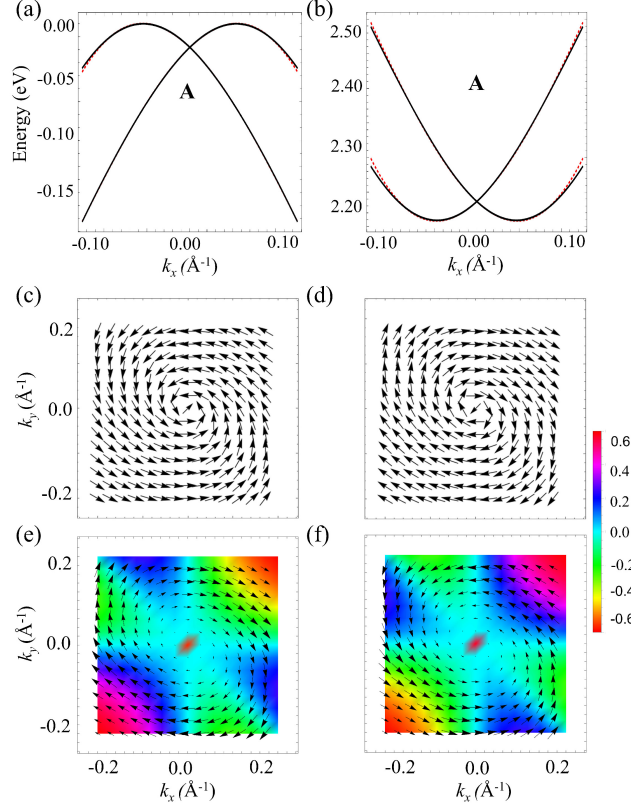


Figure 3.3: (a) VBs and (b) CBs of KIO for $R3m$ phase with SOC along A-L line (energy vs k_x). Here black solid lines and red dashed lines are obtained by DFT and parametrization of the model, respectively. (c)-(d) Spin textures of two upper most VBs and (e)-(f) two lowest CBs. The arrows and color projection represent the in-plane (x, y) and out-of-plane (z) components of texture with respect to the (k_x-k_y) plane.

rotation symmetry of the crystal. Splittings and textures can be explained by two-band effective Hamiltonian including only spin DOF. The little group associated with A point is C_{3v} , consisting of three-fold rotations C_3 , one reflection through vertical plane containing z -axis (σ_{xz}) and two reflections through diagonal planes (M_{d1}, M_{d2}) [177, 178] (besides trivial identity operation). Band dispersion relation and spin texture around k -point A in plane orthogonal to polar axis can be derived using all the symmetry-allowed terms such that $O^\dagger H(\mathbf{k})O = H(\mathbf{k})$, where O is the symmetry operation of little group [22]. The constructed two-band $\mathbf{k}, \mathbf{p}$ Hamiltonian including linear and cubic Rashba terms satisfying the C_{3v} symmetry near k -point A takes the form [179]

$$H_A(\mathbf{k}) = H_o(\mathbf{k}) + H_{SO} \quad (3.1)$$

where,

$$H_{SO} = \alpha\sigma_y k_x + \beta\sigma_x k_y + \gamma\sigma_z[(k_x^3 + k_y^3) - 3(k_x k_y^2 + k_y k_x^2)] \quad (3.2)$$

and $H_o(\mathbf{k})$ is free particle Hamiltonian. α , β are the coefficients of linear terms and γ is the coefficient of cubic term in SOC Hamiltonian. The two energy eigenvalues of Hamiltonian are

$$E(\mathbf{k})^\pm = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} \pm E_{SO} \quad (3.3)$$

where, m_x and m_y represent the effective masses in x and y directions, respectively. E_{SO} is the energy eigenvalue of SOC Hamiltonian given by $E_{SO}(\mathbf{k}) = \sqrt{\alpha^2 k_x^2 + \beta^2 k_y^2 + \gamma^2 f^2(k_x, k_y)}$, where $f(k_x, k_y) = (k_x^3 + k_y^3) - 3(k_x k_y^2 + k_y k_x^2)$. Normalized spinor wavefunctions corresponding to energy eigenvalues are given by

$$\Psi_{\mathbf{k}}^\pm = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{2\pi(\rho_\pm^2 + 1)}} \begin{pmatrix} \frac{i\alpha k_x - \beta k_y}{\gamma f(k_x, k_y) \mp E_{SO}} \\ 1 \end{pmatrix} \quad (3.4)$$

where $\rho_\pm^2 = \frac{\alpha^2 k_x^2 + \beta^2 k_y^2}{(\gamma f(k_x, k_y) \mp E_{SO})^2}$. The expectation values of spin operators are given by

$$\{s_x, s_y, s_z\}^\pm = \pm \frac{1}{E_{SO}} \{\beta k_y, \alpha k_x, \gamma f(k_x, k_y)\} \quad (3.5)$$

In-plane spin components are reproduced using α and β , whereas γ reproduces out of plane spin component. For a specific k -point, in-plane spin component is small as compared to out-of-plane if $\gamma f(k_x, k_y)$ is much larger than αk_x and βk_y , and vice versa. Spin textures calculated using DFT satisfies the model Hamiltonian predictions. Three-fold degeneracy of z -component of spin is the consequence of cubic nature of $f(k_x, k_y)$.

Figures 3.3(a) and 3.3(b) show the comparison between the DFT and $\mathbf{k}\cdot\mathbf{p}$ model predicted electronic bands calculated using Eq. 3.1 near the VBM and CBM, respectively, in the vicinity of k -point A. The $\mathbf{k}\cdot\mathbf{p}$ model produces band structure, which is in close agreement with the DFT band structure. Near the k -point A, cubic terms have smaller energy contribution as compared to the linear terms in band structure calculations. In the range $|k_i| \leq 0.125 \text{ \AA}^{-1}$ ($i = x, y$), contribution coming from cubic term is within 0.01 times contribution coming from linear terms (note that ratio of different contributions is function of $\mathbf{k}$). The energy eigenvalues of the Hamiltonian are given by $E(\mathbf{k})^\pm = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} \pm \sqrt{\alpha^2 k_x^2 + \beta^2 k_y^2 + \gamma^2 f^2(k_x, k_y)}$, which estimate only the magnitude of α , β and γ . The signs of α , β and γ are determined by the orientation of spins in Fourier space. RD coefficients are defined as $\alpha_R = \frac{\alpha - \beta}{2}$ and $\alpha_D = \frac{\alpha + \beta}{2}$, respectively. For CB, $\alpha=1.12 \text{ eV\AA}$, $\beta=-1.12 \text{ eV\AA}$ and $\gamma=-21.70 \text{ eV\AA}^3$ reproduce the DFT band structure.

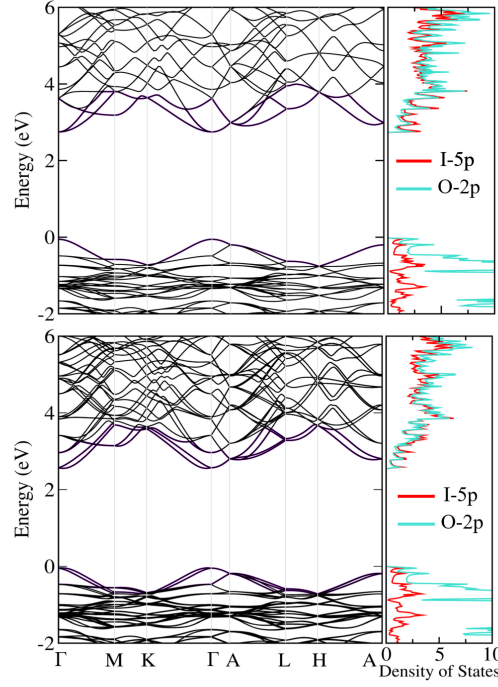


Figure 3.4: Band structure and PDOS for $R3c$ phase calculated using PBE (a) without SOC and (b) with SOC.

These parameters lead to $\alpha_R=1.12 \text{ eV\AA}$ and $\alpha_D=0 \text{ eV\AA}$, confirming the splitting is coming mainly from linear Rashba effect. For VB, $\alpha=0.63 \text{ eV\AA}$, $\beta=-0.63 \text{ eV\AA}$ and $\gamma=-1.10 \text{ eV\AA}^3$ reproduce the DFT band structure leading to purely Rashba with $\alpha_R=0.63 \text{ eV\AA}$ apart from negligible cubic contribution. The Rashba coefficients calculated using the $\mathbf{k}\cdot\mathbf{p}$ model are fairly close to the DFT predictions.

Figures 3.4(a) and 3.4(b) show the band structures and PDOS for $R3c$ phase without and with inclusion of SOC, respectively. It has a direct band gap of 2.86 eV at k -point Γ without including SOC, which is 0.41 eV larger than for the $R3m$ phase. The contribution of atomic

Table 3.2: Rashba parameters for band-splitting at k -point A for $R3m$ phase (note that $\beta=-\alpha$ in each case).

Position	m^*	α	γ	δE	δk	α_R
	(m_e)	($\text{eV\AA}$)	($\text{eV\AA}^3$)	(meV)	($\text{\AA}^{-1}$)	($\text{eV\AA}$)
VBM	-0.72	0.63	-01.10	18.10	0.054	0.67
CBM	0.34	1.12	-21.70	27.30	0.047	1.16

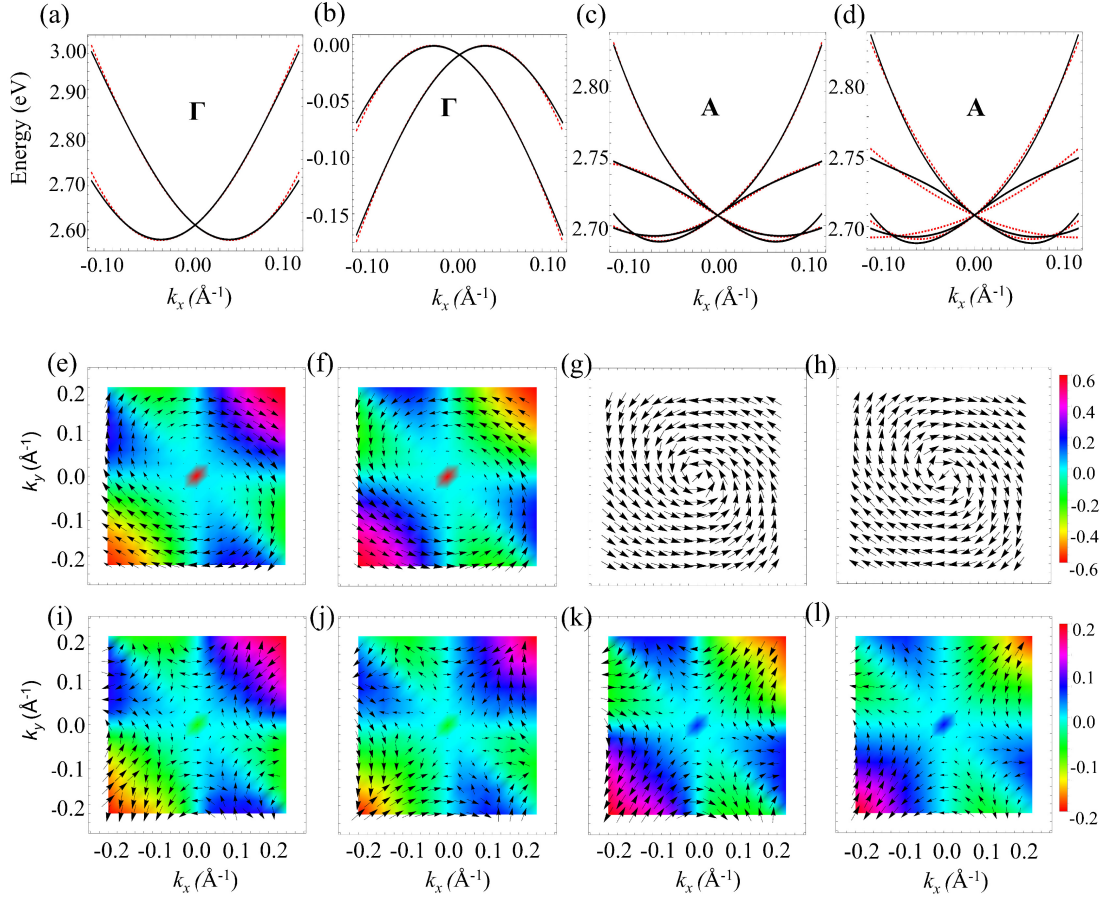


Figure 3.5: (a) VBs and (b) CBs of KIO for $R3c$ phase with SOC along Γ -M line (energy vs k_x). (c) Lowest four CBs around the k -point A with the full model given in Eq. 3.6 and (d) with modified model excluding the terms containing the orbital DOF (obtained using $\eta = \xi = \Delta = \Lambda = K = \rho = 0$ in Eq. 3.6). Here, black solid lines and red dashed lines are obtained by DFT and parametrization of the models, respectively. Spin textures of (e)-(f) two lowest CBs, (g)-(h) two uppermost VBs around k -point Γ and (i)-(l) lowest four CBs around k -point A. The arrows and color projection represent the (S_x, S_y) and S_z components of spin texture with respect to the (k_x-k_y) plane. Our spin textures are prepared using convention [(i)-(l) as examples] that if at (k_x, k_y) point, energy eigenvalues associated with (i), (j), (k) and (l) are e_{1k} , e_{2k} , e_{3k} , e_{4k} , respectively, then $e_{1k} \leq e_{2k} \leq e_{3k} \leq e_{4k}$.

orbitals in PDOS near the VBM and CBM for the $R3c$ phase are nearly similar to the $R3m$ phase. With the inclusion of SOC, the VBM and CBM shift towards k -point K. A slightly indirect band gap of 2.65 eV on including SOC confirms the importance of SOC in the calculations. A larger band gap calculated to be 3.80 eV using HSE06+SOC. Spin splitting can be seen throughout the BZ except for Γ -A, which again confirms the polarization direction parallel

to Γ -A [see Fig. 3.4b]. A dominant spin splitting can be seen along the path Γ -M, Γ -K, A-L and A-H [see Figs. 3.4 and 3.5(a)-3.5(d)]. Figures 3.5(e)-3.5(h) show the plotted spin textures near the CBM and VBM, respectively, around k -point Γ . Figures 3.5(i)-3.5(l) show the plotted spin textures for lowest four CBs, around k -point A. Near k -point Γ , in-plane spin textures form helical-type spin texture with different orientation for inner and outer bands, confirming the Rashba-type splitting of degenerate levels. A significant S_z component contribution can be seen near CBM, which is absent near the VBM. Near k -point A, the spin splitting leads to novel spin textures, which are beyond the superposition of linear RD terms. These spin textures are completely different from those obtained using two-band $\mathbf{k}\cdot\mathbf{p}$ model. These spin textures are a result of coupling of spin DOF to the orbital DOF [180, 181]. The splitting near k -point Γ can be explained by two-band effective Hamiltonian, whereas four-band Hamiltonian becomes important to understand the splitting near k -point A. The little group of k -point Γ and A is same, which is C_{3v} . The model Hamiltonian given by Eq. 3.1 can explain the band properties of the VBM and CBM near k -point Γ . Figures 3.5(a) and 3.5(b) show that DFT and $\mathbf{k}\cdot\mathbf{p}$ model predicted band structures near the k -point Γ are comparable. Rashba spin splitting energy of 6.3 and 16.5 meV is obtained for VB and CB, respectively. The δk for CB and VB is 0.042 and 0.031 $\text{\AA}^{-1}$, respectively. From DFT, the value of α_R is found to be 0.79 and 0.41 eV $\text{\AA}$ for CB and VB, respectively. For CB, fitted parameters of H_{SO} are $\alpha=0.78$ eV $\text{\AA}$, $\beta=-0.78$ eV $\text{\AA}$ and $\gamma=-13.3$ eV $\text{\AA}^3$. These parameters lead to $\alpha_R=0.78$ eV $\text{\AA}$ and $\alpha_D=0$ eV $\text{\AA}$. The corresponding parameters for VB are estimated as $\alpha=0.40$ eV $\text{\AA}$, $\beta=-0.40$ eV $\text{\AA}$ and $\gamma=-0.55$ eV $\text{\AA}^3$ leading to purely linear Rashba effect with $\alpha_R=0.40$ eV $\text{\AA}$ with negligible cubic contribution. The Rashba coefficients calculated using $\mathbf{k}\cdot\mathbf{p}$ model are fairly close to the DFT predictions. For splitting near k -point A, we have used the four-band model derived using method of invariants satisfying the C_{3v} point group symmetry [181]

$$\begin{aligned}
H_A(k) = & \alpha(k_x^2 + k_y^2) + \beta(k_x^2 + k_y^2)^2 + \delta(k_x^2 + k_y^2)^3 \\
& + \eta[(k_x^2 - k_y^2)\gamma_z + 2k_x k_y \gamma_x] + [\Delta + \Lambda(k_x^2 + k_y^2) + K(k_x^2 + k_y^2)^2]\gamma_y \sigma_z \\
& + [\kappa + \zeta(k_x^2 + k_y^2)](k_x \sigma_y - k_y \sigma_x) + \lambda k_x (k_x^2 - 3k_y^2) \sigma_z \\
& + \xi k_x (k_x^2 - 3k_y^2) \gamma_z + \rho[(k_x \gamma_x - k_y \gamma_z) \sigma_x - ((k_y \gamma_x - k_x \gamma_z) \sigma_y)]
\end{aligned} \tag{3.6}$$

where both γ_i and σ_j are the Pauli matrices, denoting the orbital and spin DOF, respectively. Here, $\gamma_i \sigma_j$ represents the Kronecker delta product of matrices γ_i and σ_j . γ_i and σ_i denote $\gamma_i \sigma_1$ and $\gamma_1 \sigma_i$, where γ_1 and σ_1 are the identity matrices of dimension 2×2 . Figure 3.5(c) shows the comparison between DFT and model predicted band structures for lowest four CBs around

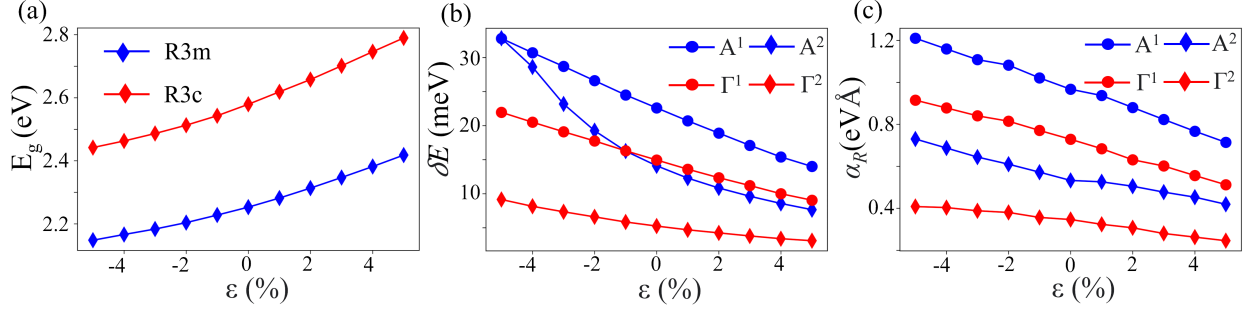


Figure 3.6: (a) Band gap (E_g), (b) Rashba spin splitting energy (δE) and (c) Rashba coefficients (α_R) as a function of strain (ϵ). The A^1 and A^2 show the information about splitting around k -point A in $R3m$ phase around the CBM and VBM, respectively. In the same manner, Γ^1 and Γ^2 show splitting in $R3c$ phase around k -point Γ .

Table 3.3: Rashba parameters for band-splitting at k -point Γ for $R3c$ phase.

Position	m^*	α	γ	δE	δk	α_R
	(m_e)	(eVÅ)	(eVÅ ³)	(meV)	(Å ⁻¹)	(eVÅ)
VBM	-0.59	0.40	-0.55	6.30	0.031	0.41
CBM	0.41	0.78	-13.27	16.50	0.042	0.79

k -point A. Figure 3.5(d) shows the DFT [same as Fig. 3.5(c)] and modified model of Eq. 3.6 excluding the terms containing orbital DOF predicted band structures. The modified model band structure largely deviates from the DFT band structures. This confirms the significance of orbital DOF and four-band $\mathbf{k}, \mathbf{p}$ Hamiltonian over usual two-band $\mathbf{k}, \mathbf{p}$ Hamiltonian to completely understand the spin splitting near k -point A. We have observed the linear splitting of ~ 0.64 and ~ 0.45 eVÅ for the bands around k -point A (calculated using the expression $E = E_0 \pm \lambda \delta k + b(\delta k)^2$). The CBM and VBM are in the vicinity of k -point A, which can be brought to k -point A using strain for possible applications of these novel spin textures.

The experimental observations show that the electronic structure, ferroelectricity, spin splitting in oxide perovskites are tunable using the strain [182]. The polarization and Rashba splitting are sensitive to uniaxial strain in oxide perovskites such as BiAlO₃ [22], KTaO₃ [183] and PbTiO₃ [184]. In view of this, we have studied the strain dependence of δE , δk and α_R in both the phases of KIO. We have considered the effect of strain within (0001) plane on spin splitting and energy levels for both the phases around the VBM and CBM. Such strain can

be obtained by growing KIO films on top of hexagonal (0001) or cubic (111) substrates [185]. The polarization direction remains along the [0001] direction throughout the full range of strain. Figure 3.6 shows the change in the band gaps, δE and α_R on application of strain. Band gap increases (decreases) under tensile (compressive) strain for $R3m$ and $R3c$ phases. δE decreases (increases) using tensile (compressive) strain for conduction and VBs. Linear trend is observed for spin splitting at the CBM and VBM in both phases. The amplitude of spin splitting can be tuned from 0.8 to 1.2 eVÅ for the CBM in $R3m$ phase. It should be noted here that a more detailed analysis would be necessary to see if other states can be stabilized under the uniaxial strain. This can be done by calculating the total formation energy of structures with different space groups as a function of strain to know which one is the most stable at a particular strain. [186]

The spin degeneracy can be restored when the structure is brought back to the parent centrosymmetric structure. The parent space group of $R3m$ is $R\bar{3}m$, which is generated by the symmetry elements of $R3m$ followed by an inversion. The polarization, P_z along the c -direction breaks the inversion symmetry. Thus, $R\bar{3}m$ phase is centrosymmetric and band splitting is absent. It is well known that in FERSC, switching the direction of polarization leads to reversal of spin texture. The full reversal of spin texture on reversing the direction of polarization is also observed in KIO. To switch the direction of polarization, transition state $R\bar{3}m$ has to be crossed, which defines the potential barrier. The parent centrosymmetric structure is generated using the program PSEUDO [187]. The calculated potential barrier to switch the polarization through $R\bar{3}m$ phase is 135 meV/f.u. for $R\bar{3}m$. Similarly, the potential barrier for $R3c$ phase is found to be 112 meV/f.u. The calculated potential barrier is comparable to 110 meV/f.u. of LaWN_3 [181] and smaller than 130 meV/f.u. of LiNbO_3 [188]. The Rashba parameters are larger for KIO than BAO, despite a significantly larger ferroelectric polarization in BAO. Therefore, we infer that larger ferroelectric polarization does not directly imply the larger splitting. A thorough analysis of symmetry and electronic structure is always required.

3.3 Rashba-Dresselhaus spin splittings in chalcogenides

In recent years, lead-based inorganic-organic hybrid halide perovskite solar cells have shown an unprecedented rise in power conversion efficiency from 3.8% to 25.7% [189, 190]. This is attributed to their exceptional properties for a solar cell absorber, such as a high absorption

coefficient of $\sim 10^5 \text{ cm}^{-1}$ in the visible wavelength range, small exciton binding energies of $\sim 20 \text{ meV}$, long charge carrier diffusion length of up to $\sim 100 \mu\text{m}$, excellent charge carrier mobilities, tunable band gap, and high defect tolerance [191, 192]. Moreover, these can be fabricated via simple solution deposition, resulting in low-cost manufacturing. However, their commercialization is impeded by several factors: (i) the efficiency decreases with increasing size of the thin films of lead halide perovskites (LHPs), (ii) the material becomes unstable upon exposure to humidity, heat, or light, and (iii) poisonous lead can harm the environment and living organisms [193]. The thermal stability of hybrid LHPs could be improved by the utilization of an inorganic cation at A site instead of an organic one, but all inorganic LHPs still suffer from long-term instability under operational conditions, especially against moisture stress [194]. These challenges, alongside the high performance of LHPs, stimulate the research in lead-free and stable perovskite-inspired materials (PIMs) [195].

The presence of ns^2 lone-pair electrons on the Pb cation can be crucial in fostering exceptional optoelectronic performance in LHPs [196]. In combination with halide anion, this lone-pair cation leads to small effective masses for electrons and holes, defect tolerance, and strong dielectric screening [197, 198]. A wide range of compounds comprising Pb^{2+} , Sn^{2+} , Ge^{2+} , Sb^{3+} , and Bi^{3+} cations containing ns^2 electronic configurations are currently of interest as light harvesters [199]. Among them, chalcogenide PIMs have emerged as a promising material having ns^2 electronic configuration as well as cation-halide combination [200, 198, 201]. Recently, Nie et al. [200] have synthesized the solar cell based on tin-antimony sulfoiodide ($\text{Sn}_2\text{SbS}_2\text{I}_3$) using a single-step, solution-based chemical deposition process, exhibiting a power conversion efficiency of 4.04%. They have also demonstrated its stability against air, moisture, and light illumination. The accomplishment of a power conversion efficiency surpassing the initially reported value for methylammonium lead-iodide [189] has significant potential. $\text{Sn}_2\text{SbS}_2\text{I}_3$ has long been known [202, 4], but the recent surge of interest in it stems from its considerable potential in various optoelectronic applications [200, 203, 204]. In view of this, we aim to provide an in-depth theoretical study of chalcogenide PIMs ($\text{Sn}_2\text{SbX}_2\text{I}_3$, $\text{X} = \text{S}, \text{Se}$) to investigate the atomistic origins of its appealing optoelectronic properties that may act as valuable guidance for further development of this emerging material class.

Note that the presence of heavy elements in PIMs, such as Sb and I, imparts a strong SOC, playing a significant role in determining the electronic properties. When the SOC is combined with the crystal's broken inversion symmetry, it results in Rashba band splitting. The Rashba

effect is considered to be a possible cause for reduced recombination rate and longer carrier lifetimes in LHPs [205, 206]. Nonetheless, it has been demonstrated [207] that employing a Rashba Hamiltonian within a tight-binding model [205] can result in an inaccurate depiction of spin orientations at the band extrema. Therefore, the Rashba effect must be carefully determined to find the right implications. In the case of organic-inorganic LHPs, the mismatch of crystal momentum between the VBM and CBM due to the Rashba effect may be the cause of the reduction in the recombination rate [208]. Moreover, the Rashba effect opens up the possibility for these materials to be used in spintronics. We, therefore, attempt to study the Rashba effect in chalcogenide PIMs, which generally enhances the efficiency of optoelectronic devices and potentially expedites their usage in spintronic devices. In this section, we analyze the RD effects in chalcogenide PIMs ($\text{Sn}_2\text{SbX}_2\text{I}_3$, $\text{X} = \text{S}, \text{Se}$) using DFT [209, 96] calculations and symmetry adapted $\mathbf{k}\cdot\mathbf{p}$ model Hamiltonian.

3.3.1 Crystal and electronic Structures

Recently, Kavanagh et al. [198] have reported that the $Cmc2_1$ phase of $\text{Sn}_2\text{SbS}_2\text{I}_3$ is more stable than the $Cmcm$ phase and the experimental $Cmcm$ phase is the result of macroscopic averaging over local $Cmc2_1$ configurations. This kind of polymorphism is also found in LHPs and goes undetected by X-ray diffraction (XRD) due to long coherence length [210, 211]. Its impact is evident in determining thermodynamic stability and optoelectronic properties. Therefore, in this work, we consider both phases ($Cmc2_1$ and $Cmcm$) of $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $Cmc2_1$ phase of $\text{Sn}_2\text{SbSe}_2\text{I}_3$ [see Figs. 3.7(a) and 3.7(b)]. The initial orthorhombic geometries of $\text{Sn}_2\text{SbX}_2\text{I}_3$ ($\text{X} = \text{S}, \text{Se}$) were obtained from Materials Project repository [212]. The lattice parameters of the optimized structures calculated using optB86b-vdW [213] exchange-correlation (ϵ_{xc}) functional are given in Table 3.4. These are in close agreement with previous experimental [202, 4, 214] and theoretical [198] results. The $Cmcm$ phase consists of $(\text{Sn}_2\text{S}_2\text{I}_2)_n$ chains along the a direction, forming a layered structure in ab plane, having I and Sb in-between the layers [see Fig. 3.7(b)]. Whereas in the $Cmc2_1$ phase, there is a small displacement of I, resulting in $(\text{Sn}_2\text{SbS}_2\text{I}_3)_n$ chains along the a direction [see Fig. 3.7(a)]. The lattice parameters of both phases are similar along a and b , with the largest difference along the c direction [see Table 3.4]. More details about bond lengths and bond angles can be seen in Table S1.

Table 3.4: Calculated lattice parameters of $\text{Sn}_2\text{SbX}_2\text{I}_3$ ($X = \text{S}, \text{Se}$). The experimental values are provided from Ref. [4] for comparison.

configurations	phase	a (Å)	b (Å)	c (Å)	c/a
$\text{Sn}_2\text{SbS}_2\text{I}_3$	$Cmc2_1$	4.27	14.16	16.40	3.84
	$Cmcm$	4.26	13.93	15.95	3.74
	experiment	4.25	13.99	16.38	3.85
$\text{Sn}_2\text{SbSe}_2\text{I}_3$	$Cmc2_1$	4.32	14.45	17.09	3.96
	experiment	4.30	14.08	17.22	4.00

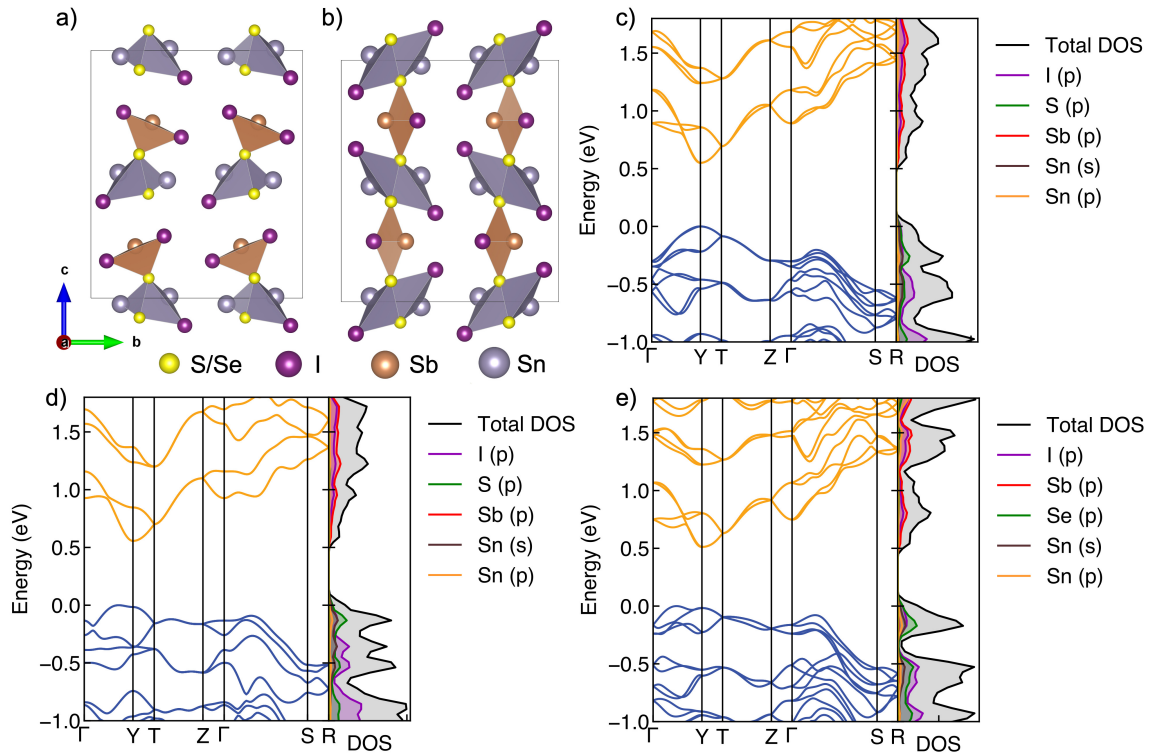


Figure 3.7: Schematic crystal structure of orthorhombic $\text{Sn}_2\text{SbX}_2\text{I}_3$ ($X = \text{S}, \text{Se}$) in (a) $Cmc2_1$ phase and (b) $Cmcm$ phase. Electronic band structure and partial density of states (pDOS) of (c) $\text{Sn}_2\text{SbS}_2\text{I}_3$ in $Cmc2_1$ phase, (d) $\text{Sn}_2\text{SbS}_2\text{I}_3$ in $Cmcm$ phase, and (e) $\text{Sn}_2\text{SbSe}_2\text{I}_3$ in $Cmc2_1$ phase using PBE+SOC.

3.3.2 Spin splitting analysis

The calculated electronic band structure and partial density of states (pDOS) using PBE ϵ_{xc} functional with the inclusion of SOC are shown in Figs. 3.7(c)-3.7(e). From pDOS, we observe

that the VBM is dominated by S/Se (p), I (p), and Sn (s) orbitals, whereas the CBM is dominated by Sb (p) and I (p) orbitals. The $Cmc2_1$ phase of $Sn_2SbS_2I_3$ has a direct band gap of 0.68 eV at Y point without including SOC. In the presence of SOC, the band gap is reduced to 0.55 eV. Therefore, the role of SOC is significant in these chalcogenide PIMs and duly considered in all the calculations. We observe that the bands are spin-degenerate throughout the BZ in the $Cmcm$ phase of $Sn_2SbS_2I_3$ as shown in Fig. 3.7(d). This is attributed to the spin degeneracy (Kramer's degeneracy) preserved by the time reversal and inversion symmetry [215]. On the other hand, in the $Cmc2_1$ phase, bands associated with CBM and VBM split around the Y point due to inversion symmetry breaking [see Fig. 3.7(c)]. To clearly visualize the splitting of bands, we plot the electronic structure around the Y point [see Figs. 3.8(a)-3.8(d)]. Note that the splitting is absent along the k_z direction due to the presence of mirror ($\overline{M}_x$) and glide ($\overline{M}_y$) planes. The $\overline{M}_x$ and $\overline{M}_y$ planes result in zero polarization along [100] and [010] planes, respectively. In accordance with the previous reports [198], we find the electric polarization along z with a magnitude of $36 \mu C/cm^2$. The spin splitting occurs only in the plane perpendicular to the polarization direction (k_x-k_y plane in our case). Furthermore, we have plotted the spin textures of CBM and VBM around the Y point [see Figs. 3.8(e)-3.8(h)]. The in-plane spin textures are chiral, with opposite orientations for the inner and outer bands, while out-of-plane spin texture is zero. The spin texture and splitting around the Y point can be understood in terms of the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian derived using the symmetry considerations [24, 87, 85]. The group of wave vector associated with Y point includes symmetry operations $\{2_{100}|00\frac{1}{2}\}(\overline{C}_{2z})$, $\{m_{100}|000\}(\overline{M}_x)$ and $\{m_{010}|00\frac{1}{2}\}(\overline{M}_y)$ (see Bilbao Crystallographic Server [130] for notation). Note that the transformation rules of $\mathbf{k}$ under the glide plane and screw axis are the same as that of the associated mirror and rotation operations, respectively [5]. The transformation rules of (k_x, k_y, k_z) and $(\sigma_x, \sigma_y, \sigma_z)$ under $\overline{C}_{2z}$, $\overline{M}_x$ and $\overline{M}_y$ are listed in the Table 3.5. The $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian characterizing the spin splitting in $k_z = 0$ plane is obtained by collecting all the symmetry invariant terms up to cubic in $\mathbf{k}$ and expressed as

$$H = H_0 + \alpha(\mathbf{k})k_x\sigma_y + \beta(\mathbf{k})k_y\sigma_x \quad (3.7)$$

where H_0 is the free particle Hamiltonian. $\alpha(\mathbf{k})$ and $\beta(\mathbf{k})$ are the splitting coefficients determining the strength of SOC, given by

$$\begin{aligned} \alpha(\mathbf{k}) &= \alpha_{(1)} + \alpha_{(3)}(k_x^2 + k_y^2) + \gamma_\alpha(k_x^2 - k_y^2) \\ \beta(\mathbf{k}) &= \beta_{(1)} + \beta_{(3)}(k_x^2 + k_y^2) + \gamma_\beta(k_x^2 - k_y^2) \end{aligned} \quad (3.8)$$

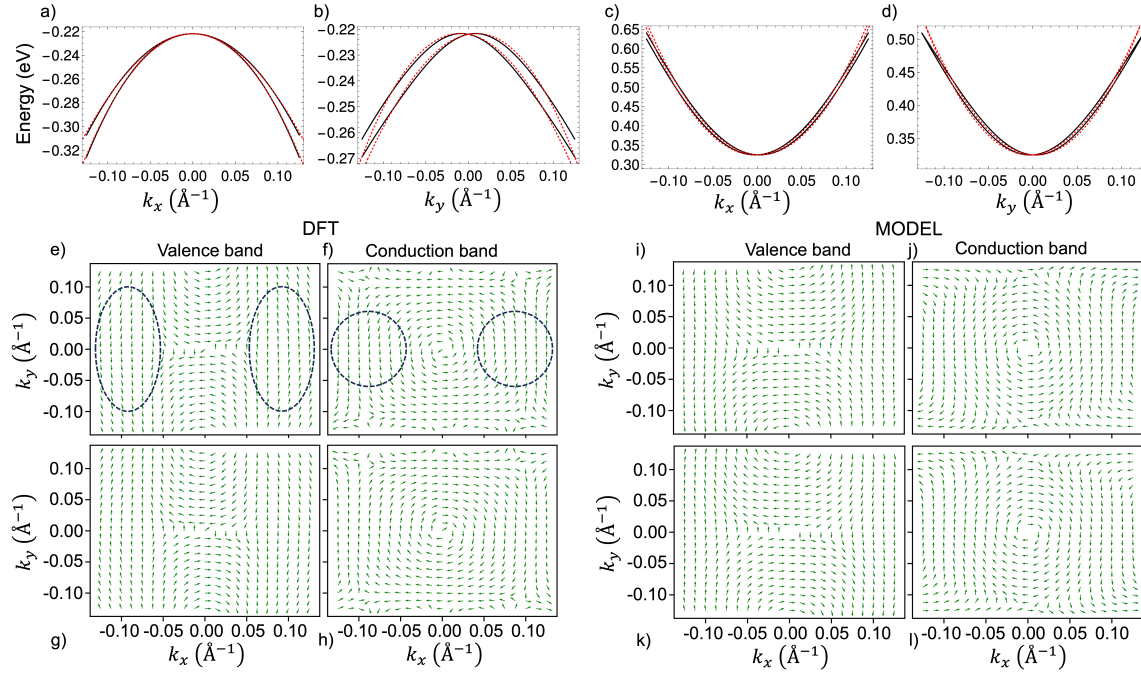


Figure 3.8: (a)-(b) VBs and (c)-(d) CBs of $\text{Sn}_2\text{SbS}_2\text{I}_3$ along k_x and k_y directions. The black lines and red dots are bands obtained using DFT and $\mathbf{k} \cdot \mathbf{p}$ model, respectively. Spin textures of (e),(g) two highest VBs, and (f),(h) two lowest CBs, computed using DFT. (i)-(l) are model-resulted spin textures, counterparts of (e)-(h). The arrows denote the in-plane (S_x, S_y) components of spin. The S_z component is zero in the considered range.

Table 3.5: The transformation rules of (k_x, k_y, k_z) and $(\sigma_x, \sigma_y, \sigma_z)$ under the operations belonging to the group of wave vector of Y point and time reversal operation (T). The $\mathbf{k}$ is referenced from the Y point.

operations	(k_x, k_y, k_z)	$(\sigma_x, \sigma_y, \sigma_z)$	invariants
$\bar{C}_{2z}$	$(-k_x, -k_y, k_z)$	$(-\sigma_x, -\sigma_y, \sigma_z)$	$k_i \sigma_j (i, j = x, y), k_z \sigma_z$
$\bar{M}_x$	$(-k_x, k_y, k_z)$	$(\sigma_x, -\sigma_y, -\sigma_z)$	$k_x \sigma_y, k_y \sigma_x, k_z \sigma_x$
$\bar{M}_y$	$(k_x, -k_y, k_z)$	$(-\sigma_x, \sigma_y, -\sigma_z)$	$k_x \sigma_y, k_y \sigma_x, k_z \sigma_y,$
T	$(-k_x, -k_y, -k_z)$	$(-\sigma_x, -\sigma_y, -\sigma_z)$	$k_i \sigma_j (i, j = x, y, z)$

where $\alpha_{(3)}$ and $\beta_{(3)}$ terms take cubic interaction into consideration. γ_α and γ_β take cubic anisotropy into consideration. Note that σ_z terms with linear dependence in $\mathbf{k}$ are forbidden by symmetry, resulting in the vanishing S_z component. We have fitted the band structure near the Y point to parameterize α and β . The results are shown in Figs. 3.8(a)-3.8(d), and correspond-

ing splitting parameters are given in Table 3.6. As evident from the Fig. 3.8(a), VBs are almost

Table 3.6: The parameterization of $\alpha_{(1)}$, $\alpha_{(3)}$, $\beta_{(1)}$, $\beta_{(3)}$, γ_α and γ_β for the lowest CBs and top VBs (around the Y point) of $\text{Sn}_2\text{SbS}_2\text{I}_3$ having $Cmc2_1$ group symmetry. The k_x and k_y ranges considered to fit our models are within $0.125 \text{ \AA}^{-1}$.

	band	$\alpha_{(1)}$ (eVÅ)	$\alpha_{(3)}$ (eVÅ ³)	γ_α (eVÅ ³)	$\beta_{(1)}$ (eVÅ)	$\beta_{(3)}$ (eVÅ ³)	γ_β (eVÅ ³)
$\text{Sn}_2\text{SbS}_2\text{I}_3$	VB	0.005	3.796	1.013	0.065	-3.595	0.508
	CB	0.115	-4.877	0.883	-0.094	5.838	1.002
$\text{Sn}_2\text{SbSe}_2\text{I}_3$	VB	0.007	5.211	2.132	0.081	-6.592	1.213
	CB	0.131	-5.126	0.658	-0.099	4.892	0.995

cubic split along k_x direction signifying crucial role of $\alpha_{(3)}$ and $\gamma_{(\alpha)}$ terms in Hamiltonian. The cubically split bands provide an additional advantage over linear splitting in spintronics, i.e., the larger spin Hall conductivity and spin transport in a system with higher spin (spin 1 and spin 3/2 quasiparticles) [129, 28, 216]. In the regime of purely linear splitting, the strength of linear RD effects is obtained using

$$\begin{aligned}\alpha_R &= \frac{\alpha_{(1)} - \beta_{(1)}}{2} \\ \alpha_D &= \frac{\alpha_{(1)} + \beta_{(1)}}{2}\end{aligned}\tag{3.9}$$

where α_R and α_D are RD parameters, respectively. For the VB, we find $\alpha_R = 0.030 \text{ eVÅ}$, and $\alpha_D = 0.035 \text{ eVÅ}$. Similarly, we obtain RD parameters $\alpha_R = 0.105 \text{ eVÅ}$, and $\alpha_D = 0.010 \text{ eVÅ}$ for the CB of $\text{Sn}_2\text{SbS}_2\text{I}_3$. Therefore, the linear Rashba effect dominates over the Dresselhaus effect for the CB splitting. This is also evident from the helical spin textures shown in Fig. 3.8(f). On the other hand, in the case of spin splitting of VB, the contribution of both linear RD is significant, with linear Dresselhaus being the dominant one. The higher CB splitting is attributed to heavier Sb (p) orbitals' contribution to the CB in comparison to the S (p) and Sn (s) orbitals' contribution to the VB [see Fig. 3.7(c)]. Furthermore, we have also plotted the spin textures of CB and VB using $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian with parameters given in Table 3.6. The $\mathbf{k}\cdot\mathbf{p}$ model-resulted spin textures are in good agreement with the DFT spin textures [see Figs. 3.8(e)-3.8(l)]. Similar spin splittings and textures are also observed in the $Cmc2_1$ phase of $\text{Sn}_2\text{SbSe}_2\text{I}_3$ (see Table 3.6 for parameters). However, the strength of splitting is slightly larger in the case of $\text{Sn}_2\text{SbSe}_2\text{I}_3$ owing to larger SOC coming from the Se atom as compared to

the S atom. We also note that $\mathbf{k}\cdot\mathbf{p}$ model spin textures may deviate from the DFT spin textures far from the Y point since the model is applicable only in the immediate proximity of the Y point. Interestingly, spin textures for CB and VB are nearly $\mathbf{k}$ -independent near $k_x = \pm 0.1\text{\AA}^{-1}$ [see dashed regions in Figs. 3.8(e) and 3.8(f)]. Such quasi-persistent spin textures promise nondephasing spin transport through persistent spin helix mechanism [217, 54]. Additionally, these spin textures are reversal through polarization switching with an energy barrier of 35 meV/atom.

3.4 Summary and outlook

We have performed the relativistic first-principles DFT calculations to study RD effects in ferroelectric rhombohedral phases of KIO with $R3m$ and $R3c$ space group symmetries. Ferroelectric and electronic properties are explored using DFT, which are also supported by symmetry-adapted $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian. Near the VBM and CBM, states are mainly derived from I-5p and O-2p orbitals. A sufficiently wide and slightly indirect band gap is calculated for $R3m$ (2.24 (PBE+SOC), 3.27 eV (HSE06+SOC)) and $R3c$ (2.65 (PBE+SOC), 3.80 eV (HSE06+SOC)) phases. Due to a significant amount of SOC, spin splitting effects are observed at both the VBM and CBM around k -points A and Γ for $R3m$ and $R3c$ phases, respectively. Helical-type in-plane spin texture confirms that the spin splitting mainly consists of Rashba-type splitting. Out of plane spin texture shows importance of cubic terms in model Hamiltonian. Two-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian satisfying C_{3v} symmetry reproduces band structure and spin texture near the CBM and VBM, that are well in agreement with the DFT results. In $R3c$ phase, the inclusion of four bands in Hamiltonian incorporating orbital DOF becomes important for complete analysis of spin splitting. Novel spin textures observed in $R3c$ phase are anomalous in sense that they differ from usual spin textures and can not be treated as linear Rashba, linear Dresselhaus or some unique combination of both. The largest Rashba coefficient is found for the CBM in $R3m$ phase. Furthermore, we have investigated the effect of strain on RD parameters and found that they increase linearly with strain. Control of spin-based properties using the external electric field makes it suitable for spintronics applications. The larger Rashba coefficient in comparison to other contemporary materials (viz. BAO and LaWN_3) makes KIO a promising addition into this class of material having Rashba-based applications. We have also investigated the spin splitting properties of chalcogenide Perovskite-Inspired Materials (PIMs)

($\text{Sn}_2\text{SbX}_2\text{I}_3$; $X = \text{S, Se}$). We observed that SOC significantly affects the electronic structure in these chalcogenide PIMs. The calculated effective masses of electrons are found to be small, suggesting good charge carrier mobility. The $Cmc2_1$ phase of $\text{Sn}_2\text{SbX}_2\text{I}_3$ ($X = \text{S, Se}$) shows Rashba and Dresselhaus effects, with the former being more dominant for CB splitting.

Symmetry-protected persistent spin textures in full-zone and full-plane with cubic splittings

4.1 Introduction

The momentum dependent spin splittings are well explained by linear Rashba (LR), linear Dresselhaus (LD) or some unique combination of LR and LD [19, 21]. In linear spin splitting including LR or LD, energy levels are dispersed with crystal momentum ($\mathbf{k}$) having the relation $E_{\mathbf{k}} = \alpha \mathbf{k}^2 \pm \tau \mathbf{k}$, where α and τ are the effective mass and linear splitting terms, respectively. The LR and LD can be described by SOC perturbed Hamiltonians, $H_{LR} = \alpha_R(\sigma_x k_y - \sigma_y k_x)$ and $H_{LD} = \alpha_D(\sigma_x k_y + \sigma_y k_x)$, respectively [19]. Here, α_R and α_D are the constants signifying the strength of LR and LD effects, respectively, and σ_i ($i = x, y, z$) are the Pauli matrices. However, the SOF arising from LR or LD will introduce spin dephasing mechanisms, limiting the experimental realization of spin currents. The persistent spin texture (PST), where spin configurations become independent of the crystal momentum ($\mathbf{k}$), enables a route to overcome spin dephasing and provides non-dissipative spin transport [21, 25, 27]. In the regime of linear splitting, PST can be obtained by tuning the strength of LR and LD effects, such that they compensate each other ($\alpha_R = \alpha_D$). In addition, PST with linear spin splitting can also be enforced by nonsymmorphic space group symmetry of the crystal and, therefore, not easily broken [21]. In recent times, cubic Rashba (CR) and cubic Dresselhaus (CD) effects have started to gain scrutiny owing to their unique benefits to spin transport like larger spin Hall conductivity as compared to linear spin splitting effects [29]. The purely cubic effects (CR or CD) can be distinguished from linear effects (LR or LD) by dispersion curve $E_{\mathbf{k}} = \alpha \mathbf{k}^2 \pm \eta \mathbf{k}^3$ [Fig. 4.1(a)]. The CR and CD effects are described by the SOC Hamiltonians given by, $H_{CR} = (k_x - ik_y)^3(\sigma_x + i\sigma_y) - (k_x + ik_y)^3(\sigma_x - i\sigma_y)$ and $H_{CD} = (k_x k_z^2 - k_x k_y^2)\sigma_x + (k_y k_x^2 -$

$k_y k_z^2 \sigma_y + (k_z k_y^2 - k_z k_x^2) \sigma_z$, respectively. The crucial experimental discoveries related to CR contain SrTiO₃(001) surface [29], asymmetric oxide heterostructure LaAlO₃/SrTiO₃/LaAlO₃, strained-Ge/SiGe quantum well and surfaces of antiferromagnets GdIr₂Si₂ and TbRh₂Si₂.

Recently, symmetry enforced purely cubic splitting (PCS) was predicted for bulk materials by deriving the two-band $\mathbf{k}, \mathbf{p}$ model of all 21 polar point group symmetries, having C_{3h} , D_{3h} and T_d ($\bar{6}$, $\bar{6}m2$ and $\bar{4}3m$ in Hermann-Mauguin notation) as the associated point group symmetries [129]. However, splitting in T_d point group corresponds to trivial CD, which can be seen in zinc-blende type crystal structures. In addition, it was also shown that the crystals with C_{3h} and D_{3h} point group symmetries show PST with PCS around the Γ point [Fig. 4.1(b)]. These types of PSTs are preserved by the symmetry and thus, are robust to spin-independent impurities and not easily get destroyed. These findings are reported for Ge₃Pb₅O₁₁, Pb₇Br₂F₁₂ and Pb₇Cl₂F₁₂ having $P\bar{6}$ space group symmetry (with C_{3h} associated point group symmetry) [129]. However, Ge₃Pb₅O₁₁ is only stable at temperatures above 450 K, and conduction band minima (CBM) of Pb₇Br₂F₁₂ and Pb₇Cl₂F₁₂ do not lie in the vicinity of Γ point [129]. Alongside these limitations, the presence of toxic element Pb is also a concern. Therefore, finding novel materials which can circumvent these limitations is essential.

4.2 Cubic-ordered full-plane PSTs in hexagonal bulk materials

In this section, using state-of-the-art first-principles based DFT calculations, duly supplemented with the effective model Hamiltonian obtained using the $\mathbf{k}, \mathbf{p}$ invariant approach, we reveal the PCS in a large family of materials with D_{3h} point group symmetry. We find that the in-plane mirror and three-fold rotation symmetry of the crystal lead to the PCS around Γ and A points in the BZ. In addition, the PSTs are observed in a larger region and preserved in whole Γ –M–K plane [see Figs. 4.1(c)–4.1(d) for the plane]. More importantly, K₃Ta₃B₂O₁₂ shows large spin splitting of CBs around the Γ , M, and A points. Our calculations also show that magnitude of the spin splitting can be tuned with the application of uniaxial strain preserving the full-plane PST.

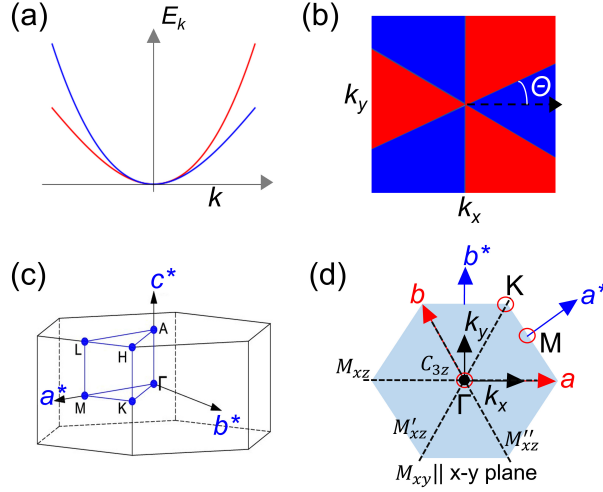


Figure 4.1: (a) Schematic illustration of band structure due to purely cubic spin splitting. Here, the band energies E_k vary with k in the form, $E_k = \alpha k^2 \pm \eta k^3$. (b) Schematic PST due to cubic spin splittings. The color represents the out-of-plane (z -) component of spin textures (note that in-plane (x -, y -) spin components are zero). Here, the red and blue colors denote the spins in the state $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively. Here, $|\uparrow\rangle$ and $|\downarrow\rangle$ are the eigenstates of σ_z with eigenvalues $+1$ and -1 , respectively. Θ is the angular difference between line separating the sectors with eigenvalues $+1$ and -1 , and $k_y = 0$. (c) First BZ of the hexagonal structure. Blue lines highlight the path used for band structure calculation. (d) BZ of the hexagonal structure within the $(k_x - k_y)$ plane, where k_x and k_y are the cartesian reciprocal lattice vectors. The lattice vectors are denoted by a and b , whereas the reciprocal ones are represented by a^* and b^* , respectively. The symmetry elements (C_{3z} , M_{xy} and M_{xz}) of the D_{3h} point group are also shown. The black solid dot and dashed lines represent the rotation axis and mirror planes, respectively.

4.2.1 Symmetry analysis and electronic band structures

We have screened lead-free experimentally synthesized non-magnetic materials having band gap greater than 1.0 eV with space groups $P\bar{6}$, $P\bar{6}m2$, $P\bar{6}2m$, $P\bar{6}2c$ and $P\bar{6}c2$, from AFLOW [218] and Materials Project [219] data repositories. There is rather a large family of materials which crystallize in these space groups, and can show PST with PCS. In particular, we are interested in materials, which are dynamically stable, have suitable band edge positions, wide band gap and exhibit giant splitting. Therefore, we have particularly focused on $K_3Ta_3B_2O_{12}$ ($P\bar{6}2m$), $KTaGe_3O_9$ ($P\bar{6}c2$) with D_{3h} point group symmetry and $Sr_7Br_2H_{12}$ ($P\bar{6}$) with C_{3h} point group

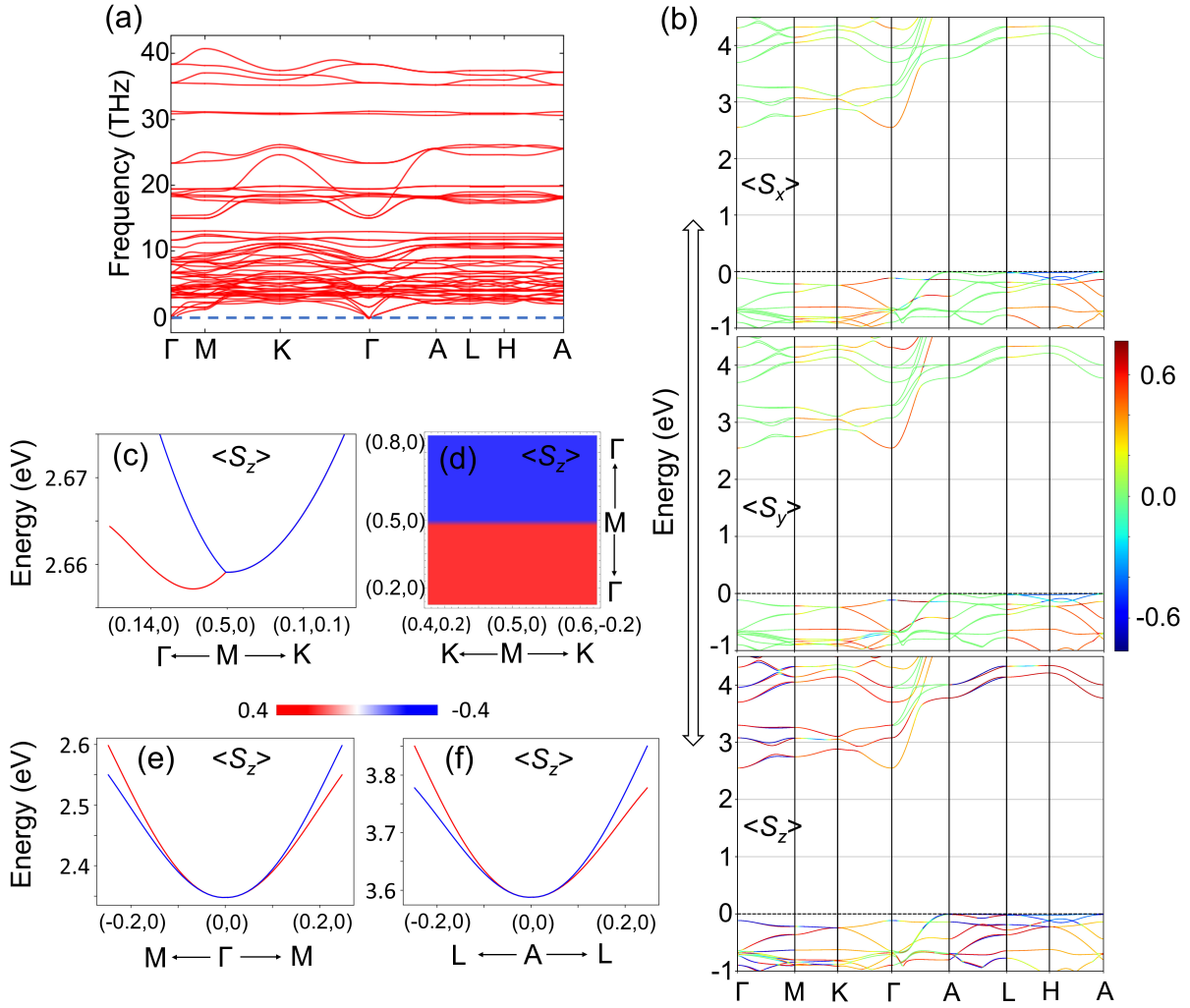


Figure 4.2: (a) Calculated phonon dispersion for $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$. (b) Spin-resolved band structures along high-symmetry-path are shown. The color bar indicates the expectation values of the S_x , S_y and S_z spin components. (c) The calculated spin-resolved band structure of lower CBs along the path $K-M-\Gamma$. (d) Spin texture of lower CB around the M point in $k_z = 0$ plane. Note that there should be two spin-textures associated with two bands. Here, the only one branch associated with the outer band is shown. The inner branch has an opposite spin orientation with respect to outer branch at every (k_x, k_y) point. The spin resolved band structures around (e) Γ point (along $M-\Gamma-M$) and (f) A point (along $L-A-L$). The k -point (k_x, k_y) ranges considered to compute the band structure and spin textures around the high symmetry point are indicated in the units of reciprocal lattice vectors $(\frac{2\pi}{|a|}, \frac{2\pi}{|b|})$, where a and b are the real lattice vectors.

symmetry. The symmetry elements of D_{3h} point group are shown in Fig. 4.1(d). The three-fold rotation axis along z -direction (C_{3z}), the vertical mirror plane containing the x -axis (M_{xz}) and the horizontal mirror plane perpendicular to the z -axis (M_{xy}) generate the D_{3h} point group. The C_{3h} point group is subgroup of D_{3h} and contains C_{3z} and M_{xy} as symmetry elements. Our relaxed crystal structures are in good agreement with the experimentally synthesized crystal structures. The calculated lattice parameters (a , c) deviate from experimental ones [220, 221, 222] by (1.2%, 1.2%), (0.3%, 2.1%) and (1.5%, 1.4%) for $K_3Ta_3B_2O_{12}$, $KTaGe_3O_9$ and $Sr_7Br_2H_{12}$, respectively. Subsequently, the dynamical stability of these materials is tested by analyzing their phonon spectra. Figure 4.2(a) shows the phonon spectrum for $K_3Ta_3B_2O_{12}$ along the high-symmetry-path given in Fig. 4.1(c). The absence of negative frequencies in the phonon dispersion plots confirms the dynamical stability of these structures at low temperature.

After that, we have calculated the band structures using PBEsol ϵ_{xc} functional with inclusion of SOC. Figure 4.2(b) shows spin projected band structures of $K_3Ta_3B_2O_{12}$. A band gap of 2.51 eV is calculated with CBM and valence band maximum (VBM) at Γ and A points, respectively. Since PBEsol is known to underestimate the band gap, we have also calculated the band gap using more sophisticated hybrid ϵ_{xc} functional HSE06. The obtained band gap using HSE06 ϵ_{xc} functional is 4.01 eV. Similarly, we have also calculated band gaps of $KTaGe_3O_9$ and $Sr_7Br_2H_{12}$. The HSE06 band gaps come out to be 4.74 eV and 4.84 eV for $KTaGe_3O_9$ and $Sr_7Br_2H_{12}$, respectively.

4.2.2 Spin splitting and effective $k.p$ Hamiltonian

Inclusion of SOC leads to splitting of bands throughout the BZ. In $K_3Ta_3B_2O_{12}$, splitting is predominantly present for lower CB along Γ –M, A–L directions [Fig. 4.2(b)] and nearly absent for upper VB. This is due to the fact that lower CB mainly consists of heavier Ta-5d orbitals, whereas O-2p orbitals contribute to upper VB. Along the path Γ –M–K– Γ ($k_z = 0$ plane), the band dispersion is entirely specified by the S_z component. On the contrary, the in-plane (S_x, S_y) spin component is almost absent along that path. The observed PST is distinct from the widely observed PST, which occurs locally around specific k -points or along lines of first BZ. The in-plane mirror symmetry of crystal (M_{xy}) enforces spin components to satisfy the relation $(S_x, S_y, S_z) \rightarrow (-S_x, -S_y, S_z)$, leading to zero in-plane components. This leads to out-of-plane SOF, which is considered to be the z -axis. Figures 4.2(c) and 4.2(d) show the CBs and associated spin textures near the M point, respectively. The split bands are predominantly

Table 4.1: The transformations of $(\sigma_x, \sigma_y, \sigma_z)$ and (k_x, k_y, k_z) under the generators of the C_{2v} , D_{3h} , and C_{3h} point group and time-reversal operator (T). The first row shows the point group operations and the corresponding point group symmetries. The last row shows the symmetry invariant terms. Note that we have included the terms upto cubic in $\mathbf{k}$ and higher order contributions are found to be insignificant.

Operations	$C_{3z} = e^{-i\pi/3\sigma_z}$ (D_{3h}, C_{3h})	$M_{xz} = i\sigma_y$ (D_{3h}, C_{2v})	$M_{xy} = i\sigma_z$ (D_{3h}, C_{3h}, C_{2v})	$T = i\sigma_y K$
k_x	$-k_x/2 + \sqrt{3}k_y/2$	k_x	k_x	$-k_x$
k_y	$-\sqrt{3}k_x/2 - k_y/2$	$-k_y$	k_y	$-k_y$
k_z	k_z	k_z	$-k_z$	$-k_z$
σ_x	$-\sigma_x/2 + \sqrt{3}\sigma_y/2$	$-\sigma_x$	$-\sigma_x$	$-\sigma_x$
σ_y	$-\sqrt{3}\sigma_x/2 - \sigma_y/2$	σ_y	$-\sigma_y$	$-\sigma_y$
σ_z	σ_z	$-\sigma_z$	σ_z	$-\sigma_z$
Invariants	$(k_x\sigma_y - k_y\sigma_x),$ $k_y(3k_x^2 - k_y^2)\sigma_z,$ $k_x(k_x^2 - 3k_y^2)\sigma_z$	$k_i^m k_y \sigma_x, k_i^m k_y \sigma_z,$ $k_i^m k_x \sigma_y, k_i^m k_z \sigma_y$ ($i = x, y, z; m = 0, 2$)	$k_i^m k_x \sigma_z, k_i^m k_y \sigma_z,$ $k_i^m k_z \sigma_x, k_i^m k_z \sigma_y$ ($i = x, y, z; m = 0, 2$)	$k_i \sigma_j$ ($i, j = x, y, z$)

linear in $\mathbf{k}$. For deeper insights, the band dispersion can be deduced by identifying all the symmetry allowed terms such that $H(\mathbf{k}) = O^\dagger H(\mathbf{k}) O$, where O is operations belonging to little group of high-symmetry-point and time-reversal (T) [223]. The invariant Hamiltonian need to satisfy the condition given below

$$H_G(\mathbf{k}) = D(O)H(O^{-1}\mathbf{k})D^{-1}(O), \quad \forall O \in G, T \quad (4.1)$$

where $D(O)$ is the representation of operation O . The little group of M point is C_{2v} , consisting of mirror planes M_{xz} and M_{xy} besides identity operation (E). The $\mathbf{k}, \mathbf{p}$ Hamiltonian around the M point, following the transformation rules listed in Table 4.1, is given by [19]

$$H_{C_{2v}}(\mathbf{k}) = H_0(\mathbf{k}) + \gamma k_y \sigma_z + \delta k_z \sigma_y \quad (4.2)$$

where $H_0(\mathbf{k})$ is the part of Hamiltonian describing the band dispersion, depending on the parameter α and β as:

$$H_0(\mathbf{k}) = E_0 + \alpha k_x^2 + \beta k_y^2 \quad (4.3)$$

α and β are connected to the effective masses (m_x^* , m_y^*) with expressions $|\alpha| = \frac{\hbar^2}{2m_x^*}$ and $|\beta| = \frac{\hbar^2}{2m_y^*}$, respectively. γ and δ are the linear SOC splitting coefficients. For dispersion relation in $(k_x - k_y)$ plane around M point, Eq. 4.2 takes the form

$$H_{C_{2v}}(\mathbf{k}) = H_0(\mathbf{k}) + \gamma k_y \sigma_z \quad (4.4)$$

The eigenstates corresponding to Eq. 4.4 are given by

$$\Psi_{\mathbf{k}\uparrow} = e^{i\mathbf{k}\cdot\mathbf{r}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (4.5)$$

and

$$\Psi_{\mathbf{k}\downarrow} = e^{i\mathbf{k}\cdot\mathbf{r}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (4.6)$$

The corresponding eigenvalues are given as

$$E_{C_{2v}}^{\pm}(\mathbf{k}) = E_0 + \alpha k_x^2 + \beta k_y^2 \pm \gamma k_y \quad (4.7)$$

The spin textures determined by the expression $S_{\pm} = \frac{\hbar}{2} \langle \Psi_{\mathbf{k}\uparrow,\downarrow} | \sigma | \Psi_{\mathbf{k}\uparrow,\downarrow} \rangle$ are given as

$$S_{\pm} = \pm \frac{\hbar}{2} (0, 0, 1) \quad (4.8)$$

Eq. 4.8 shows that only S_z component is present around M point agreeing with DFT spin texture [Fig. 4.2(d)]. By fitting the DFT band structure and spin texture around the M point, we find that $\gamma = 3.11$ eVÅ. This splitting is significantly larger as compared to other bulk systems such as in BiTeCl ($\alpha_R = 1.2$ eVÅ) [224], BiAlO₃ ($\alpha_R = 0.74$ eVÅ) [22] and LaWN₃ ($\alpha_R = 2.7$ eVÅ) [181, 225].

Figure 4.2(e) shows the splitting around Γ point. The spin split bands around Γ are purely cubic in $\mathbf{k}$ with only z -component being non-vanishing [see Fig. 4.2(b)]. The splittings around the Γ points can be understood in terms of effective $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian. Here, the little group of wave vector of Γ point remains the D_{3h} , containing identity (E), C_{3z} and four mirror planes (M_{xy} , M_{xz} , M'_{xz} and M''_{xz}). The symmetry-adapted Hamiltonian for $(k_x - k_y)$ can be expressed as (see Table 4.1)

$$H_{D_{3h}}(\mathbf{k}) = H_0(\mathbf{k}) + \lambda k_y (3k_x^2 - k_y^2) \sigma_z \quad (4.9)$$

where, λ is the cubic SOC splitting coefficient. The eigenstates corresponding to this Hamiltonian are $\Psi_{\mathbf{k}\downarrow}$ and $\Psi_{\mathbf{k}\uparrow}$. The cubic split eigenvalues of Equation 4.9, are obtained as

$$E_{D_{3h}}^{\pm}(\mathbf{k}) = E_0 + \alpha k_x^2 + \beta k_y^2 \pm 3\lambda k_x^2 k_y \mp \lambda k_y^3 \quad (4.10)$$

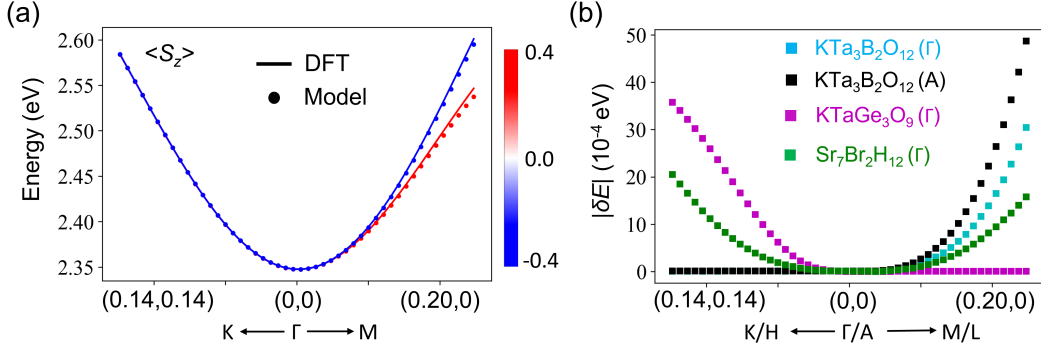


Figure 4.3: (a) CBs of $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ around the Γ point projected over z -component of spin direction. (b) Spin splitting energies (δE) of $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ (CBM), KTaGe_3O_9 (VBM) and $\text{Sr}_7\text{Br}_2\text{H}_{12}$ (VBM). Band structure and δE are plotted along $(\frac{2\pi}{a}0.14, \frac{2\pi}{b}0.14) - (0,0) - (\frac{2\pi}{a}0.14, 0)$ direction of the momentum space, which is along $\text{K(H)} - \Gamma(\text{A}) - \text{K(M)}$ direction. The δE defines the energy different between spin-up and spin-down bands.

The expectation values for the spin operators are the same as given by Equation 4.8, confirming the unidirectional spin texture around Γ point. Note that the Hamiltonian given by Equation 4.9 depends upon the choice of coordinate system and is valid only for space groups $P\bar{6}2m$ and $P\bar{6}2c$. The symmetry allowed term for D_{3h} point group associated with $P\bar{6}m2$ and $P\bar{6}c2$ is $\zeta k_x(k_x^2 - 3k_y^2)\sigma_z$ instead of $\lambda k_y(3k_x^2 - k_y^2)\sigma_z$. This is particularly due to the fact that mirror operation present in $P\bar{6}m2$ and $P\bar{6}c2$ is M_{yz} instead of M_{xz} . Additionally, $P\bar{6}$ space group is linked to the C_{3h} point group and at Γ point, little group remains C_{3h} . The effective two-band Hamiltonian following the transformation rules given in Table 4.1, upto the third order in $\mathbf{k}$ in the $(k_x - k_y)$ plane is given by [129]

$$H_{C_{3h}}(\mathbf{k}) = H_0(\mathbf{k}) + \zeta k_x(k_x^2 - 3k_y^2)\sigma_z + \lambda k_y(3k_x^2 - k_y^2)\sigma_z \quad (4.11)$$

and the corresponding energy eigenvalues with eigenstates ($\Psi_{\mathbf{k}\uparrow}, \Psi_{\mathbf{k}\downarrow}$) are

$$E_{C_{3h}}^{\pm}(\mathbf{k}) = E_0 + \alpha k_x^2 + \beta k_y^2 \pm \zeta k_x^3 \pm 3\lambda k_x^2 k_y \mp 3\zeta k_y^2 k_x \mp \lambda k_y^3 \quad (4.12)$$

The additional cubic splitting term with coefficient ζ arises for C_{3h} point group, because the symmetry is reduced as compared to the D_{3h} . The Bloch states $\Psi_{\mathbf{k}\uparrow}$ and $\Psi_{\mathbf{k}\downarrow}$ are the eigenstates of σ_z leading to zero in-plane (S_x, S_y) spin polarization around Γ and M points. The S_z component of polarization is non-vanishing, leaving to PST over full $\Gamma - \text{M} - \text{K}$ plane in $P\bar{6}$, $P\bar{6}m2$, $P\bar{6}2m$, $P\bar{6}2c$ and $P\bar{6}c2$ space group materials. The splitting observed around M and Γ points

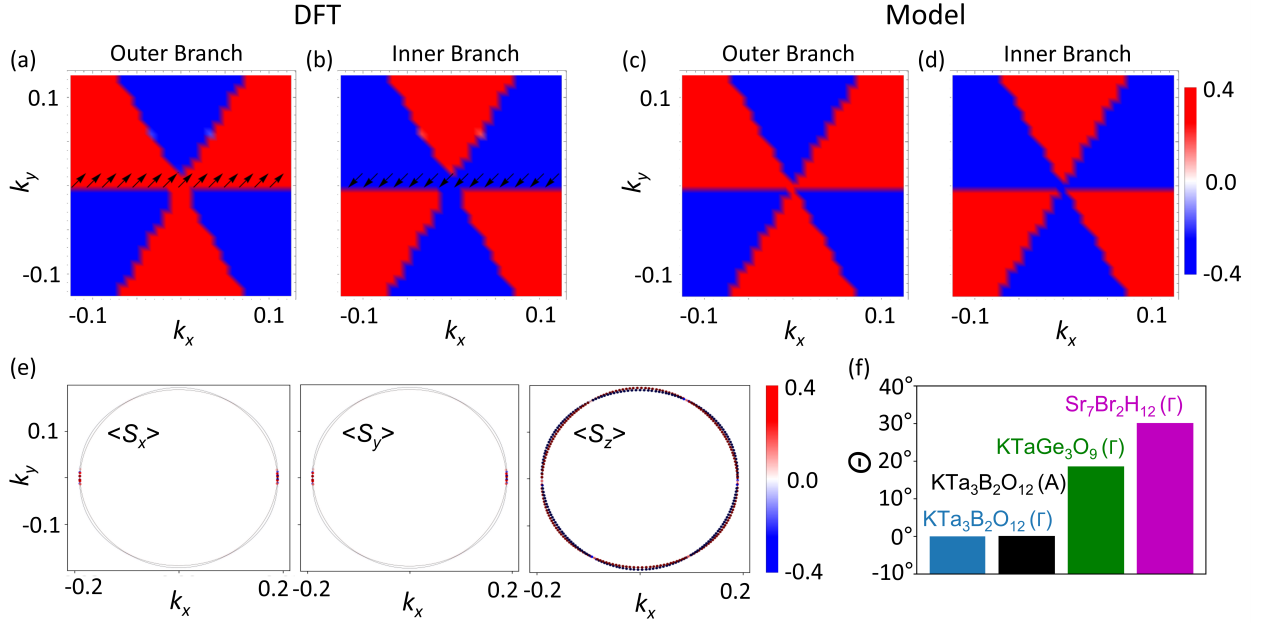


Figure 4.4: Spin textures of the CBs for $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ around the Γ point obtained by DFT [(a)-(b)] and $\mathbf{k} \cdot \mathbf{p}$ model [(c)-(d)]. Our spin textures are prepared using the convention [(a)-(d) as examples] that the energy of the outer branch is smaller or equal as compared to the energy of inner branch at any (k_x, k_y) point in the considered range. (e) Constant energy contours projected over the spin components having energy of $E_F + 2.38$ eV. Here, the red and blue dots denote the spins in the state $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively. (f) The calculated values of Θ for spin textures of $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$, KTaGe_3O_9 and $\text{Sr}_7\text{Br}_2\text{H}_{12}$.

is linear and cubic in nature, respectively. The $\mathbf{k} \cdot \mathbf{p}$ model and DFT give the same nature of spin splitting and textures. It is also worth emphasizing that the above two-band models are also applicable to the other $\mathbf{k}$ -points, whose little group is identical to the Γ or M points. In $P\bar{6}$, $P\bar{6}m2$, $P\bar{6}2m$, $P\bar{6}2c$ and $P\bar{6}c2$ space groups, the little group of A and L points are same as for Γ and M points, respectively. Here, the PST over entire L–A–H high-symmetry-path with PCS is also observed [Figs. 4.2(b) and 4.2(f)].

We have compared the band structures and spin textures of $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ around Γ point with HSE06, PBE, PBEsol and PBE+U (here, U is the Hubbard parameter) ϵ_{xc} functionals to validate the choice of functional. The value of U is taken to be 2.5 eV to include the on-site Coulomb repulsion energy for Ta-5d orbitals, in accordance with previous studies [226]. It is found that all the spin splitting properties except band gap calculated with HSE06, PBE, PBE+U are within $\pm 5\%$ as compared to PBEsol. Therefore, our calculations are based on

computationally efficient PBEsol ϵ_{xc} functional. Firstly, we have calculated the band structure for the split bands along k_x and k_y directions. Then, we have fitted the band structure to $\mathbf{k}\cdot\mathbf{p}$ model and the results are shown in Fig. 4.3(a) for $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$. Our model fits the DFT band structure very well. The observed splitting is found to be highly anisotropic and depends upon the space group symmetry of the material. The bands are spin split along Γ –M direction and degenerate along Γ –K direction. Anisotropic effective mass could lead to the anisotropic splitting, but in our case, the effective mass is observed to be isotropic in both Γ –K and Γ –M directions. To further analyze the anisotropy, we have plotted the magnitude of the energy difference ($|\delta E| = |E(k, \uparrow) - E(k, \downarrow)|$) between the split bands [see Fig. 4.3(b)]. The splitting is completely absent in Γ –K and A–H directions for $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ and Γ –M direction for KTaGe_3O_9 . The splitting for $\text{Sr}_7\text{Br}_2\text{H}_{12}$ is present along both Γ –M and Γ –K directions with different magnitudes. The different contributions coming from the terms with splitting coefficients ζ and λ lead to anisotropic splitting along Γ –M and Γ –K directions.

Furthermore, the spin textures around the Γ and A point for the considered systems are also obtained using DFT and $\mathbf{k}\cdot\mathbf{p}$ models. Figures 4.4(a) and 4.4(b) are the obtained spin textures of $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ around Γ point. The spin textures are momentum ($\mathbf{k}$) independent with non-zero out-of-plane components with a mere in-plane component around Γ point in $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$. Figures 4.4(c) and 4.4(d) show the spin textures calculated using $\mathbf{k}\cdot\mathbf{p}$ model and are in accordance with the DFT results. It is interesting to note that the spin textures of considered configurations are different from each other. The border lines separating the $+|s_z|$ and $-|s_z|$ sectors vary with materials under consideration. To understand this, the spin-projected constant energy contours of inner and outer bands are computed as shown in Fig. 4.4(e). Here, by spin-projected means expectation values of spin operators are computed for each k -point on constant energy contours. In fact, the border lines are the directions along which the energies of two bands with opposite spins become equal [Fig. 4.4(e)]. We have introduced the parameter Θ to distinguish the spin textures, as shown in Fig. 4.1(b). These directions can be estimated from $\mathbf{k}\cdot\mathbf{p}$ models by evaluating the $\Theta = \tan^{-1}(k_y/k_x)$ with $k_x \geq 0$ and given by

$$\tan(\Theta) = \begin{cases} -\frac{\zeta}{\lambda} - \frac{(\zeta^2 + \lambda^2)^{2/3}}{\lambda(\zeta + i|\lambda|)^{1/3}} - \frac{(\zeta^2 + \lambda^2)^{1/3}(\zeta + i|\lambda|)^{1/3}}{\lambda} \\ -\frac{\zeta}{\lambda} + \frac{(1-i\sqrt{3})[(\zeta^2 + \lambda^2)^{1/3}(\zeta + i|\lambda|)^{1/3}]}{2\lambda} + \frac{(1+i\sqrt{3})(\zeta^2 + \lambda^2)^{2/3}}{2\lambda(\zeta + i|\lambda|)^{1/3}} \\ -\frac{\zeta}{\lambda} + \frac{(1+i\sqrt{3})[(\zeta^2 + \lambda^2)^{1/3}(\zeta + i|\lambda|)^{1/3}]}{2\lambda} + \frac{(1-i\sqrt{3})(\zeta^2 + \lambda^2)^{2/3}}{2\lambda(\zeta + i|\lambda|)^{1/3}} \end{cases} \quad (4.13)$$

Figure 4.4(f) shows Θ for the considered configurations. It is found to be consistent with DFT

Table 4.2: The materials showing PCS with PST along with their parameters of Equation 4.11. The splitting is observed for lower CBs (CB) or higher VBs (VB) around the high-symmetry-points (HSP) Γ and A.

Materials	CB/VB	HSP	E_0 (eV)	α (eVÅ ²)	ζ (eVÅ ³)	λ (eVÅ ³)	Ref
BaHfSi ₃ O ₉	VB	Γ	-0.19	3.05	0.65	0.00	
BiTa ₇ O ₁₉	VB	Γ	0.00	-3.79	2.35	0.00	
BiTa ₇ O ₁₉	CB	Γ	2.82	-1.20	0.55	0.00	
LaTa ₇ O ₁₉	VB	Γ	-0.19	-3.28	0.95	0.00	
LaTa ₇ O ₁₉	CB	Γ	3.56	-1.23	9.55	0.00	
KCaP ₃ O ₉	VB	Γ	-0.15	1.96	0.85	0.00	
KMgP ₃ O ₉	VB	Γ	-0.19	2.13	1.00	0.00	
KTaGe ₃ O ₉	VB	Γ	-0.35	1.44	8.05	0.00	
RbNbGe ₃ O ₉	VB	Γ	-0.11	1.26	4.30	0.00	
TlTaGe ₃ O ₉	VB	Γ	-0.15	1.59	6.35	0.00	
TlTaGe ₃ O ₉	CB	Γ	3.58	1.86	1.52	0.00	This work
K ₃ Ta ₃ B ₂ O ₁₂	CB	Γ	2.34	5.04	0.00	6.85	
K ₃ Ta ₃ B ₂ O ₁₂	CB	A	5.37	5.05	0.00	8.13	
K ₄ Au ₆ S ₅	VB	Γ	0.00	-0.95	0.00	5.55	
K ₄ Au ₆ S ₅	CB	Γ	1.62	8.07	0.00	2.01	
RbS	VB	Γ	0.00	-0.91	0.00	1.06	
W ₆ CCl ₁₈	CB	Γ	1.04	0.51	0.00	9.10	
Sr ₇ Cl ₂ H ₁₂	VB	Γ	0.00	-1.13	2.35	1.80	
Sr ₇ Br ₂ H ₁₂	VB	Γ	0.00	-1.07	3.21	2.45	
Pb ₇ Br ₂ F ₁₂	CB	A	3.43	-3.11	-0.91	-4.36	
Pb ₇ Cl ₂ F ₁₂	CB	A	3.63	5.11	1.23	8.18	
Pb ₇ Br ₂ F ₁₂	CB	Γ	3.76	-1.11	-2.92	-5.04	
Pb ₇ Cl ₂ F ₁₂	CB	Γ	3.98	-2.08	1.75	8.65	[129]
Ge ₃ Pb ₅ O ₁₁	CB	Γ	2.13	1.27	-5.24	-3.43	

results. The angular difference between any two border lines of spin textures is calculated to be 60°, leading to the threefold rotation symmetry, which is in line with the threefold rotation

symmetry of the crystal. Our calculations show that there is rather a big class of materials that support PST with PCS. All of these materials along with the calculated parameters are reported in Table 4.2. Table 4.2 also includes the already reported parameters of Ge₃Pb₅O₁₁, Pb₇Cl₂F₁₂ and Pb₇Br₂F₁₂ for comparison. The splitting observed around Γ point for K₃Ta₃B₂O₁₂ ($\lambda = 6.85 \text{ eV}\text{\AA}^3$) is larger as compared to Ge₃Pb₅O₁₁ ($\chi = -5.24 \text{ eV}\text{\AA}^3$), Pb₇Br₂F₁₂ ($\lambda = -5.04 \text{ eV}\text{\AA}^3$) and comparable to Pb₇Cl₂F₁₂ ($\lambda = 8.65 \text{ eV}\text{\AA}^3$). The splitting in K₃Ta₃B₂O₁₂ around A point is $\lambda = 8.13 \text{ eV}\text{\AA}^3$, larger than that around Γ point. Note that orbitals contribution determines whether the PSTs with significant splitting occurs in the VB or CB. Giant splitting occurs when the heavy atom orbitals contribute for the splitting bands. For example, splitting of VB is nearly absent as compared to CB in K₃Ta₃B₂O₁₂, since the mostly O-2p contribute for VB. The magnitude of splitting in these materials can be further increased by doping heavier elements with large SOC [227] and introducing strain [184, 228, 85] to make its experimental detection more easily accessible (i.e., spin-resolved photoemission spectroscopy).

4.3 Coupled spin-valley physics and full-zone PSTs in 2D WSi₂N₄ family

The advancement in 2D materials also engenders the potential of realizing physical properties desirable in spintronics and valleytronics. In condensed matter physics, discussion of the symmetry in crystalline solids plays a pivotal role in understanding the physical properties. For instance, inversion and time-reversal symmetry together force the bands to be doubly degenerate throughout the BZ. The coupling of inversion symmetry breaking with SOC lifts the band degeneracy mainly through Rashba and Dresselhaus (RD) effects. However, if time-reversal symmetry breaks along with inversion symmetry breaking, the spin-valley effects are induced. The presence of well-separated multiple energy extremal points in momentum-space, generally referred to as valleys, constitutes a binary index for low energy carriers [37]. Therefore, it can be exploited for information processing and encoding. The lifting of band degeneracy results in non-trivial momentum-dependent spin textures, which are mainly governed by the type of splitting. In general, the SOC introducing these spin splitting effects, also introduces two kinds of spin dephasing mechanisms, viz. Dyakonov-Perel [229] and Elliot-Yafet [230] mechanisms. One of the possible ways to overcome these spin dephasing mechanisms is persistent spin texture (PST), in which spin directions become independent of the crystal momentum ($\mathbf{k}$) [27].

PST is obtained by trading off the strength of the linear RD effects in heterostructures and surfaces. It has also been shown that non-symmorphic space group symmetry could be exploited to obtain PST around specific high symmetry points and paths [21]. Also, cubic spin splittings can lead to symmetry-protected PST around the zone center in bulk materials [129]. Analogous to charge, utilizing the spin and valley DOF through the non-dissipative spin transport is a vital ingredient of spintronics and valleytronics.

The 2D MoSi_2N_4 , WSi_2N_4 and MoSi_2As_4 , host massive Dirac fermions with strong spin valley coupling near the corners of BZ. Additionally, the valley fermions manifest valley-contrasting Berry curvature, and valley-selective optical circular dichroism [50, 49, 53]. This can be attributed to the intrinsic broken inversion symmetry coupled with large SOC arising from d -orbitals of transition metal. Under an in-plane electric field, carriers in different valleys drift in opposite directions, leading to the valley Hall effect. MoSi_2N_4 shows exceptional piezoelectricity, photocatalytic water splitting and high carrier mobility of 270-1200 cm^2/Vs , which is better than widely used TMDs [231]. Stacking of MoSi_2N_4 monolayers generates dynamically stable bilayer and bulk materials with thickness-dependent properties [52]. Most of the studies focus on the valley splitting in monolayers around the corners of the BZ. However, the complete analysis of SOC induced spin splitting is still unclear.

This section reports fully relativistic calculations within the framework of DFT on the SOC-driven spin splitting in WA_2Z_4 ($\text{A}=\text{Si, Ge; Z}=\text{N, P, As}$) family. Our calculations are supplemented by the effective $\mathbf{k}\cdot\mathbf{p}$ model derived from the method of invariants. The calculations reveal the PST in the whole region of BZ in a single layer of these materials. The full zone persistent spin texture (FZPST) is protected by the surface inversion symmetry (SIS) $\{(x,y,z)\rightarrow(x,y,-z)\}$. In addition to spin-valley locked splitting around the corners of BZ, we observe a cubic splitting around the center of BZ. Significant splitting around the M point is linear in $\mathbf{k}$, which is found to be complementary to the linear RD effects. It is a well-known fact that SIS hinders the conventional linear Rashba spin splitting which is later observed under the application of out-of-plane electric field. The $\mathbf{k}\cdot\mathbf{p}$ analysis shows that PST along M-K path is robust to the external electric field. It is generally expected that the presence of inversion symmetry in the bulk WSi_2N_4 , causes the spin splitting and polarization to vanish. However, our calculations show the 100% spin polarization of doubly degenerate bands in centrosymmetric bulk and even layered WSi_2N_4 , which are spatially segregated. We demonstrate that such hidden spin polarization arises by the inversion asymmetric site point group of W atom.

Thus, WA₂Z₄ family broaden the pool of promising materials in the fields of spintronics and valleytronics.

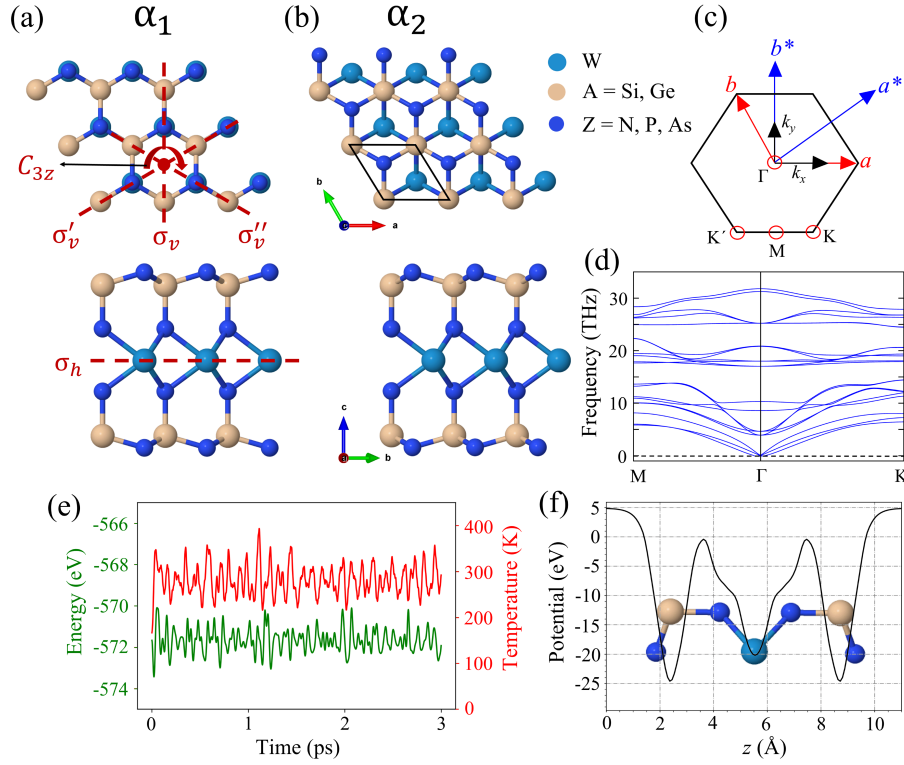


Figure 4.5: Crystal structures of (a) α_1 -WA₂Z₄ and (b) α_2 -WA₂Z₄ monolayers with symmetry operations highlighted using red dashed line. The solid black lines indicate the corresponding unit cell. (c) The first BZ and k -points (Γ , M, K and K') are shown using red circles. (d) The phonon band dispersions of α_2 -WSi₂N₄ monolayer. (e) Variation of total energy and temperature for α_2 -WSi₂N₄ monolayer during AIMD simulation for 3 ps at 300 K. (f) Planar average of the electrostatic potential energy of the α_2 -WSi₂N₄ monolayer as a function of out-of-plane axis.

4.3.1 Crystal structures and stability

The optimized crystal structure of WA₂Z₄ monolayers are shown in Figs. 4.5(a) and 4.5(b), which can be viewed as the WZ₂ layer sandwiched between two A-Z bilayers. Depending on the stacking of A-Z bilayers, different types of crystal structures are possible. Many layered materials are influenced by these stacking effects [232]. In our work, we have considered the two most stable phases i.e., α_1 and α_2 , which differ by the position of N atoms. These two

phases share the same hexagonal lattice structure with space group $P\bar{6}m2$. The associated point group symmetry is D_{3h} , containing identity operation (E), three-fold rotation (C_{3z}) having z as the principal axis, mirror operations perpendicular to principal axis (M_{xy}) and parallel to principal axis (M_{xz}) [Fig. 4.5(a)]. The optimized lattice constants of WA_2Z_4 monolayers are provided in Table 4.3. As expected, the lattice constants increase with increasing atomic number of the group IV and V atoms. Thus, WSi_2N_4 and WGe_2As_4 exhibit the smallest and largest lattice constants i.e., 2.88 Å and 3.63 Å, respectively. The same coordination environment in α_1 and α_2 structures leads to slightly different lattice constants (within 0.5%). Our lattice constants are in well agreement with already reported experimental and theoretical studies [47, 48, 49, 233, 52].

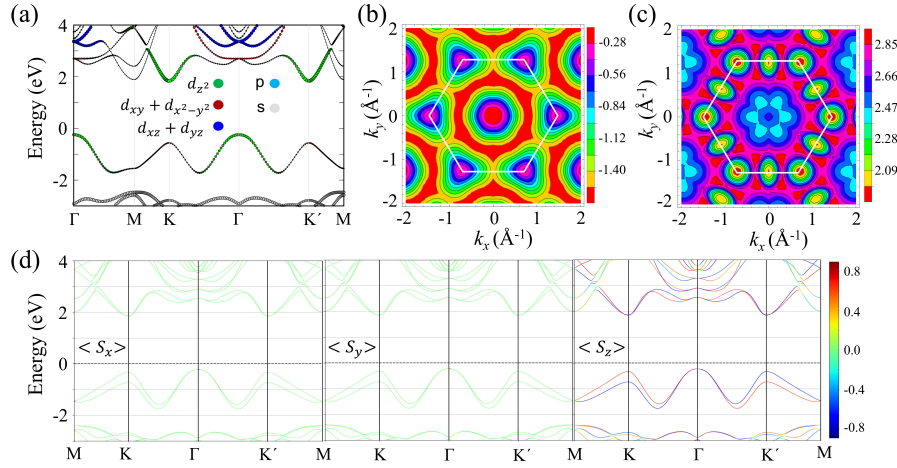


Figure 4.6: (a) Orbital-resolved electronic band structure of α_2 - WSi_2N_4 monolayer without including SOC. Symbol size is proportional to the particular orbital weightage. The constant energy contours of (b) topmost VB and (c) lowest CB in the momentum-space. The white hexagon is the first BZ. (d) Spin-resolved electronic band structure of α_2 - WSi_2N_4 monolayer. The color bar shows the x -, y - and z - components of spin polarization.

To confirm the energy feasibility of WA_2Z_4 monolayers, the formation energy per atom (E_{for}) is calculated as follows

$$E_{for} = \{E_{tot} - (n_W E_W + n_A E_A + n_Z E_Z)\} / (n_W + n_A + n_Z) \quad (4.14)$$

where E_{tot} is the total ground state energy of WA_2Z_4 monolayer. E_W , E_A and E_Z are the chemical potentials of isolated W, A and Z atoms, respectively. n_W , n_A and n_Z are the total number of W, A and Z atoms in the unit cell, respectively. As seen from Table 4.3, the neg-

Table 4.3: Optimized lattice constant ($a = b$) of the unitcell of WA₂Z₄ monolayers. The calculated formation energy per atom (E_{for}), dipole moment per unit cell (P_y), band gaps without and with SOC using PBE (E_g^{PBE} , $E_g^{PBE+SOC}$) and HSE06 ($E_g^{HSE+SOC}$, $E_g^{HSE+SOC}$). The calculated band gaps using G₀W₀ performed on top of PBE functional with inclusion of SOC (E_g^{GW}).

	Phase	a (Å)	E_{for} (eV)	P_y (eÅ)	E_g^{PBE} (eV)	$E_g^{PBE+SOC}$ (eV)	E_g^{HSE} (eV)	$E_g^{HSE+SOC}$ (eV)	E_g^{GW} (eV)
WSi ₂ N ₄	α_1	2.881	-0.746	1.77	2.33	2.32	3.11	3.09	3.78
	α_2	2.894	-0.772	1.80	2.08	2.06	2.69	2.64	3.36
WGe ₂ N ₄	α_1	2.976	-0.532	1.82	1.68	1.64	2.13	2.05	2.76
	α_2	2.988	-0.543	1.83	1.33	1.31	1.76	1.71	2.38
WSi ₂ P ₄	α_1	3.413	-0.265	2.03	0.94	0.69	1.22	0.85	1.37
	α_2	3.423	-0.252	2.04	0.55	0.32	0.87	0.76	0.93
WGe ₂ P ₄	α_1	3.486	-0.292	2.31	0.70	0.45	0.94	0.56	1.02
	α_2	3.498	-0.273	2.32	0.47	0.23	0.74	0.38	0.73
WSi ₂ As ₄	α_1	3.561	-0.079	2.11	0.78	0.52	1.03	0.60	1.02
	α_2	3.575	-0.060	2.13	0.50	0.22	0.77	0.39	0.67
WGe ₂ As ₄	α_1	3.624	-0.019	2.39	0.60	0.33	0.85	0.38	0.79
	α_2	3.632	-0.017	2.40	0.45	0.16	0.70	0.37	0.63

ative value of E_{for} shows the energy feasibility of WA₂Z₄ monolayers. The WA₂N₄ is most stable in α_2 phase, while α_1 phase has the lowest energy in the case of WA₂P₄ and WA₂As₄, which is consistent with the previous reports [48]. However, some previous studies concern only the α_2 -phase for WA₂P₄ and WA₂As₄ [49, 233, 52]. Therefore, the complete analysis of both phases is more realistic approach. Further, to examine the dynamical stability, we have plotted the phonon dispersion plots for the concerned compounds [see Fig. 4.5(d)]. The unit cell of WA₂Z₄ monolayer consists of seven atoms [see Fig. 4.5(b)]. As a consequence, phonon plots show three acoustic and eighteen optical branches. As the general property of 2D materials, quadratic dispersion is found in out-of-plane ZA mode around the Γ point. The absence of imaginary frequencies in phonon plots confirms the dynamical stability of the WA₂Z₄ monolayers. To further check the room temperature stability, *ab initio* molecular dynamics (AIMD)

simulations are performed at 300 K for 3 ps with a time step of 1 fs [see Fig. 4.5(e)]. The resultant small energy, temperature fluctuations and no structural disruption, confirm the thermal stability of WA_2Z_4 monolayers.

Polarization properties play a critical role in determining the intrinsic electronic properties, therefore, we investigate these effects in WA_2Z_4 . Firstly, charge transfer using Bader techniques is performed. Significant charge transfer is found in these monolayers, where Z atoms receive charge from W and A atoms. Different electronegativities lead to different amount of charge received by different Z atoms. For instance, outer N gets a charge of $2.23 e^-$ from Si, whereas As receives only $0.75 e^-$. Due to SIS, charge transfer is same for the innermost and outermost layers. Therefore, planar average electrostatic potential shown in Fig. 4.5(f) is symmetric along z -direction, centering W atom. Furthermore, the only in-plane electric dipole moment (along y -direction) is observed [Table 4.3].

4.3.2 Electronic structure

As the physics in WA_2Z_4 monolayers is essentially the same, therefore, taking $\alpha_2\text{-WSi}_2\text{N}_4$ as a representative, we investigate the electronic properties of this class of materials. Figure 4.6(a) shows the orbital-projected electronic band structure of $\alpha_2\text{-WSi}_2\text{N}_4$ without SOC calculated using GGA-PBE functional. It has an indirect band gap of 2.08 eV, which is consistent with the previous findings [47, 48, 233, 52]. The W- d orbitals dominate the states near band edges. The VBM at Γ and CBM at K point mainly consist of d_{z^2} orbitals, whereas, d_{xy} and $d_{x^2-y^2}$ contribute to the top valence states at K/K' point. To clearly visualize these two bands, constant energy contours are plotted in momentum-space, as shown in Figs. 4.6(b) and 4.6(c). It is found that the energies near CBM and VBM are elliptically wrapped. On the other hand, energies are triangularly wrapped for the VB around K/K' point, similar to MoS_2 family [37]. In addition to WSi_2N_4 , WGe_2N_4 also has an indirect band gap with band edge positions similar to WSi_2N_4 . On contrary, WA_2P_4 and WA_2As_4 have a direct band gap at K/K' point.

When SOC is included, as seen in Fig. 4.6(d), the band structure is strongly modified and a sizable spin splitting is observed throughout the BZ, which is the consequence of intrinsic inversion symmetry breaking. The band gap of $\alpha_2\text{-WSi}_2\text{N}_4$ decreases to 2.06 eV owing to the SOC induced spin splitting. As PBE is known to underestimate the electronic band gap, the band structures are also calculated using more sophisticated functional HSE06 and G_0W_0 approach. The values of band gaps using different functionals are compared in Table 4.3. To

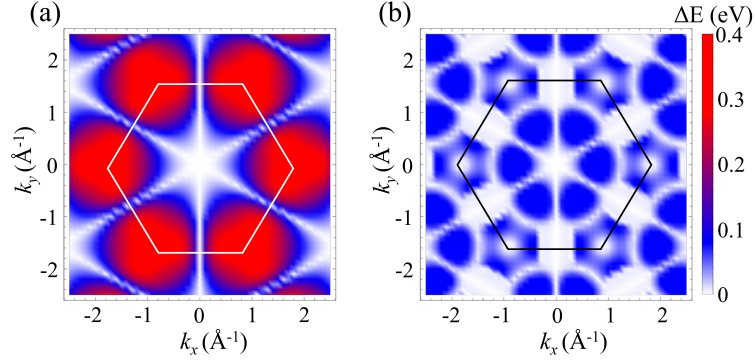


Figure 4.7: The spin splitting ($\Delta E = |E(k, \uparrow) - E(k, \downarrow)|$) of (a) topmost VB and (b) lowest CB mapped over the full BZ.

appraise the optical absorption of WSi₂N₄, we calculate the real and imaginary parts of the dielectric tensor. The dielectric tensor (ϵ) is in-plane isotropic due to the D_{3h} . Therefore, we consider only the ϵ_{xx} by performing BSE calculation on top of G₀W₀@PBE+SOC. The first absorption peak is observed at 2.49 eV, therefore, it is responsive to the energy spectrum in the visible region.

The transport properties of electrons are mainly governed by the conduction and VBs. Figure 4.7 shows spin splitting ($\Delta E = |E(k, \uparrow) - E(k, \downarrow)|$) for the topmost VBs and lowest CBs in the entire momentum-space. Splitting present in the VB is significantly larger as compared to the CB. For this reason, we mainly focus on the VBs. The splitting is observed in the full BZ except for the high symmetry path Γ –M, where the eigenstates are at least two-fold degenerate. The degenerate bands split around the time-reversal invariant Γ and M points. Importantly, spin splitting around M and Γ point is anisotropic in nature. Maximum spin splitting observed around M point is 35 meV along the M–K line, which mainly originates from the strong hybridization of d_{xy} and $d_{x^2-y^2}$ orbitals. Similar features of spin splitting are also observed in the whole WA₂Z₄ family. The DFT results are further examined using symmetry analysis.

4.3.3 Full-zone PST

To better understand the spin splitting properties, we have constructed the 2-band $\mathbf{k}\cdot\mathbf{p}$ model using the method of invariants, which describes the dispersion around Γ , M and K points. The minimal $\mathbf{k}\cdot\mathbf{p}$ model is derived by including the spin DOF. According to Bloch's theorem, the wave function at an arbitrary k-point can be written as:

$$|\Psi_k\rangle = e^{ik\cdot r}|\phi_k(r)\rangle \quad (4.15)$$

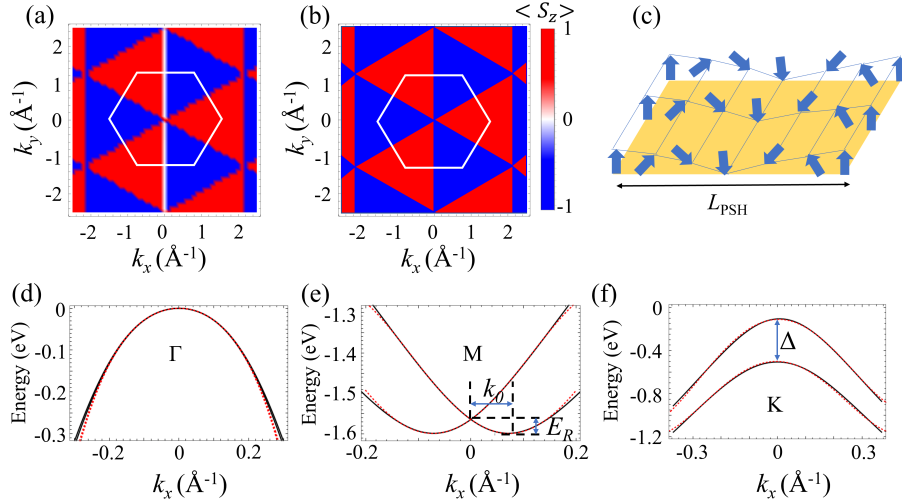


Figure 4.8: The spin textures of topmost VBs associated with the outer branch using (a) DFT and (b) $\mathbf{k}\cdot\mathbf{p}$ models. The energy of the outer branch is smaller or equal as compared to the energy of inner branch at the $\mathbf{k}$ -point in the considered range. (c) Schematic diagram of PSH state. The L_{PSH} represents the wavelength of spatially periodic mode. The band structure of topmost VBs around (d) Γ , (e) M, and (f) K points. Here, the black solid lines and red dots represent the band structure computed using DFT and $\mathbf{k}\cdot\mathbf{p}$ models, respectively.

where $\phi_k(r)$ is the periodic part of the wave function satisfying the crystal symmetry D_{3h} . At the Γ point ($k = 0$), the wave function will have D_{3h} point group symmetry. At other points, symmetry is reduced from the D_{3h} point group due to the phase factor. If we focus on an arbitrary k -point, mirror symmetry operations lead to the transformation of k vectors (Table 4.1) $M_{xy}(k_x, k_y, k_z) = (k_x, k_y, -k_z)$. An arbitrary k -point in the k_x - k_y plane (as in 2D materials) is invariant under M_{xy} . Therefore, the Hamiltonian at an arbitrary k -point will still preserve M_{xy} symmetry, which is crucial to observing persistent spin textures. Other mirror symmetry operations, for example, M_{xz} , are not preserved at an arbitrary k point. In addition, note that other parts of the Hamiltonian (for example, the free-particle Hamiltonian) will also satisfy the underlying symmetry operations.

The little group of Γ point is D_{3h} . The symmetry allowed Hamiltonian considering the terms up to third order in momentum reads as [87]

$$H_{\Gamma}(\mathbf{k}) = H_0(\mathbf{k}) + \lambda k_x(3k_y^2 - k_x^2)\sigma_z. \quad (4.16)$$

The lowest order symmetry allowed splitting term is cubic in $\mathbf{k}$. Around Γ point, bands split along k_x (Γ –K) direction and doubly degenerate along k_y (Γ –M) direction. On the other hand, the little group of M point is C_s , containing the M_{xy} and M_{xz} operations. The effective

$\mathbf{k}, \mathbf{p}$ model for band dispersion around M point is given by

$$H_M(\mathbf{k}) = H_0(\mathbf{k}) + \alpha k_x \sigma_z \quad (4.17)$$

The splitting is linear in $\mathbf{k}$ around M point and can be treated as complimentary to linear Rashba or linear Dresselhaus. In addition, the splitting is strongly anisotropic in nature i.e., bands are degenerate along k_y (M– Γ) direction and are lifted along k_x (M–K) direction. At the K/K' point, associated little group is C_{3h} . Thus, $\mathbf{k}, \mathbf{p}$ model is given by

$$H_K(\mathbf{k}) = H_0(\mathbf{k}) + k_x(3k_y^2 - k_x^2) + \sigma_z[\Delta + \eta(k_x^2 + k_y^2) + \zeta k_x(3k_y^2 - k_x^2)] \quad (4.18)$$

At K/K' point, Zeeman-type splitting in the VB is predicted by the non-zero coefficient Δ in $H_K(\mathbf{k})$. The Δ observed for time-reversal conjugate valleys K/K' is same, whereas, the nature of spin splitting is opposite in nature. The properties which are odd under the time-reversal will have opposite nature at K and K' valleys. The spin polarization is one such feature [Fig. 4.6(d)]. Hence, the spin DOF and valleys are distinctly locked at inequivalent valleys. Therefore, the flip of only one binary index is forbidden. This strong coupling between spin and valley may enable the long-life valley and spin relaxation.

Figures 4.8(a) and 4.8(b) show the spin textures computed using DFT and $\mathbf{k}, \mathbf{p}$ models, respectively. It is clearly seen that in-plane (S_x, S_y) spin components are absent and band dispersion is fully described by the S_z component. The spin polarization of Bloch states is either parallel or anti-parallel to z -direction leading to the case of PST. These spin textures are different from widely reported locally existing persistent spin textures and are preserved in the whole BZ [234, 25, 228, 235]. These full-zone persistent spin textures (FZPST) can be explained using the symmetry arguments. The group of arbitrary k -point in full BZ is C_s containing the M_{xy} operation, besides the trivial identity. This imparts a condition on the spin expectation values at an arbitrary $\mathbf{k}$ -point as follows

$$M_{xy}^{-1} s(\mathbf{k}) = s(\mathbf{k}) \quad (4.19)$$

and therefore

$$(S_x, S_y, S_z) = (-S_x, -S_y, S_z) \quad (4.20)$$

This condition is satisfied only when the in-plane (S_x, S_y) spin components are zero, leading to FZPST along the z -direction. This is in accordance with DFT and $\mathbf{k}, \mathbf{p}$ model predictions. In spintronic devices that rely on SOC-induced spin splitting, precise control of the Fermi

level is often necessary to access the regions in the BZ where the desired spin textures exist. This necessitates complex gating or doping strategies, adding complexity to device fabrication and operation. In contrast, materials with PST throughout the BZ eliminate this constraint, simplifying device design and potentially leading to more robust and easily controllable spintronic devices. Efforts to fine-tune the Fermi level in SOC-based devices can sometimes lead to increased scattering and reduced carrier mobility due to the introduction of impurities or defects. By avoiding this Fermi level engineering, spintronics devices could potentially exhibit enhanced carrier mobility and longer spin lifetimes, which are crucial for efficient spin transport and manipulation. The requirement for specific Fermi level tuning in SOC-based devices often limits the choice of materials to those with suitable band structures and doping properties. PST is present throughout the BZ, opens up the possibility of using a wider range of materials, potentially including those that were previously unsuitable due to their electronic structure. Devices that rely on precise Fermi level control can be sensitive to external perturbations like temperature changes or voltage fluctuations, which can shift the Fermi level and disrupt the desired spin textures. Materials with PST throughout the BZ are inherently more robust to such perturbations, as the robust spin orientation are preserved due symmetry and are not localized to specific energy ranges.

The SOC Hamiltonian can be written as, $H_{\text{SOC}}(\mathbf{k}) = \mathbf{\Omega}(\mathbf{k}) \cdot \boldsymbol{\sigma}$, where $\mathbf{\Omega}(\mathbf{k})$ is the spin-orbit field (SOF). In the present case, spin precess around the unidirectional SOF leading to a spatially periodic persistent spin helix (PSH) mode [27]. The $SU(2)$ conservation laws in the PSH state imply that the spin expectation values have an infinite lifetime [217]. Since S_z is a conserved quantity, the fluctuation in the z -component of spin polarization with wave vector can only decay by diffusion, thus protecting the spins from dephasing. Figure 4.8(c) shows the schematic diagram of PSH, where L_{PSH} is the wavelength of PSH. The angular frequency (ω) of precession around SOF can be expressed as $\omega = -\gamma B$, where γ is the gyromagnetic ratio. The strength of the effective magnetic field is $B = 2|\mathbf{\Omega}|/\gamma\hbar$ [27]. Therefore, the PSH length is given by

$$L_{\text{PSH}} = \frac{\pi\hbar^2}{m^*\alpha} \quad (4.21)$$

The length of PSH mode can be calculated by evaluating the band dispersion parameters m^* and α . The PSH mechanism leads to the long-range spin transport without dissipation, enabling better efficiency in spintronics devices. In order to quantify the strength of splitting effects, we parameterize the splitting coefficients (λ , α , Δ , η and ζ) by fitting the DFT band structures. In

Table 4.4: The calculated SOC parameters, viz. α , Δ and wavelength of PSH mode (L_{PSH}) of upper VBs for WA₂Z₄ family.

	phase	α (eVÅ)	Δ (eV)	L_{PSH} (nm)
WSi ₂ N ₄	α_1	0.87	0.384	5.03
	α_2	0.92	0.397	4.84
WGe ₂ N ₄	α_1	1.20	0.435	4.51
	α_2	1.21	0.437	4.49
WSi ₂ P ₄	α_1	1.19	0.407	4.42
	α_2	1.22	0.429	4.31
WGe ₂ P ₄	α_1	1.37	0.450	4.08
	α_2	1.33	0.442	4.07
WSi ₂ As ₄	α_1	1.47	0.459	3.99
	α_2	1.61	0.496	3.21
WGe ₂ As ₄	α_1	1.74	0.499	3.16
	α_2	1.79	0.507	2.89

general, we are interested in coefficients having the largest contribution in band splitting, i.e., λ , α , and Δ . Figures 4.8(d)-4.8(f) show the comparison between the DFT and model resulted band splits. The splitting observed around Γ point is very tiny ($\lambda = 0.21 \text{ eVÅ}^3$), as the energy contribution coming from the term cubic in $\mathbf{k}$ is very small i.e., $k_x \ll 1 \text{ Å}$. The linear splitting observed around M point is $\alpha = 0.92 \text{ eVÅ}$. The energy eigenvalues of Hamiltonian given in Eq. 4.17 can be written as

$$E_{\text{M}}^{\pm} = \frac{\hbar^2}{2m^*}(|k| \pm k_0)^2 + E_R \quad (4.22)$$

where E_R and k_0 are the shifting energy and wave vector, respectively [see Fig. 4.8(e)]. The α can also be estimated using E_R and k_0 as follows

$$\alpha = \frac{2E_R}{k_0} \quad (4.23)$$

The values of $E_R = 35 \text{ meV}$ and $k_0 = 0.075 \text{ Å}$, lead to $\alpha = 0.93 \text{ eVÅ}$. In addition, we calculate the L_{PSH} from the Eq. 4.21 and it is found to be 4.84 nm for α_2 -WSi₂N₄. Table 4.4 shows the calculated values of α , Δ and L_{PSH} for the WA₂Z₄ family. The effect of SOC increases

with increasing atomic weight, therefore, the splitting is in the order $\text{Ge} > \text{Si}$ and $\text{As} > \text{P} > \text{N}$. The observed values of α are larger than traditional TMDs (0.05 - 0.40 eVÅ) [236], WO_2Cl_2 monolayer (0.90 eVÅ) [237], defective PtSe_2 (0.20 - 1.14 eVÅ) [238] and $(\text{Mo}, \text{W})\text{X}_2$ ($\text{X}=\text{S}, \text{Se}$) (0.14 - 0.26 eVÅ) [239].

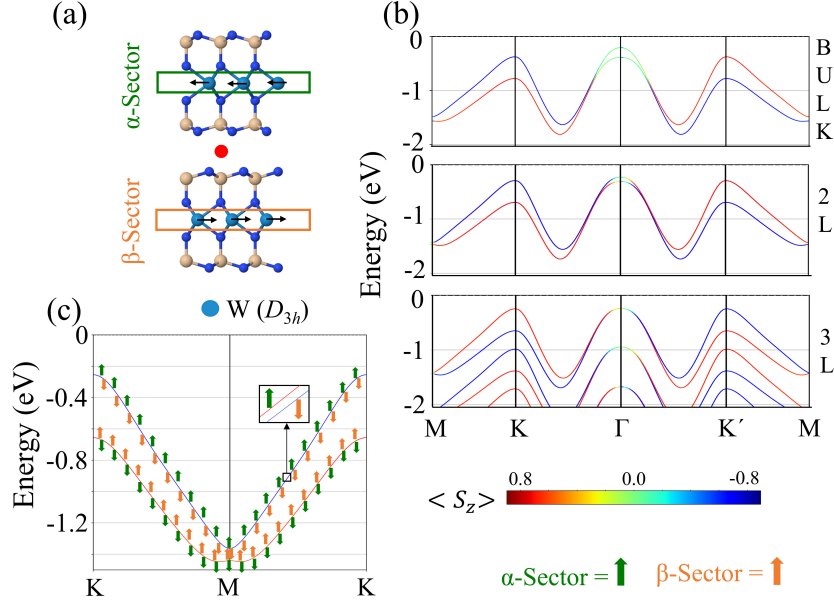


Figure 4.9: (a) Side view of the bulk crystal structure of WSi_2N_4 with site point group of W atom. The red dot represents the inversion center. The two boxed real-space sectors forming the inversion partners are used for spin projection are considered as α -sector and β -sector. The black arrows on W atoms represent the direction of dipole moment on particular atomic sites. (b) The spin-projected top VBs of bulk WSi_2N_4 , bilayer (2L) and trilayer (3L). The color bar shows the out-of-plane (z -) component of spin textures. (c) The spin- and atom- projected band structure of top VBs along K-M-K path. The green and orange color shows the band is coming from α - and β -sectors, respectively. The up and down arrows shows the z -component of spin polarization. Note that the in-plane (S_x, S_y) spin components are zero along that path.

4.3.4 Hidden full-zone PST

The previous theoretical study reports the possibility of experimental realization of layered bulk WSi_2N_4 family, using the bottom up synthesis method [52]. We have considered the layer dependence of the spin polarization in layered WSi_2N_4 family. The bulk WSi_2N_4 has an indirect band gap of 1.97 eV having CBM and VBM at K and Γ , respectively [52]. Figure 4.9(a)

shows the unit cell of bulk WSi₂N₄ having $P6_3/mmc$ space group symmetry. The associated point group symmetry is D_{6h} and have a point of inversion as shown in Fig. 4.9(a). The presence of inversion and time reversal symmetries lead to the bands to be two-fold degenerate throughout the BZ. As expected, the top VBs are two-fold degenerate as shown in Fig. 4.9(b). In current view, the RD effects are observed only when the inversion symmetry is absent. Thus, it is unwise to look for spin splitting and spin polarization in centrosymmetric bulk WSi₂N₄. Therefore, the degree of spin polarization is expected to be zero in inversion symmetric even layered and bulk WSi₂N₄, as reported in Ref. [52]. In contrast, we report the existence of hidden spin polarization for bulk WSi₂N₄, which can be attributed to the hidden Dresselhaus (D-2) effect [240]. The key point here is that SOC is anchored on particular nuclear sites in the solid, thus it is the individual atomic site symmetry in solid that forms a good starting point to describe the SOC-induced spin-polarization. The net spin polarization of the bulk crystal is sum of the local polarization over the atomic sites. The D-2 effect arises when the site point group of an atom within a 3D crystal lacks inversion asymmetry and the crystal as a whole is centrosymmetric [240].

In present case, the inversion symmetry is present in bulk space group but not in the site point groups [Fig. 4.9(a)]. One such atomic site is W atom, where site point group is inversion asymmetric D_{3h} , contributing mainly to the low-energy spectrum. The two W layers connected by the inversion symmetry are indicated as sectors S_α and S_β . The two sectors are individually inversion asymmetric and produce equal dipole moment but in opposite directions [Fig. 4.9(a)]. Therefore, the net dipole moment of bulk WSi₂N₄ becomes zero, which is the central property of centrosymmetric structures. Figure 4.9(c) shows the band structure projected on the spin components and real space sectors S_α and S_β . If we consider only one sector, the large band splitting (~ 0.4 eV) between the spin-up and spin-down states is observed along K-M-K path. The interactions between the sectors form a pair of bonding and antibonding states, therefore, open a band gap at the band crossing M point [241]. Although the bands are doubly degenerate as a consequence of bulk inversion asymmetry, the branches of doubly degenerate bands have opposite spin polarizations, which are separated in the real space [Fig. 4.9(c)]. As already discussed, S_z is a good quantum number, therefore, the spins are fully out-of-plane and up and down spins locate at the energy bands. The weak van der Waals interaction among inversion partners causes slight spin mixture from another layer and slightly larger separation of the degenerate bands. However, most of the spin at the K valley remains on each layer. The real

space segregation of spin polarized bands originates from the separate local sites Dresselhaus SOC. The bulk spin polarization in such systems can be observed by controlling the stacking directions probing beams [242, 243, 244]. The extra advantage of D-2 effect is that the spins can be controlled by manipulating the interaction between two inversion parts. One such example is that a small electric field ($\sim 1 \text{ mV/\AA}$) is required to reverse the spin polarization as compared to linear Rashba effect [245].

The results similar to the bulk are expected to be observed for even number of layers of WSi_2N_4 , having centrosymmetric $P6_3/mmc$ space group symmetry. Therefore, we have examined the results for bilayer- WSi_2N_4 . The real space segregated hidden spin polarization is also observed in doubly degenerate bands of topmost VBs [Fig.4.9(b)]. The band splitting similar to monolayer is observed in odd number of layers of WSi_2N_4 having non-centrosymmetric $P\bar{6}m2$ space group symmetry [i.e., see band structure for trilayer in Fig.4.9(b)].

4.4 Summary and outlook

We have shown the existence of PST in bulk materials having D_{3h} and C_{3h} point group symmetries. The PSTs are observed in full Γ –M–K plane, as long as in-plane mirror symmetry remains intact and differs from trivial PST. Taking $\text{K}_3\text{Ta}_3\text{B}_2\text{O}_{12}$ as a test case, we have observed purely cubic splitting around the Γ point of an order $\approx 6.85 \text{ eV\AA}^3$, which is larger than the already reported splitting. Around M point, bands are linearly split with an order of $\approx 3.11 \text{ eV\AA}$. The observed splitting is found to be anisotropic in nature. The nature and anisotropy of splitting are also studied using the $\mathbf{k}\cdot\mathbf{p}$ model via symmetry analysis. Our calculations show that there exists a large family of materials which possess full plane PST in purely cubical regime. In addition, strain engineering tunes the observed PST by varying the magnitudes of SOC splitting coefficients. These spin textures known for non-dissipative spin transport, together with PCS, form another prospective aspect. The large SOC splitting coefficients, wide band gap, suitable band edge positions, strain tunability and room temperature stability make them suitable for room temperature applications. The complete realization of original device of these applications may enrich the field of spintronics.

In addition, we have revealed the interesting spin splitting properties of WA_2Z_4 family. The formation energies, phonon spectra and AIMD calculations confirm the stability of these materials. The PBE, HSE06 and the excited state methods G_0W_0 and BSE show that these

materials are semiconducting, having a band gap in visible region. In addition to valley dependent properties at the corners of BZ, we have observed cubic and linear split bands around the time-reversal invariant Γ and M points, respectively. The in-plane mirror symmetry (M_{xy}) leads to out-of-plane FZPST, therefore, enabling dissipationless long range transport through spatially periodic mode PSH mechanism. The effect of EEF is duly considered on band gap and spin splitting. The EEF leads to linear Rashba-type helical spin texture around the VBM. The impact of layer thickness is studied in aforementioned effects. We have found the hidden spin polarization in the bulk and even layered WSi_2N_4 , which can be attributed to the D-2 effect. The D-2 effect arises because the local site point of W atom lacks inversion symmetry; however, the global space group is centrosymmetric. The PST is robust to electric field and thickness along the M-K direction. We believe that this work will provide highly efficient spintronics and valleytronics devices for room temperature applications.

Reducing symmetry to modulate spin and valley physics in 2D materials

5.1 Introduction

The successful investigation of graphene has spurred the discovery of extraordinary properties and promising applications in the field of two-dimensional materials [246, 247, 248]. Afterwards, numerous two-dimensional materials such as silicene, germanene, transition metal dichalcogenides (TMDs) and so on have been explored [249, 250, 251, 252, 253, 254]. 2D materials with Janus structure possess different physical and chemical properties on each side due to mirror symmetry breaking, which make them exciting [255, 256]. The asymmetric crystal potential causes an intrinsic electric field in these Janus 2D materials, leading to spin-valley splitting and Rashba spin splitting when combined with SOC [236, 257]. Additionally, Janus materials show great applications in photocatalytic water splitting, magnetic skyrmions, and out-of-plane piezoelectricity [258, 259, 260]. The experimental synthesis of MoSSe from MoSe₂ through the replacement of Se atom by S atom, further triggered the prediction of more Janus 2D materials [261, 262]. Only TMD and metal monochalcogenides Janus materials have been considerably studied so far. Therefore, it is necessary to expand this family to have a more in-depth understanding.

Recently, the MA₂Z₄ (M=Cr, Mo, W, V, Nb, Ta, Ti, Zr or Hf; A=Si or Ge; and Z=N, P, As) 2D family of the septuple-atomic layer has been proposed [48]. Particularly, 2D van der Waals (vdW) layered MoSi₂N₄ and WSi₂N₄ have been successfully fabricated by the chemical vapor deposition method [47]. It has been found that WA₂Z₄ materials have high tensile strength with excellent ambient stability. Subsequently, several predictions of these Janus 2D materials and their excellent physical properties have been carried out. This includes the quantum spin Hall

state in SrAlGaTe_4 [156], high electron mobility, efficient photocatalysis, Rashba spin splitting, out-of-plane piezoelectricity in the MoSiGeN_4 [263, 149, 264] and intrinsic ferromagnetism in the VSiGeN_4 [265, 266]. Therefore, this class of materials is expected to provide intriguing physical phenomena, particularly in valleytronics and spintronics.

Nowadays, spin and valley are considered as extra DOF, which are distinct from the electronic charge and provide an interesting avenue in semiconductor devices [37]. This draws a number of emerging quantum applications such as valley Hall effect and valley-dependent orbital magnetic moment. The broken inversion symmetry is compulsory for valleytronics, since Berry curvature vanishes in centrosymmetric materials [267]. Also, strong SOC in inversion asymmetric materials induces Rashba spin splitting, which is a critical ingredient in spin field-effect transistors (SFETs) [268, 235, 269]. Thus, the Rashba effect is extensively studied for SFETs and spin-to-charge interconversion. The spin-valley locking and the Rashba effect arising from the SOC are bringing tremendous attention to the flourishing field of valleytronics and spintronics. These effects have been noticed in graphene [270], TMDs [37], h -MN ($M=\text{Nb, Ta}$) [271] and bismuth thin films [234]. However, the scarcity of 2D materials showing these phenomena with appreciable spin-valley polarization and significant Rashba effect holds back the field of spin valleytronics.

External perturbations are used successfully to improve the performance of monolayer devices by modifying the band dispersion. Some groundbreaking discoveries related to strains include band gap reduction [272, 273, 274, 275], direct to indirect band transition [276], funneling of photogenerated excitons [277], tunnel resistance modulation [278], enhancement in Rashba splitting [279, 87, 235, 228], and coexistence of negative Poisson's ratio and magnetism [280]. The uniaxial strain can also lower the symmetry, inducing the band splitting and modulation of Berry curvature dipole and valley magnetization [281]. The strain superlattices can open the significant energy gap and shift the Dirac points in graphene [282]. Furthermore, several experimental and theoretical investigations predict the direct to indirect band gap transition in MoS_2 under the tensile strain between 2 to 3% [272, 283, 284]. Most importantly, 2D materials are able to sustain significant reversible elastic strain, i.e., graphene (25%) [285, 286, 287] and MoS_2 (11%) [288, 289, 290], making strain-dependent effects easy accessible in experiments.

5.2 Symmetry control of spin-valley physics in 2D Janus WSiGeZ₄

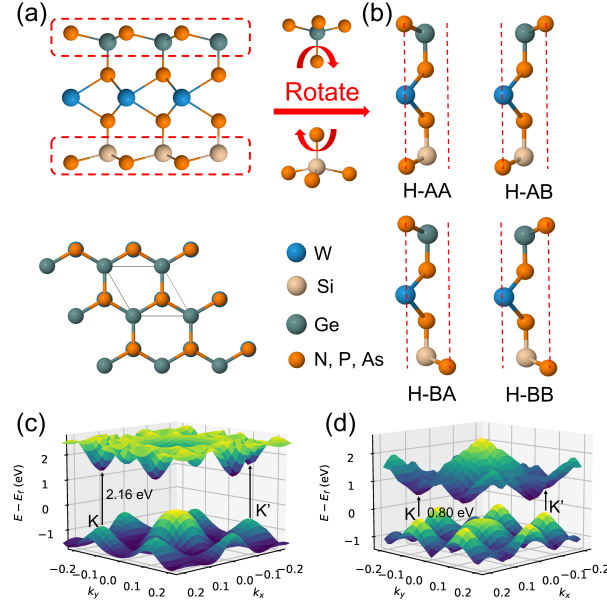


Figure 5.1: (a) Side and top views of lattice structure corresponding to monolayer H-BB WSiGeZ₄. (b) Side views of various stacking orders for three constituent parts in the monolayer WSiGeZ₄. The 3D view of the top valence band (VB) and bottom conduction band (CB) in monolayer (c) H-BB WSiGeN₄ and (d) H-AA WSiGeP₄.

In this section, we have investigated the effect of stacking of A-Z layers to modulate the electronic properties, focusing on their spintronics and valleytronics aspects. We have taken the unexplored Janus WSiGeZ₄ as an example to study these effects. The first-principles calculations predict that these materials have Dirac-type valleys located at the corners of Brillouin zone (BZ), connected by TRS. The valleys show contrasting physics, i.e., spin polarization, optical circular dichroism and Berry curvature. The broken surface inversion symmetry induces Rashba spin splitting at the center of the BZ. The findings imply that symmetry control enhances Berry curvature by more than 300%. Furthermore, Rashba splitting increases significantly by modifying the out-of-plane asymmetry. The underlying mechanism behind the unconventional enhancement is duly investigated through microscopic orbital contribution and macroscopic charge transfer. This method is more effective compared to the strain and electric field, in modulating the Berry curvature and Rashba splitting. The high carrier mobilities and tunable electronic properties suggest their great potential in spintronics and valleytronics.

Table 5.1: Optimized lattice constant (a) for the unit cell of WSiGeZ₄ monolayer. The calculated formation energy per atom (E_{for}), dipole moment per unit cell (P_y , P_z), band gaps in presence of SOC using PBE (E_g^{PBE}) and HSE06 (E_g^{HSE}). The calculated band gaps using G₀W₀ performed on top of PBE functional with inclusion of SOC ($E_g^{GW@PBE}$).

	Phase	a (Å)	E_{for} (eV)	P_y (eÅ)	P_z (eÅ)	E_g^{PBE} (eV)	E_g^{HSE} (eV)	$E_g^{GW@PBE}$ (eV)
WSiGeN ₄	H-AA	2.929	-0.639	1.710	0.024	2.01	2.48	3.27
	H-AB	2.931	-0.643	-0.930	0.021	1.88	2.36	3.11
	H-BA	2.934	-0.651	-2.488	0.028	1.83	2.31	3.03
	H-BB	2.940	-0.658	1.716	0.026	1.66	2.15	2.87
WSiGeP ₄	H-AA	3.452	-0.279	2.016	0.042	0.56	0.58	1.19
	H-AB	3.459	-0.259	-1.085	0.032	0.46	0.51	1.06
	H-BA	3.462	-0.271	-2.989	0.058	0.39	0.47	0.97
	H-BB	3.468	-0.262	2.031	0.043	0.25	0.42	0.75
WSiGeAs ₄	H-AA	3.594	-0.113	2.103	0.096	0.41	0.45	0.89
	H-AB	3.599	-0.072	-1.204	0.084	0.33	0.39	0.82
	H-BA	3.601	-0.086	-3.104	0.124	0.28	0.36	0.76
	H-BB	3.605	-0.053	2.118	0.101	0.18	0.29	0.58

5.2.1 Crystal structure and electronic properties

WA₂Z₄ structure, built by septuple atomic layers in the sequence Z-A-Z-W-Z-A-Z having D_{3h} point group symmetry, can be regarded as one layer of WZ₂ sandwiched by two layers of A-Z [48]. The intermediate WZ₂ is structurally similar to 1H-TMD [48, 54]. The WA₂Z₄ structure breaks inversion symmetry and preserves horizontal mirror symmetry (σ_h). When they form the Janus structure by replacing A atom with a different same group atom, σ_h is broken, leading to inversion symmetry breaking with C_{3v} symmetric point group [263, 149]. Figure 5.1(a) shows the fully optimized crystal structure of the WSiGeZ₄. Theoretically, several intermediate structures are obtained by varying the stacking of the intermediate layer of 1H-WZ₂ and two A-Z layers [47, 48, 291, 292, 293, 294, 295]. As shown in Fig. 5.1(b), we have considered the four structures (H-AA, H-AB, H-BA, and H-BB) depending upon the stacking

order of the three constituent (Z-Si, Z-W-Z, and Ge-Z) monolayers. As shown in Table 5.1, the lattice parameters of H-AA, H-AB, H-BA and H-BB are only slightly different. This is because of same coordination environment and similar valence electron states. The lattice constant of Janus WSiGeZ₄ monolayer is approximately the average of WSi₂Z₄ and WGe₂Z₄. It is evident that the lattice constant increases with the increasing atomic number of the pnictogen.

We have obtained the formation energy per atom (E_{for}) to confirm the energy feasibility, using the expression

$$E_{for} = \frac{E_{tot} - (n_W E_W + n_{Si} E_{Si} + n_{Ge} E_{Ge} + n_Z E_Z)}{(n_W + n_{Si} + n_{Ge} + n_Z)} \quad (5.1)$$

where E_{tot} is the total ground state energy of the WSiGeZ₄ monolayer, E_W , E_{Si} , E_{Ge} , and E_Z are the chemical potentials of W, Si, Ge, and Z atoms, respectively. n_W , n_{Si} , n_{Ge} , and n_Z are the number of W, Si, Ge, and Z atoms in the unit cell, respectively. As clear from Table 5.1, all the considered phases are energetically feasible. Nevertheless, the ground state configurations are different. For instance, the H-BB phase is most favorable for WSiGeN₄, but WSiGeP₄ and WSiGeAs₄ are most stable in the H-AA phase. The absence of imaginary phonon mode in the entire BZ confirms the dynamical stability of phases H-AA, H-AB, H-BA, and H-BB. There are two main factors contributing to the origin of vertical polarization. The first one is the asymmetry arising from the replacement of one Si by Ge atom, and another is the asymmetry arising from the rotation of Si-Z and Ge-Z layers (see Fig. 5.1(b)). Table 5.1 summarizes the calculated electric dipole moment per unit cell.

The three-dimensional band structures of the monolayer H-BB WSiGeN₄ and H-AA WSiGeP₄ are shown in Figs. 5.1(c) and 5.1(d), respectively. The monolayer H-BB WSiGeN₄ has an indirect band gap with VBM and CBM at Γ and K/K' points, respectively. The monolayer H-AA WSiGeP₄, and WSiGeAs₄ are the direct band gap semiconductors with band edges located at K/K' points. The monolayer WSiGeN₄, WSiGeP₄ and WSiGeAs₄ have valley-like peaks at the K and K' points. The two valleys at K and K' are inequivalent due to structural asymmetry and TRS, although they have degenerate energy, as discussed in the coming sections.

5.2.2 Valley physics

To investigate the valleys in the monolayer WSiGeZ₄, band structures with SOC are calculated as shown in Figs. 5.2(a), 5.2(b), and 5.2(c). We have observed that monolayer H-BB WSiGeN₄ is still an indirect band semiconductor and monolayer H-AA WSiGeP₄ and WSiGeAs₄ remain

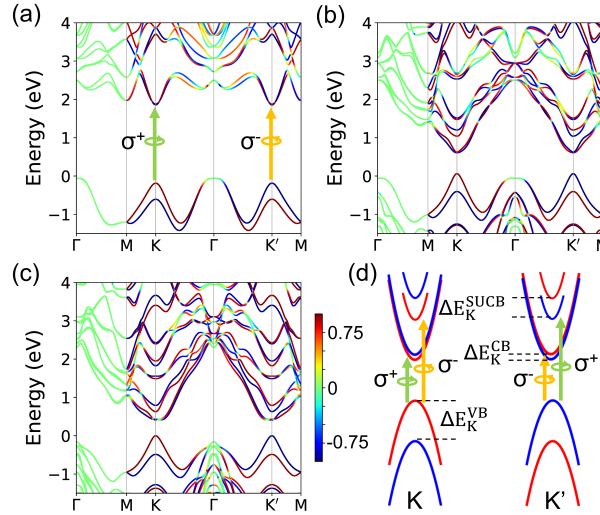


Figure 5.2: The spin resolved band structure of monolayer (a) H-BB WSiGeN₄, (b) H-AA WSiGeP₄ and (c) H-AA WSiGeAs₄ calculated using PBE+SOC. The energy levels with positive and negative spin magnetization are sketched in the red and blue curves, respectively. (d) Schematic of valley selective excitation. Length of arrows and circles depict the energy and chirality of incident photon, respectively.

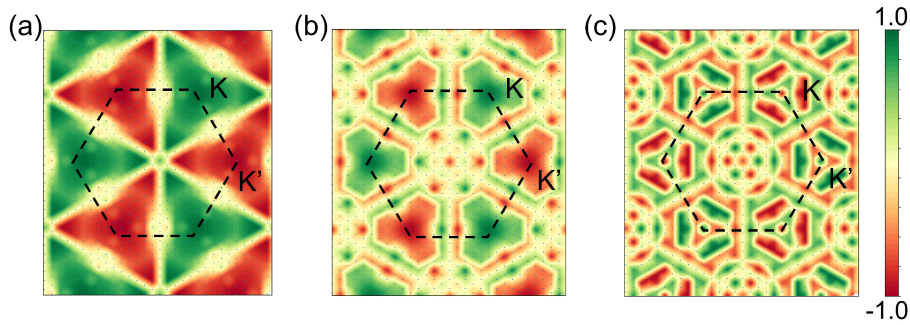


Figure 5.3: The degree of circular polarization for transition between VB to CB in monolayer (a) H-BB WSiGeN₄ and (b) H-AA WSiGeP₄ mapped over the BZ. (c) The circular polarization for transition between VB to SUCB in monolayer H-AA WSiGeP₄. The black dotted lines represents the first BZ.

direct band semiconductors. Band gaps obtained using PBE functional are listed in Table 5.1. We have also used the more accurate HSE06 functional and G_0W_0 approach to validate the band structure results (see Table 5.1). We have found that apart from the band gap, all the band features are similar irrespective of the choice of functional. The band gaps increase for the HSE06 and G_0W_0 methods due to the inclusion of exact exchange and self-energy, respectively. As seen in Figs. 5.2(a), 5.2(b) and 5.2(c), SOC mainly causes spin splitting of the

degenerate bands. The spin splitting is a direct consequence of the inversion symmetry breaking, which lifts the spin degeneracy at each generic k -point. Since the TRS is preserved, the spin polarization at K and K' points are opposite because the time-reversal operation connects the K and K' points. Additionally, properties that are odd under time-reversal operation will have opposite natures at K and K' points. This concludes the existence of a valley degree of freedom.

The circular polarization for optical transition between the pair of states $|n\mathbf{k}\rangle$ and $|m\mathbf{k}\rangle$ is given by [49]

$$\eta(\mathbf{k}) = \frac{|M_+|^2 - |M_-|^2}{|M_+|^2 + |M_-|^2} \quad (5.2)$$

where $M_{\pm}$ is the optical transition matrix element for the incident light with $\sigma_{\pm}$ polarization. The $M_{\pm}$ can be expressed as $M_{\pm} = \frac{1}{\sqrt{2}}(M_x \pm M_y)$, where $M_{x/y} = m_e \langle m\mathbf{k} | v_{x/y} | n\mathbf{k} \rangle$. $\eta = +1$ and $\eta = -1$ represent the optical absorption of only right hand circularly polarized (RHCP) and left hand circularly polarized (LHCP) light, respectively. Figure 5.3(a) shows the degree of circular polarization of excitation from first occupied VB to first unoccupied CB in the case of monolayer H-BB WSiGeN₄. As seen, the circular dichroism is perfectly valley selective. The absorption of RHCP and LHCP photon will take place at K and K' points, respectively. Therefore, the circularly polarized optical pumping can control the electron and hole population of either valley. In the case of the monolayer H-BB WSiGeN₄, the direct band gap at K/K' point is 2.16 eV. Therefore, either valley can be selectively excited by the circularly polarized photon with the energy around 2.16 eV.

In case of monolayer H-AA WSiGeP₄ and WSiGeAs₄, the picture remains the same. However, there are no additional states apart from K/K' near the CBM and VBM, thus, there will be no scattering states. Figure 5.3(b) shows the circular polarization for optical transition between VB to CB in the case of monolayer H-AA WSiGeP₄. The valleys are perfect and show complete valley contrasting physics, i.e., selective valley excitation. The valley selective optical transition occurs from VB to CB when the energy of the circularly polarized incident photon is around 0.56 and 0.41 eV for monolayer H-AA WSiGeP₄ and WSiGeAs₄, respectively. Furthermore, there exist additional valleys at the second unoccupied conduction band (SUCB) near the CBM (see Figs. 5.2(b) and 5.2(c)). Also, the spin polarization for the SUCB at K and K' points is opposite. Therefore, if the incident photon's energy is larger than the direct band gap, then the transition from VBM to SUCM takes place (see Fig. 5.2(d)). The circular polarization from the VB to SUCM is also valley specified, as shown in Fig. 5.3(c). The LHCP and RHCP

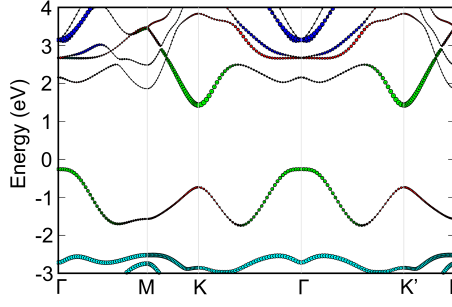


Figure 5.4: Orbital projected band structure of monolayer H-BB WSiGeN₄ without SOC. Fermi level is set to zero in the energy axis. The fatness of band structure corresponds to W- d_{z^2} (green), W- $d_{x^2-y^2}$ and W- d_{xy} (red), W- d_{yz} and W- d_{xz} (blue), and N- p (cyan) orbitals.

from VBM to SUCM will be absorbed at K and K' valleys, respectively. Note that the chirality of light for the transition taking place from VB to CB or VB to SUCB is opposite in the same valley (see Fig. 5.2(d)). Therefore, we can selectively pump an electron from VB to CB or SUCB by using optically selective light. This shows that SUCB in monolayer H-AA WSiGeP₄ and WSiGeAs₄ add another dimension to the valley physics.

The low power $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian including the orbital and spin DOF explains the valley splitting around C_3 symmetric K/K' points. Figure 5.4 shows the orbital-projected band structure of monolayer H-BB WSiGeN₄. The VB and SUCB states mainly consist of in-plane orbitals (d_{xy} , $d_{x^2-y^2}$). Whereas, the out-of-plane orbital (d_{z^2}) mainly contribute to the CBM. Similar contributions are also observed for monolayer H-AA WSiGeP₄ and WSiGeAs₄. The $\mathbf{k} \cdot \mathbf{p}$ model Hamiltonian employing the basis $|d_{xy}-\tau i d_{x^2-y^2}\rangle \otimes |s_z\rangle$, $|d_{z^2}\rangle \otimes |s_z\rangle$ and $|d_{xy}+\tau i d_{x^2-y^2}\rangle \otimes |s_z\rangle$ and containing the terms up to linear in $\mathbf{k}$ is given by [37, 50, 49]

$$H_\tau = \begin{pmatrix} \epsilon_a + \tau \lambda_a S_z & \gamma_2 k^- & \gamma_1 k^+ \\ \gamma_2 k^+ & \epsilon_c & \gamma_3 k^- \\ \gamma_1 k^+ & \gamma_3 k^+ & \epsilon_v + \tau \lambda_v S_z \end{pmatrix} \quad (5.3)$$

where $k^\pm = k_x \pm \tau i k_y$ and k_x or k_y is measured from K and K' point. The $\tau = \pm 1$ is the valley index and γ_i are the optical matrix elements. The ϵ_c , ϵ_v , and ϵ_a are the energy levels at K/K' point. $\Delta = \epsilon_c - \epsilon_v$ is the direct band gap. $2\lambda_a$ (ΔE_K^{SUCB}) and $2\lambda_v$ (ΔE_K^{VB}) represent the splitting of SUCB and VB (see Fig. 5.2(d)). For the case of monolayer H-BB WSiGeN₄, SUCB is far away from the CBM. Therefore, the two band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian is sufficient, which reads as [37]

$$H_\tau = \begin{pmatrix} \epsilon_c & \gamma_3 k^- \\ \gamma_3 k^+ & \epsilon_v + \tau \lambda_v S_z \end{pmatrix} \quad (5.4)$$

Table 5.2: The observed spin splitting of VB (ΔE_K^{VB}), CB (ΔE_K^{CB}), SUCB (ΔE_K^{SUCB}) and the Berry curvature (Ω_K) at K point.

	Phase	ΔE_K^{VB} (meV)	ΔE_K^{CB} (meV)	ΔE_K^{SUCB} (meV)	Ω_K ($\text{\AA}^2$)
WSiGeN ₄	H-AA	415	3	-	16.1
	H-AB	415	4	-	17.2
	H-BA	417	9	-	17.5
	H-BB	418	12	-	18.1
WSiGeP ₄	H-AA	431	6	184	75
	H-AB	426	4	186	133
	H-BA	435	6	174	161
	H-BB	436	9	184	335
WSiGeAs ₄	H-AA	480	18	164	108
	H-AB	481	25	217	151
	H-BA	492	26	180	205
	H-BB	502	28	236	411

To quantize the SOC effect, we have calculated the magnitude of spin splitting at the top of VB, the bottom of CB and SUCB (see Table 5.2). The valley splitting observed for the top VB and SUCB is significantly larger than the lowest CB. The $W-d_{xy}$ and $W-d_{x^2-y^2}$ orbitals under the influence of in-plane electric dipole moment produce spin splitting at the K point [296]. The CB is mainly contributed by $W-d_{z^2}$ and the contributions from $W-d_{xy}$ and $W-d_{x^2-y^2}$ are nearly zero. Therefore, spin splitting is predominant for the VB and the SUCB, and very tiny for the CB. The trend for spin splitting at valleys is observed as $\text{WSiGeN}_4 < \text{WSiGeP}_4 < \text{WSiGeAs}_4$, which is attributed to the increase in SOC for heavier elements.

Incommensurate lattices can bring about interfacial strain during support on a substrate or vdW heterostructures formation. Therefore, the role of strain is also addressed in this study. We have applied the biaxial compressive and tensile strain in the deformation range of 6% to investigate the evolution of band edges. Figures 5.5(a), 5.5(b) and 5.5(c) show the variation of spin splitting at valleys of CB and VB for monolayer WSiGeZ_4 . We see that the ΔE_K^{CB} is

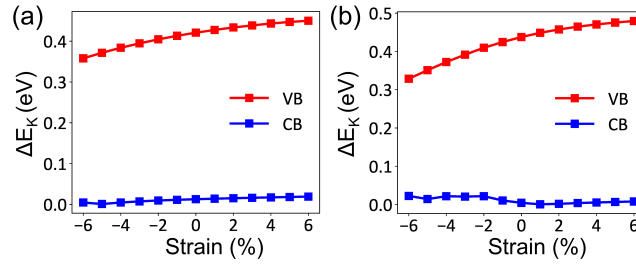


Figure 5.5: The variation of spin splitting of the VB and CB at K/K' valleys with respect to the biaxial strain in monolayer (a) H-BB WSiGeN₄ and (b) H-AA WSiGeP₄.

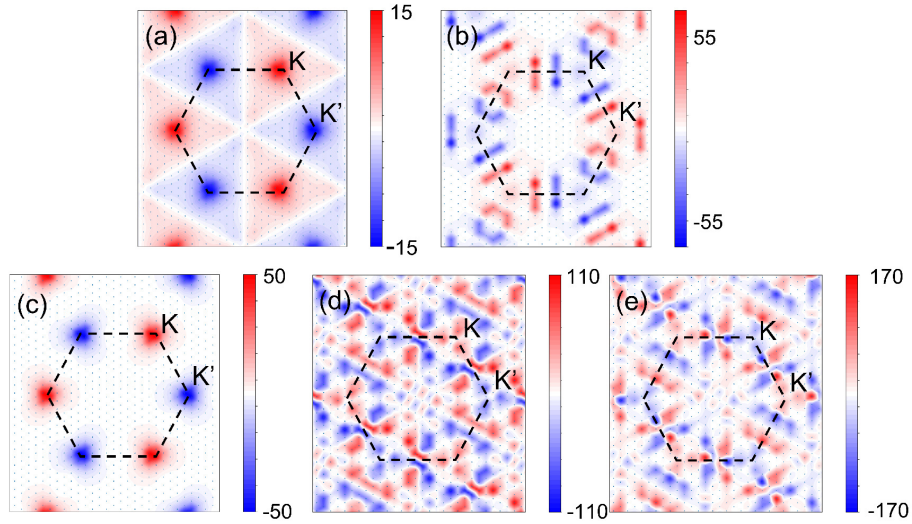


Figure 5.6: Berry curvature distribution over BZ for (a) VB, (b) CB in monolayer H-BB WSiGeN₄. Berry curvature distribution of (c) VB, (d) CB and (e) SUCB in monolayer H-AA WSiGeP₄. The black dotted lines denote the first BZ.

independent of the strain, whereas the ΔE_K^{VB} slightly increases (decreases) with the application of tensile (compressive strain).

5.2.3 Berry curvature modulation

To confirm the nonequivalence of valleys at K and K' points, we have studied the non-zero out-of-plane Berry curvatures. The velocity of the charge carriers in the presence of non-zero Berry curvature is given by $\hbar v_n(\mathbf{k}) = v_g - v_\perp$. Here, v_g denotes the group velocity, which is defined as $v_g = \nabla_{\mathbf{k}} \epsilon_n(\mathbf{k})$, where $\epsilon_n(\mathbf{k})$ is the energy of $|n\mathbf{k}\rangle$ state. In addition to the group velocity, Berry curvature leads to a transverse velocity denoted by $v_\perp$. The transverse velocity is given by $v_\perp = -\frac{e}{\hbar} E \times \Omega_n(\mathbf{k})$, where E is the in-plane electric field, and $\Omega(\mathbf{k})$ is the out-of-plane Berry curvature [49]. For 2D systems, Berry curvature only has a z -component and for $|n\mathbf{k}\rangle$ state, it is expressed as [49]

$$\Omega_n(\mathbf{k}) = -2\text{Im} \sum_{n' \neq n} \frac{\langle n\mathbf{k} | v_x | n'\mathbf{k} \rangle \langle n'\mathbf{k} | v_y | n\mathbf{k} \rangle}{(\epsilon_{n'} - \epsilon_n)^2} \quad (5.5)$$

where the summation is over all the occupied bands. ϵ_n and $\epsilon_{n'}$ are the energy levels for $|n\mathbf{k}\rangle$ and $|n'\mathbf{k}\rangle$ states, respectively. The time-reversal operation applies the opposite Berry curvature at time-reversal conjugate momenta ($\Omega_n(-K) = -\Omega_n(K)$). Figures 5.6(a) and 5.6(b) show the Berry curvature of the VB and CB mapped in the first BZ for monolayer H-BB WSiGeN₄. Figures 5.6(c), 5.6(d) and 5.6(e) show the Berry curvature of monolayer H-AA WSiGeP₄ for VB, CB, and SUCB, respectively. Berry curvature is mostly confined around the valleys and has been found to be the highest at K and K' points. It has also been observed that the Berry curvature rapidly decreases to zero while moving away from the K and K' points. The opposite nature of Berry curvature near the K and K' points can distinguish the charge carriers at different valleys. The opposite Berry curvature leads to the spatial separation of charge carriers coupled with different valleys. Thus, the charge from different valleys will accumulate on opposite edges, leading to valley Hall effect. The TRS leads to the case of no net charge current at the linear order. However, there could exist a valley Hall effect after the electron doping. As for hole doping, one has to reach the energy level of K/K' point which is lower in energy compared to the Γ point for monolayer WSiGeN₄. The monolayer WSiGeP₄ and WSiGeP₄ are more suitable for the case of hole doping, as the valence states lie at the K/K' point.

The transverse velocity can be amplified using the larger Berry curvature. Thus, faster charge transport and lesser recombination can be achieved. Therefore, a larger value of Ω_K

is always desired, and Berry curvature modulation is indispensable in the field of valleytronics [297]. Using Eqs. 5.4 and 5.5, the Berry curvature of VBs can be expressed as

$$\Omega_v(\mathbf{k}) = \tau \frac{2a^2t^2\Delta}{(4a^2t^2\mathbf{k}^2 + \Delta^2)^{3/2}} \quad (5.6)$$

where a , t and Δ are the lattice constant, nearest-neighbor hopping integral, and direct band gap, respectively. Therefore, the Berry curvature can be enhanced by tuning the parameters a , t and Δ . Figure 5.7(a), 5.7(b) and Table 5.2 show the modulation of Berry curvature via different stacking orders. Surprisingly, the Berry curvature can be enhanced up to 400% compared to its ground state. For the case of monolayer H-AA WSiGeP₄, it increases Berry curvature from 80 Å² to 335 Å² by changing the phase to the H-BB. Similarly, Berry curvature is also enhanced to 411 Å² for monolayer H-BB WSiGeAs₄. However, modification is almost negligible in the case of monolayer H-BB WSiGeN₄ due to the small size of the N atom. The H-BB phase has the smallest value of Δ at the K point, thereby highest Berry curvature is obtained for this phase. The percentage change in the direct gap is highest in the case of the WSiGeAs₄ monolayer, therefore, the strongest tuning is obtained using symmetry control for WSiGeAs₄ monolayer.

It is crucial to understand the underlying mechanism behind the Berry curvature modulation. The Berry curvature can be seen as proportional to $\Omega_v(k = 0) \propto \Delta^{-2}$ (see Eq. 5.6). The direct band gap (Δ) follows the trend H-BB < H-BA < H-AB < H-AA (see Table 5.1); therefore, the Berry curvature peak follows the more pronounced trend H-BB > H-BA > H-AB > H-AA. This trend is more significant for WSiGeN₄ and WSiGeAs₄, as the direct band gaps are more sensitive to the stacking order. Table 5.3 shows the orbital contribution at K point for the VB for monolayer WSiGeP₄. A similar trend is also observed for the monolayer WSiGeAs₄ and WSiGeN₄. The W- d and P- p orbitals contribute to valence states, where W- d_{xy} and W- $d_{x^2-y^2}$ have the largest contributions. Rotation of Si/Ge-Z layers leads to a change in the orbital contribution, hence, the strength of the SOC. The contribution coming from heavy W- d is highest in the case of the H-BB phase. Thus, the highest SOC strength leads to the largest strength of Berry curvature at the K/K' point for the H-BB phase. The contribution of W- d orbitals follows the trend, H-BB > H-BA > H-AB > H-AA and the same trend is followed by the Berry curvature. This shows that microscopic orbital contribution has a strong correlation with the Berry curvature.

Another efficient way to modify the orbital contribution is by applying strain [297, 281]. Hence, the effect of tensile and compressive biaxial strain on the Berry curvature of VB is also analyzed. Figures 5.7(c) and 5.7(d) show the Berry curvature of unstrained and strained cases

Table 5.3: Orbital contribution to the VB at K/K' point of monolayer H-AA WSiGeP₄.

Phase	p_x	p_y	p_z	d_{xy}	d_{yz}	d_{z^2}	d_{xz}	$d_{x^2-y^2}$
H-AA	0.055	0.000	0.055	0.271	0.002	0.000	0.002	0.271
H-AB	0.055	0.009	0.055	0.271	0.003	0.002	0.003	0.271
H-BA	0.058	0.013	0.058	0.280	0.004	0.001	0.004	0.280
H-BB	0.057	0.025	0.057	0.303	0.001	0.000	0.001	0.303

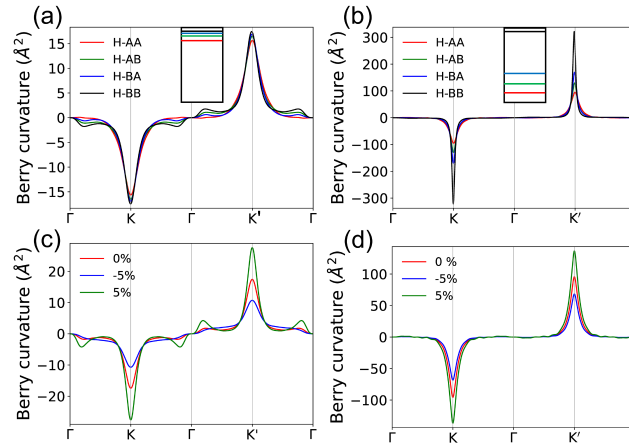


Figure 5.7: Modulation of Berry curvature by varying stacking orders in monolayer (a) WSiGeN₄ and (b) WSiGeP₄. The insets in (a) and (b) show the position of Berry curvature at K' point. The effect of biaxial strain on the Berry curvature in monolayer (c) H-BB WSiGeN₄ and (d) H-AA WSiGeP₄.

for the VB in monolayer H-BB WSiGeN₄ and H-AA WSiGeP₄. The strain could also tune the Berry curvature efficiently. Under the tensile strain, the direct band gap and the magnitude of wavevector are reduced. Therefore, the magnitude of the Berry curvature increases. In the case of WSiGeN₄, Berry curvature increases from 15 $\text{\AA}^2$ to 25 $\text{\AA}^2$ under 5% tensile strain. Whereas, it increases from 80 $\text{\AA}^2$ to 129 $\text{\AA}^2$ in WSiGeP₄ and is significantly smaller than the Berry curvature 335 $\text{\AA}^2$ obtained by symmetry control.

5.2.4 Rashba effect

The presence of strong SOC in addition to the breaking of surface inversion symmetry along z -direction leads to the Rashba spin splitting of VB around Γ point. The spin-projected band structure of top VBs of monolayer H-AA WSiGeP₄ is depicted in Fig. 5.8(a). The bands

describe unique Rashba type dispersion, which can be explained by linear Rashba Hamiltonian. The helical nature of in-plane spin textures as shown in Fig. 5.8(b), confirms the presence of the Rashba effect around the Γ point. Moreover, a small out-of-plane spin component has three-fold rotation symmetry in-line with the symmetry of the crystal.

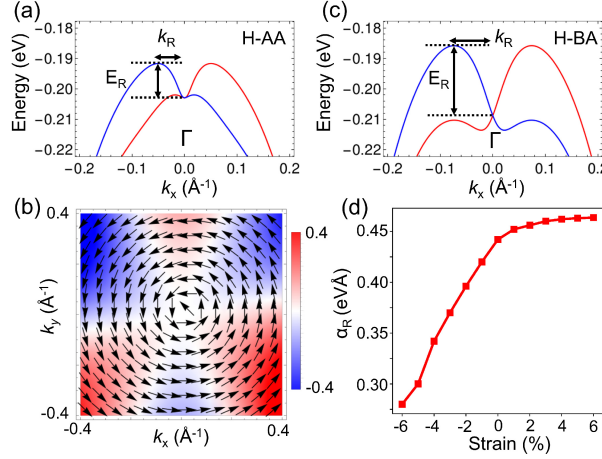


Figure 5.8: (a) The spin-projected band structures and (b) associated spin texture of top VBs in H-AA WSiGeP₄. (c) The spin-projected band structure of top VBs in H-BA WSiGeP₄. (d) The variation of Rashba coefficients under the application of biaxial strain.

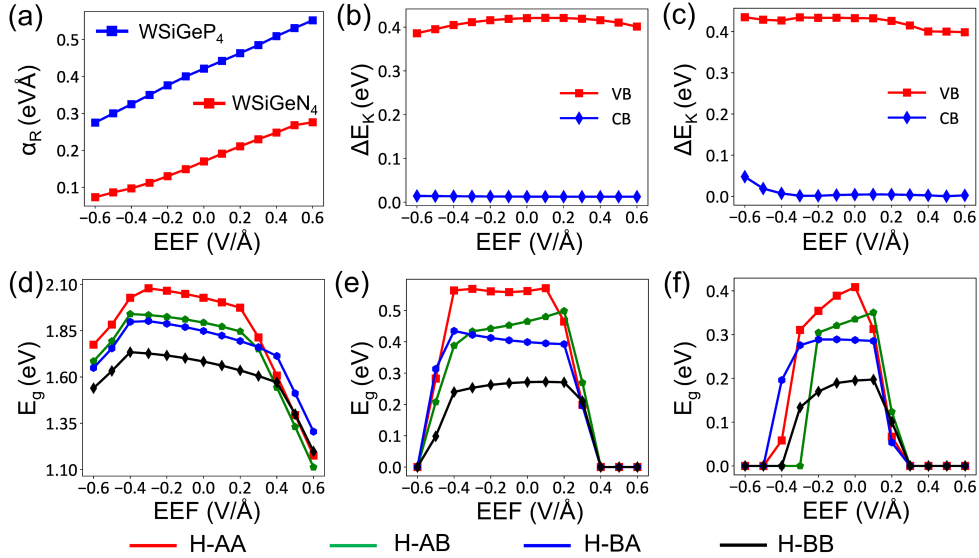


Figure 5.9: (a) The variation of Rashba coefficient (α_R) under the application of out-of-plane EEF. Zeeman spin splittings at K/K' points as a function of EEF in monolayer (b) H-BB WSiGeN₄ and (c) H-AA WSiGeP₄. Modulation of band gaps with strain in monolayer (d) H-BB WSiGeN₄, (e) H-AA WSiGeP₄ and (f) H-AA WSiGeAs₄.

To understand the band structure and spin texture, we have constructed a $\mathbf{k}\cdot\mathbf{p}$ model Hamil-

tonian near the Γ point. The little group of the Γ point is C_{3v} , and the corresponding Hamiltonian is expressed as [299, 300, 228]

$$H_{\Gamma}(\mathbf{k}) = H_o(\mathbf{k}) + \alpha_R(k_x\sigma_y - k_y\sigma_x) + \gamma(k_y^3 - 3k_xk_y^2) \quad (5.7)$$

where $H_o(k)$ is the free particle Hamiltonian, and α_R is the linear Rashba coefficient. γ is the parameter signifying the contributions from the cubic term in the splitting and takes the out-of-plane spin contributions into consideration. We have observed that the energy contribution coming from the cubic term is much smaller than the linear term. The fitting of the DFT band structure by $\mathbf{k}\cdot\mathbf{p}$ model hamiltonian allows the calculation of α_R . Within the linear Rashba term, the α_R is also estimated by $\alpha_R = \frac{2E_R}{k_R}$, where E_R and k_R are the Rashba energy splitting and momentum shift, respectively [299]. The calculated values of E_R and k_R are 11.2 meV and 0.55 $\text{\AA}^{-1}$, respectively [see Fig. 5.8(a)]. Thus, for monolayer H-AA WSiGeP₄, α_R is 0.41 eV $\text{\AA}$. A larger value of α_R makes the Rashba effect more accessible experimentally. Therefore, greater magnitude of α_R is always desired. Consequently, we have studied the impact of symmetry on the strength of Rashba effect. Table 5.4 shows E_R , k_R , and α_R of monolayer WSiGeN₄ and WSiGeP₄ in different configurations. H-BA structure has the largest value of E_R and α_R . As shown in Fig. 5.8(c), E_R increases to 22.9 meV from 11.2 meV when the structure changes to H-BA from H-AA. The value of α_R is also significantly enhanced from 0.41 eV $\text{\AA}$ to 0.61 eV $\text{\AA}$. Similar results have also been obtained for WSiGeN₄ and WSiGeAs₄. The observed trend of α_R is H-BA > H-BB > H-AA > H-AB.

According to the Rashba model, spin splitting occurs in the plane perpendicular to the electric field. The net vertical electric field acting on the metal atom W, determines the strength of the Rashba effect. Therefore, the larger the out-of-plane intrinsic electric field, the more prominent is the in-plane spin splitting. In case of H-BA, the out-of-plane intrinsic electric field arising due to the formation of Janus and the position of Z atoms support each other. Therefore, the strongest Rashba spin splitting is observed for the H-BA phase as it has the highest out-of-plane asymmetry.

Additionally, the effect of biaxial strain on α_R is also studied, and the variation is shown in Fig. 5.8(d). The value of α_R decreases from 0.41 eV $\text{\AA}$ to 0.28 eV $\text{\AA}$ under a compressive strain of 6%. The tensile strain of 6% increase α_R to 0.46 eV $\text{\AA}$, which is significantly smaller than the increment observed using the symmetry control. The strain is also an effective way to modulate the band edge positions and band gaps. For the case of WSiGeN₄, the band gap remains indirect in the range of -6% to 6%. The band gap remains direct for WSiGeP₄ and WSiGeAs₄

Table 5.4: The calculated parameters (E_R , k_R and α_R) for Rashba spin splitting around Γ point.

	Phase	E_R (meV)	k_R ($\text{\AA}^{-1}$)	α_R (eV $\text{\AA}$)
WSiGeN ₄	H-AA	5.7	0.060	0.19
	H-AB	3.0	0.068	0.09
	H-BA	9.4	0.067	0.28
	H-BB	5.6	0.066	0.17
WSiGeP ₄	H-AA	11.2	0.055	0.41
	H-AB	8.57	0.079	0.22
	H-BA	22.9	0.075	0.61
	H-BB	16.9	0.079	0.43

Table 5.5: The acoustic phonon limited carrier mobility and other relevant parameters for WSiGeZ₄ monolayer. The x and y directions correspond to armchair and zigzag directions, respectively. m_o is rest mass of the electron.

	Carrier	m_x/m_o	m_y/m_o	E_x (eV)	E_y (eV)	C_{2D} (Nm ⁻¹)	μ_x (cm ² V ⁻¹ s ⁻¹)	μ_y (cm ² V ⁻¹ s ⁻¹)
WSiGeN ₄	e_K	0.460	0.499	5.82	6.832	493.1	2355.1	942.2
	h_Γ	1.838	1.816	5.70	5.147	493.1	98.3	119.7
WSiGeP ₄	e_K	0.975	0.594	13.18	10.32	225.5	37.3	99.9
	h_K	0.484	0.448	9.49	6.98	225.5	237.0	473.5
WSiGeAs ₄	e_K	3.260	1.673	11.92	10.88	178.2	3.5	8.2
	h_K	0.542	0.477	9.59	8.91	178.2	150.1	197.6

in the range of -3% to 3%. In general, the band gap shows decrement under tensile strain. However, under compressive strain, the band gap increases up to 2% and decreases afterward. Furthermore, WSiGeAs₄ shows semiconductor to metal transitions under a compressive strain of larger than 3%.

5.2.5 The role of electric field

An external electric field (EEF) is commonly used to tune the strength of Rashba effect in spintronics devices [301, 302]. Therefore, the effect of EEF is also investigated in this study. We have applied the out-of-plane EEF in the range of $-0.6 \text{ V/\AA}$ to $0.6 \text{ V/\AA}$ to analyze the variation of Rashba coefficient (α_R) and Zeeman splittings (ΔE_K^{CB} and ΔE_K^{VB}). Figure 5.9(a) shows the variation of α_R as a function of EEF for monolayer H-BB WSiGeN₄ and H-AA WSiGeP₄. When the EEF points from Ge to Si (taken to be positive direction), which is consistent with the local electric field, it enhances the Rashba SOC. Whereas, the opposite direction of EEF reduces the strength of Rashba SOC, as the effects of the EEF and the local electric field cancel each other. The value of α_R varies from $0.28 \text{ eV/\AA}$ to $0.55 \text{ eV/\AA}$ in case of monolayer H-AA WSiGeP₄, while it varies from $0.08 \text{ eV/\AA}$ to $0.25 \text{ eV/\AA}$ for monolayer H-BB WSiGeN₄. The variation of Zeeman splittings at the K point are shown in Figs. 5.9(b) and 5.9(c). The $d_{x^2-y^2}$ and d_{xy} orbitals under the influence of in-plane electric field contribute to the Zeeman splitting at K point. Therefore, the out-of-plane EEF hardly affects the ΔE_K^{CB} and ΔE_K^{VB} . The evolution of band gap as a function of EEF is provided in Figs. 5.9(d), 5.9(e) and 5.9(f). We have noticed that the band gaps are almost insensitive to small EEFs (in the range $-0.3 \text{ V/\AA}$ to $0.3 \text{ V/\AA}$). It is also interesting to note that the CBM for monolayer WSiGeZ₄ shifts to the M point under large EEF, this is because the Si atom starts contributing to the CBM. Therefore, band gaps decrease sharply under large EEFs. In the case of WSiGeP₄ and WSiGeAs₄, giant Stark effect closes the band gap and semiconductor to metal transition takes place.

5.2.6 Carrier mobility

Estimation of carrier mobilities is essential for exploring the potential use of any material for application in electronic devices [303, 149]. The carrier mobility (μ_{2D}) of the WSiGeZ₄ monolayer is calculated using the deformation potential (DP) theory. According to DP theory [304], μ_{2D} is expressed as

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{k_B T m^* m_d E_l^2} \quad (5.8)$$

where m_d and m^* are the average effective mass ($\sqrt{m_x m_y}$) and the effective mass along the transport direction, respectively. C_{2D} is Young's elastic modulus, which is calculated from the elastic tensor C_{ij} . The E_l is the DP constant defined by $E_l = \delta E / \delta l$. Here, δE is the change in the position of the CBM or VBM with respect to the vacuum level and $\delta l = \Delta l / l$ is

the relative strain. The calculated elastic constants and carrier mobilities are listed in Table 5.5. The carrier mobilities in these monolayers are anisotropic and show considerable variation. For instance, the most significant carrier mobility observed is 2355.1 cm²V⁻¹s⁻¹ for the electron in monolayer H-BB WSiGeN₄, and the smallest carrier mobility observed is as tiny as 3.514 cm²V⁻¹s⁻¹ for the electron in monolayer H-AA WSiGeAs₄.

5.3 Probing the uniaxial strain-dependent valley drift and Berry curvature in monolayer MoSi₂N₄

The strain engineering of monolayer MoSi₂N₄ has been gaining attention recently [50, 305, 231, 292]. These previous reports are based on the biaxial or uniaxial out-of-plane strain, where the valley extremum remains at K/K' point, preserving the three-fold rotation symmetry [50, 305, 292]. However, the effect of reduced symmetry of valleys in monolayer MoSi₂N₄ remains unexplored. Recent theoretical and experimental studies have shown that the non-linear Hall effect can occur even in time-reversal symmetric systems under reduced symmetry [306, 307, 308, 281]. Therefore, the mechanical tunability of its valleys and associated properties in monolayer MoSi₂N₄ under uniaxial deformation potential provides an ideal avenue to prospect.

This section demonstrates strain-induced electron and hole valley drifts and their effects in monolayer MoSi₂N₄. We theoretically apply in-plane lattice deformation up to 10% along three crystallographic non-equivalent directions, i.e., armchair (AC), intermediate (IM), and zigzag (ZZ). The energy valley drifts are responsive to the strain directions. For example, drifts are more pronounced for strain along the ZZ direction than the IM and AC directions. Additionally, electron valleys are more sensitive to the deformation when compared to the hole valleys. The group theoretical perspective and microscopic orbital contribution explain the underlying mechanism behind the asymmetric nature of valley drifts. Afterward, we provide the effect of asymmetric valley drifts on Berry curvature distribution and optical circular dichroism.

5.3.1 Lattice under strain

The monolayer MoSi₂N₄ has the hexagonal lattice structure built by septuple atomic layers in the sequence N-Si-N-Mo-N-Si-N (see Fig. 5.10). The lattice can be regarded as 2H-MoN₂

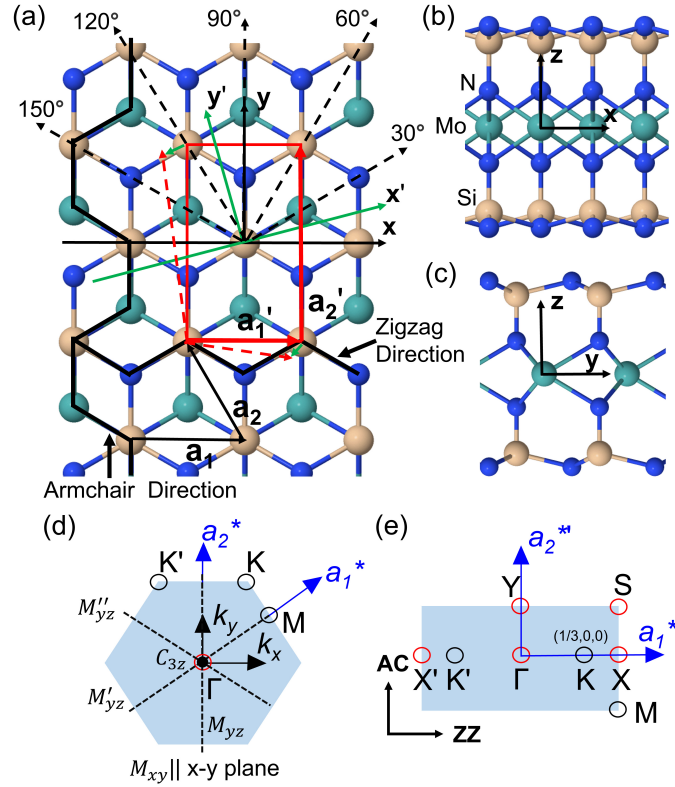


Figure 5.10: (a) Top and [(b),(c)] side views of monolayer MoSi_2N_4 . The x , y , and z axes are shown in each case. a_1 and a_2 are the hexagonal lattice vectors, while a'_1 and a'_2 are lattice vectors of the orthorhombic cell. The rotated Cartesian frame for strain along an arbitrary direction is shown using green lines. After applying strain along x' direction and allowing relaxation along perpendicular y' direction, the orthorhombic unit cell is shown using red dashed lines. The effect of strain on the strained lattice is exaggerated for clear illustration and is much smaller for our considered range. x and y directions are zigzag (ZZ) and armchair (AC), respectively. The atomic arrangement is ZZ along 0° , 60° and 120° , whereas AC along 30° , 90° and 150° directions. The first (d) hexagonal and (e) orthorhombic BZ are shown. M_{xy} and M_{yz} are the mirror planes, and C_{3z} is the three-fold rotation axis. The high symmetry points Γ , M, and K of hexagonal BZ are mapped in the orthorhombic BZ (see Eq. 5.9).

monolayer sandwiched between two silicene-like Si-N monolayers [47]. There are two alternative choices for the unit cell of monolayer MoSi_2N_4 having the $\text{P}\bar{6}m2$ space group. As shown in Fig. 1(a), the choices are the $\text{P}\bar{6}m2:h$ (7 atoms hexagonal lattice) and $\text{P}\bar{6}m2:o$ (14 atoms orthorhombic lattice). It is very efficient to perform DFT calculations in the $\text{P}\bar{6}m2:h$ setting. However, the $\text{P}\bar{6}m2:o$ is of great convenience in terms of symmetry perspective for strained lattice along AC or ZZ directions, and therefore considered in our study. Firstly, we have mapped

the arbitrary k-point (k_1, k_2) of hexagonal BZ on the basis of orthorhombic reciprocal vectors. The results are expressed as

$$(k_1, k_2)_h \implies (k_1, k_1 + 2k_2)_o \quad (5.9)$$

The location of Γ , M, and K points are shown in Fig. 5.10(d), and corresponds to $(0, 0, 0)$, $(1/2, 1/2, 0)$, and $(1/3, 0, 0)$ in orthorhombic BZ, respectively. Firstly, we have fully relaxed the structure using the conjugate gradient algorithm such that the force on each atom is smaller than 0.001 eV/Å. The simulated lattice parameter (a_1) was found to be 2.912 Å, being consistent with the previous experimental [47, 309] and theoretical studies [48, 49, 50, 51, 52, 53].

To simulate the strained lattice of monolayer MoSi₂N₄ along x (ZZ) and y (AC) directions, we change the corresponding lattice vector to satisfy the relation, $\epsilon_x = \frac{a'_1 - a_1}{a'_1}$ and $\epsilon_y = \frac{a'_2 - a_2}{a'_2}$, where $a'_1(a'_2)$ and $a''_1(a''_2)$ are the lattice constant along $x(y)$ direction without and with strain respectively (see Fig 5.10(a)). For the application of strain along an arbitrary direction, we rotate the coordinate system such that x' points along the direction of strain. After that, we apply strain, relax the structure along y' direction, and then return to the original Cartesian system. Due to the C_{3z} and M_{yz} symmetry, only the direction between $\theta = 0^\circ$ and 30° are of interest, where θ is measured anticlockwise with respect to the ZZ direction. Therefore, we have considered $\theta = 0^\circ$ (ZZ), $\theta = 15^\circ$ (IM), and $\theta = 90^\circ$ (equivalent to 30°) (AC) directions. For the uniaxially strained lattice, D_{3h} symmetry reduces to C_{2h} , containing a two-fold rotation operation (C_{2z}) and mirror symmetry containing the x - y plane. Moreover, additional diagonal mirror planes arise for the strain along AC and ZZ directions, leading to D_{2d} point group symmetry.

The elastic energy density for orthorhombic lattices is expressed as [310, 311]

$$U_{ortho} = \frac{1}{2}C_{11}\epsilon_{xx}^2 + \frac{1}{2}C_{22}\epsilon_{yy}^2 + C_{12}\epsilon_{xx}\epsilon_{yy} + C_{44}\epsilon_{xy}^2. \quad (5.10)$$

C_{ij} and ϵ_{ij} are components of elastic constants and strain tensors, respectively. Employing Eq. 5.10, the direction-dependent Young's modulus and Poisson's ratio are obtained as [310]

$$\begin{aligned} Y_{2D}(\theta) &= \frac{\Delta}{C_{11}s^4 + C_{22}c^4 + (\frac{\Delta}{C_{44}-2C_{12}})c^2s^2} \\ \nu_{2D}(\theta) &= \frac{(C_{11} + C_{22} - \frac{\Delta}{C_{44}})c^2s^2 - C_{12}(s^4 + c^4)}{C_{11}s^4 + C_{22}c^4 + (\frac{\Delta}{C_{44}-2C_{12}})c^2s^2} \end{aligned} \quad (5.11)$$

where $\Delta = C_{11}C_{22} - C_{12}^2$, $c = \cos(\theta)$ and $s = \sin(\theta)$. The dynamical and mechanical stabilities of strained lattices are confirmed using phonon spectrum and elastic constants, respectively.

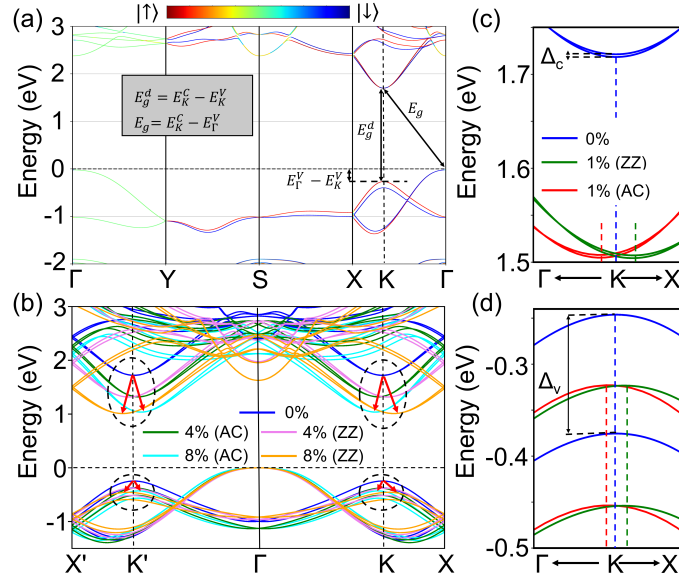


Figure 5.11: (a) Spin-projected band structures of the monolayer MoSi₂N₄ in the presence of SOC. (b) Evolution of band structures under the uniaxial strain of strength 4% and 8% along the ZZ and AC directions. The red arrows represent the valley drifts. (c) and (d) are the zoomed versions of low CBs and top VBs of monolayer MoSi₂N₄ with 1% uniaxial stain, respectively. The vertical dashes represent the location of energy extreme in k -space

5.3.2 Monolayer MoSi₂N₄

Spin-projected band structure of monolayer MoSi₂N₄ is shown in Fig. 5.11. It has a band gap of 1.72 eV, having VBM and CBM at the Γ and K point, respectively. The calculated band gap is smaller than the experimental value of 1.94 eV [47] due to self-interaction error, while it is in good agreement with previous theoretical PBE results [48, 49, 50, 51]. In Refs [55, 305, 312], band gaps are improved using hybrid HSE06 and many-body perturbation theories (GW, BSE). We have conducted a comparison between the results using the PBE and HSE06 to validate the choice of functional. The results calculated using HSE06 are within $\pm 4\%$ as compared to the PBE, excluding band gaps. Therefore our calculations are based on the computationally efficient PBE functional. The VB (VB) at K points lies lower in energy than VBM with an offset ($\Delta_{\Gamma-K} = E_\Gamma^V - E_K^V$) value of 0.24 eV (see Fig. 5.11(a)). Spins eigenstates are polarized along the z -direction except for the Γ -Y line and can be explained by the symmetry aspects [51]. Horizontal-mirror symmetry (M_{xy}) commutes with the Hamiltonian, therefore eliminating the spin-polarization along the x - y plane and preserving along the z direction. For any k -point along Γ -Y direction, $H(k)$ exhibits C_{2v} point group symmetry and

does not contain the spin operator leading to degenerate eigenvalues. It has Dirac-type valley bands near the K/K' points. Due to the strong SOC and broken inversion symmetry, valley Fermions exhibit strong spin-valley coupling, valley-selective optical circular polarization, and valley-contrasting Berry curvature [50, 49, 51]. The VB valley is the spin split of order ~ 130 meV, whereas the CB valley is nearly spin degenerate. These effects are well explained by the previous DFT calculations [50, 49, 51, 88], tight-binding (TB) models [51], and two-band and three-bands $k.p$ models [50, 49].

5.3.3 Valley drifts

Figure 5.11(b) shows the evolution of band structures under the strain along AC and ZZ directions. We find a robust strain-valley coupling between the strain and low-energy states. Uniaxial strain shifts the electron and hole valleys away from the K/K' point. Figures 5.11(c) and 5.11(d) shows the valley drift response of low CB and top VB under the uniaxial strain in the limit of 1% along ZZ and AC directions. Here, we observe that electron valleys responses are stronger when compared to the hole sector. In addition, the parabolicity of bands is more heavily deformed than the hole bands. This phenomenon can be explained by the changing geometric effects and orbital hybridization of relevant Bloch states due to reduced symmetry of the lattice. The strain modifies the scalar potential for the corresponding Bloch bands contributing to the low-energy holes and valley states at the K/K' point.

For a clear illustration of valley drifts, we have plotted the constants energy contours of VB and CB near the K point. The results are shown in Figs. 5.12(a) and 5.12(b). Except for the immediate vicinity of the K point, the dispersion is not isotropic. The trigonal warping effect of energy bands is visible, resulting from the C_{3z} . The trigonal warping effect is more pronounced for the VB when compared to the CB. When applying the uniaxial strain, an increase in the warping effect near the K point is observed due to the continuous reduction in C_{3z} and translation symmetry along its mutually perpendicular direction. The bands are elliptically warped (due to the appearance of two-fold rotation symmetry) in the immediate proximity of K when uniaxial strain is applied and increases with an increasing strain field. The elliptical warping of band topology is anti-symmetric in such a way that the major axis is along the k_x - and k_y -direction for strain along ZZ and AC directions, respectively. For lattice strained along the IM direction, the major axis of elliptical warping makes an angle of 30° . The anisotropic nature of electronic bands leads to different effective masses, charge transport, and optical absorption in

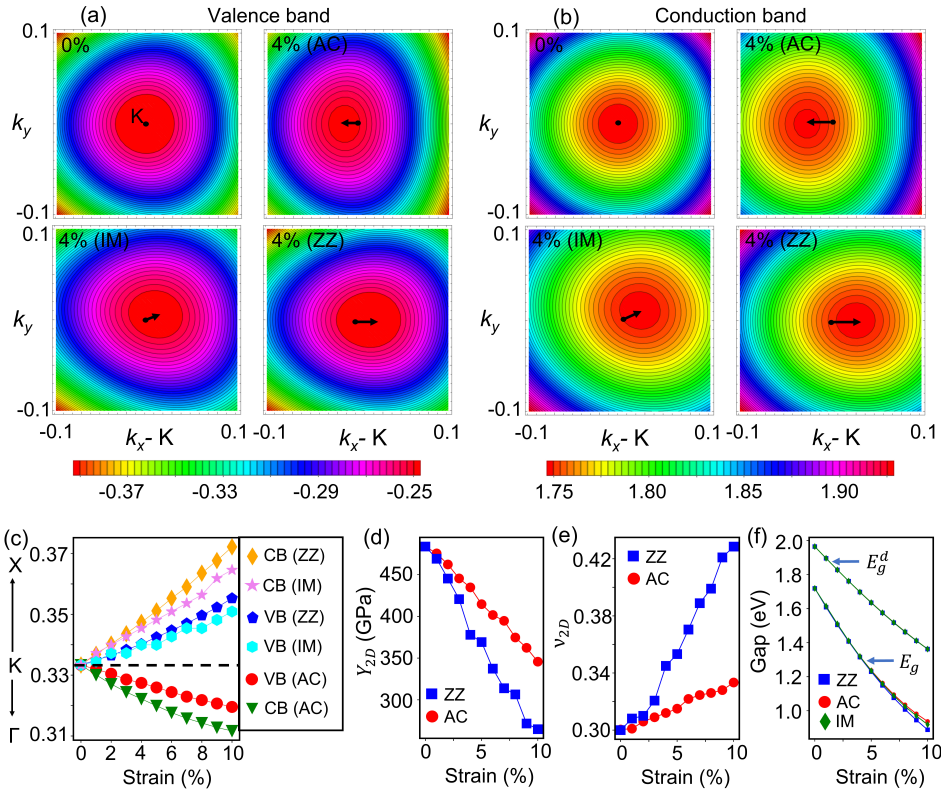


Figure 5.12: (a) Contour plot showing isoenergy contours of the VB around the K point for the unstrained case (0%) and with the uniaxial strain of 4% along AC, IM, and ZZ directions of monolayer MoSi_2N_4 . Black arrows show the directions of valley drifts. (b) The same as in (a) for the CB. (c) Momentum drift of the CB and VB near the K point. Valley extremum as a function of uniaxial strain applied along the AC, IM, and ZZ direction. Note that only the k_x component of drift along $\text{K} \rightarrow \text{X}$, $\cos(30^\circ)$ of the net drift is shown in (c) for the IM case. The k_y component ($\sin(30^\circ)$ of the net drift) is also there and duly considered in all the calculations. The variation of (d) Young's modulus, (e) Poisson ratio, (f) direct and indirect band gap as a function of strain.

different directions. In addition, the energy extreme of the valley drifts away from the K point. In general, the direction of valley drift is 2θ (with respect to $\text{K} \rightarrow \text{X}$ direction) when strain is applied along θ direction. Particularly, the direction of valley drift is $\text{K} \rightarrow \Gamma$ and $\text{K} \rightarrow \text{X}$ for AC and ZZ direction, respectively (shown by black arrows in Fig. 5.12(a) and 5.12(b)). To quantify the valley drifts, we plot the valley extreme as a function of strain in Fig. 5.12(c). The VB drift off the K point with the rate $1.38 \times 10^{-3} (\frac{2\pi}{a})/\%$ for strain along the AC direction, whereas the rate of drift is $2.19 \times 10^{-3} (\frac{2\pi}{a})/\%$ for the ZZ direction. For uniaxial strain along the IM direction, drift is in-between that of AC or ZZ direction with the rate of $1.99 \times 10^{-3} (\frac{2\pi}{a})/\%$. Similarly, the

rate of electron valley drifts are $2.17 \times 10^{-3} (\frac{2\pi}{a})/\%$, $3.43 \times 10^{-3} (\frac{2\pi}{a})/\%$ and $3.89 \times 10^{-3} (\frac{2\pi}{a})/\%$ for strain along the AC, IM, and ZZ directions, respectively. The electron valley drifts are nearly ~ 1.7 times that of hole valley drifts.

Here, we notice that the drift response is more extensive when the lattice is stretched along the ZZ direction. That is because the stretching of the Mo-N bond is asymmetric when the lattice is stretched along AC or ZZ direction (see Figs. 5.10(b) and 5.10(c)). To understand this, we plot Young's modulus ($Y_{2D}(\theta)$) and Poisson's ratio ($\nu_{2D}(\theta)$) as a function of strain in Figs. 5.12(d) and 5.12(e). For unstrained monolayer MoSi₂N₄, Young's modulus 485.7 GPa is in good agreement with the experiment value of 491.4 ± 139.1 GPa [47] and theoretical value of 479 GPa [231]. The drop in Young's modulus is significant when strain is along ZZ direction. Drastic variation in elastic constants leads to significant cell deformation. Therefore electron and hole valley drifts are more pronounced when uniaxial strain is applied along the ZZ direction.

Figure 5.12(f) shows the evolution of direct (E_g^d) and indirect (E_g) band gaps. The band gap energies are red-shifted under the uniaxial tensile strain. The shift in the band gap is nearly direction independent for the smaller strains in the range of 0-5%. However, band gaps are red-shifted at a faster rate for the larger uniaxial strains along the ZZ directions and are attributed to the more enormous variation in mechanical constants. The red-shift rates of the indirect and direct gaps are 0.067 eV/% and 0.53 eV/%, respectively. These unequal rates lead to the enhancement in the VB energy offset ($\Delta_{\Gamma-K}$). $\Delta_{\Gamma-K}$ increases from 0.24 to 0.43 eV under the uniaxial strain of 10%. The optical absorption and photoluminescence experiments study these variations in the band gaps and are widely explored for graphene [313, 282, 314] and TMDs [272, 315].

The degeneracy of each band is determined by the irreducible representations of point group symmetry of monolayer that is contained in the full rotation symmetry group [5]. The representation of the a full rotation group will be a reducible representation of the D_{3h} and can be written as $\Gamma_{l=2} = A' \oplus E' \oplus E''$, where A' , E' , and E'' are the irreducible representations of D_{3h} . Therefore, the five-fold degenerate Mo- d orbitals split into three categories at the Γ point: $A'(d_{z^2})$, $E'(d_{x^2-y^2}, d_{xy})$, and $E''(d_{xz}, d_{yz})$ under the effect of trigonal crystal field. The group of wavevector at the K/K' point reduces to the C_{3h} . Further, we constructed the Bloch state using the linear combination of atomic orbitals approach, $\Psi_{l,m}^\eta(r, k) = \sum_{R_\eta} e^{ik \cdot R_\eta} Y_l^m(r - R_\eta)$, where Y_l^m are the spherical harmonics and R_η is the position of Mo, N and Si atoms. We then

Table 5.6: The irreducible representations and basis functions for the little group $C_{3h}(= C_3 \times \sigma_h)$ of K/K' point [5]. The sign $\pm$ corresponds to $\pm K$ points. The last column contains the energy bands to which basis functions contribute.

C_{3h}	C_3	σ_h	Mo	N	Band
A'	1	1	$ \Psi_{2,\mp 2}^{\text{Mo}}\rangle$	$\frac{1}{\sqrt{2}}(\Psi_{1,\mp 1}^{\text{N1}}\rangle + \Psi_{1,\mp 1}^{\text{N2}}\rangle)$	VB
A''	1	-1	$ \Psi_{2,\pm 1}^{\text{Mo}}\rangle$	$\frac{1}{\sqrt{2}}(\Psi_{1,\mp 1}^{\text{N1}}\rangle - \Psi_{1,\mp 1}^{\text{N2}}\rangle)$	CB+1
E'_1	$\omega^\pm$	1	$ \Psi_{2,0}^{\text{Mo}}\rangle$	$\frac{1}{\sqrt{2}}(\Psi_{1,\pm 1}^{\text{N1}}\rangle + \Psi_{1,\pm 1}^{\text{N2}}\rangle)$	CB
E'_2	$\omega^\mp$	1	$ \Psi_{2,\pm 2}^{\text{Mo}}\rangle$	$\frac{1}{\sqrt{2}}(\Psi_{1,0}^{\text{N1}}\rangle - \Psi_{1,0}^{\text{N2}}\rangle)$	CB+2
E''_1	$\omega^\pm$	-1	$ \Psi_{1,0}^{\text{Mo}}\rangle$	$\frac{1}{\sqrt{2}}(\Psi_{1,\pm 1}^{\text{N1}}\rangle - \Psi_{1,\pm 1}^{\text{N2}}\rangle)$	VB-2
E''_2	$\omega^\mp$	-1	$ \Psi_{2,\mp 1}^{\text{Mo}}\rangle$	$\frac{1}{\sqrt{2}}(\Psi_{1,0}^{\text{N1}}\rangle + \Psi_{1,0}^{\text{N2}}\rangle)$	VB-1

identify how the Bloch wavefunction $\Psi_{l,m}^\eta(r, k)$ transforms under the symmetry operations of C_{3h} . Table 5.6 classifies the Bloch state at the BZ corners according to the irreducible representations of C_{3h} . The M_{xy} mirror symmetry allows hybridization only between A' and E' orbitals, opening a gap at the K point [43]. As seen from Figs. 5.13(a) and 5.13(b), the VB and CB states mainly originate from the hybridization of Mo- d and N- p orbitals. The Bloch state contributing to CB at the K/K' point is $|\Psi_{2,0}^{\text{Mo}}\rangle$, whereas the states for VB are $|\Psi_{2,-2}^{\text{Mo}}\rangle$ and $|\Psi_{2,2}^{\text{Mo}}\rangle$ at the K and K', respectively. The periodic parts of the Bloch wavefunctions for the CB and VB at the K point are predominantly composed of $|d_{z^2}\rangle$ and $|d_{x^2-y^2}-id_{xy}\rangle$, respectively. The uniaxial strain modifies the crystal field between metal and Mo-N trigonal coordination environment. Therefore, strain modifies the bandwidths of contributing orbitals and energy of the Bloch states. The energy of d and p orbitals along the strain direction increases with increasing strain. The out-of-plane orbitals (d_{z^2}) are more influenced by the in-plane strain when compared to the in-plane orbital ($d_{x^2-y^2}, d_{xy}$). Therefore the effect of strain is more prominent for electron valleys leading to larger valley drift for CB. Stretching of orbitals along the strain direction leads to the charge density redistribution and increases with the increasing strain field. To compare the ZZ and AC directions, we plot the ground state charge density difference between the unstrained lattice and the lattice with 4% of strain. The charge density difference near Mo and inner N atoms is more prominent in the ZZ case compared to the AC case. Strong charge density redistribution leads to sharper changes in the valley drifts, elastic constants, and band gaps for the lattice stretched along the ZZ direction.

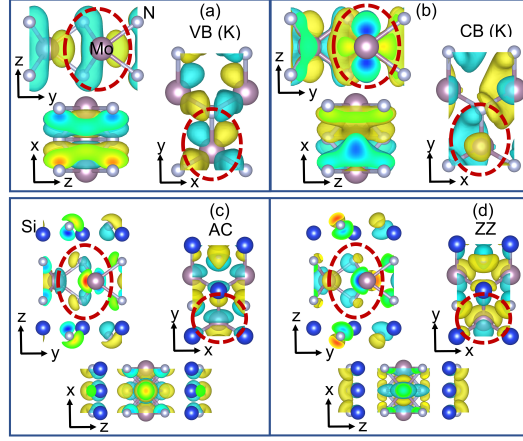


Figure 5.13: The real part of the wavefunction of (a) VB and (b) CB at the K point for monolayer MoSi_2N_4 without strain. Note that in (a) and (b), we show only the Mo-N₂ network since the contribution coming from the upper and lower Si-N layer is almost zero. The charge density difference between the unstrained and 4% strained lattice along the (c) AC and (d) ZZ directions. The electron accumulation is shown in cyan, and electron depletion is shown in yellow.

5.3.4 Berry curvature modulation

We further investigate the Berry curvatures in monolayer MoSi_2N_4 under uniaxial strain. Berry curvature is analogous to the magnetic field in momentum space and has a pivotal impact on the electronic transport properties. For example, the integral of Berry curvature gives Hall conductivity. The Berry curvature is evaluated using the expression

$$\Omega(k) = i\nabla_k \times \langle u(k) | \nabla_k | u(k) \rangle \quad (5.12)$$

where $|u(k)\rangle$ is the periodic part of the Bloch wavefunction. We plot the total Berry curvature of all the occupied bands in Fig. 5.14(a). Berry curvature distribution is peaked around valleys with opposite values at K and K' points. The contrasting nature of Berry curvatures at the valleys is attributed to the TRS, enabling the separation of charge carriers depending on their valley index. The introduction of strain alters the occupation of different orbitals contributing to Bloch states and leading to modification in the electronic energies and Berry curvature. The Berry curvature profile is strongly modified when the lattice is strained along ZZ or AC direction. The Berry curvature peak drifts away from K/K' point, similar to the energy valley drift. The Berry curvature peak is enhanced up to a factor of ~ 1.5 under the strain of 8% along ZZ and AC directions. The increased berry curvature flux density and drift would influence the valley transport when the external transverse electric field is applied since the berry curvature

directly enters into the equation of motion and engenders an anomalous velocity term $\sim E \times \Omega$. Therein, the strong response of valleys to the strain notably alters the valley-contrasting physics in the monolayer MoSi_2N_4 .

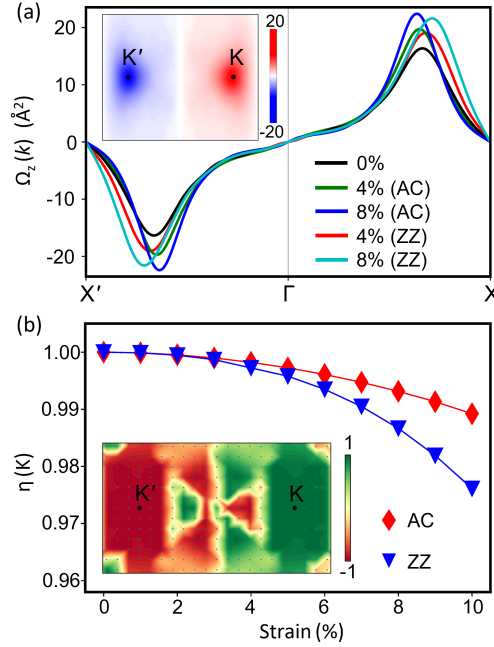


Figure 5.14: (a) Berry curvature distribution summed for all VBs along the path $X'-K'-\Gamma-K-X$ in monolayer MoSi_2N_4 . Inset in (a) shows the mapping of Berry curvature under first BZ. (b) The degree of circular polarization of excitation from VB to CB at the K point. Inset in (b) shows the mapping of the degree of circular polarization in the first BZ.

5.3.5 Circular dichroism under strain

The electron and hole population in two nonequivalent valleys are controlled by circularly polarized optical pumping. The electromagnetic interaction that gives rise to dipole transition is $H_{em} = \frac{e}{mc} P \cdot A$, where P is the momentum operator, and A is the magnetic vector potential of incident light [5]. Then, the probability of dipole transition between the VB ($v(k)$) and CB ($c(k)$) is $|\langle v(k) | H_{em} | c(k) \rangle|^2$. Group theory tells when the dipole transition is allowed or forbidden [5]. The wavefunctions $v(k)$ and $c(k)$ at the K point transforms as the irreducible representations A' and E'_1 , respectively (see Table 5.6). $P_{\pm} (= P_x \pm iP_y)$ are the chiral momentum operator representing right/left-hand circularly polarized light. $P_{\pm} (= P_x \pm iP_y)$ transforms as $C_3 P_{\pm} C_3^{\dagger} = \omega^{\mp} P_{\pm}$ [49]. P_+ transforms according to the irreducible representation E'_2 . $A' \otimes E'_2 \otimes E'_1$ contains only the fully symmetrical irreducible representation A' . Therefore,

right-hand circularly polarized light will be absorbed at the K point, whereas absorbance of left-hand circularly polarized light will be forbidden. A similar analysis shows that only left-hand circularly polarized light will be absorbed at the time-reversal conjugate K' point. The degrees of circular polarization ($\eta(k)$) are expressed as

$$\eta(k) = \frac{|P_+|^2 - |P_-|^2}{|P_+|^2 + |P_-|^2}. \quad (5.13)$$

The degree of circular polarization is computed directly by evaluating optical matrix elements $|\langle v(k) | H_{em} | c(k) \rangle|^2$ using an ab initio approach, not from a model Hamiltonian. The wavefunction coefficients are obtained directly from density functional theory (DFT) simulations as implemented in VASP. For each type of strain, wavefunctions are calculated using DFT, and then the optical matrix elements are computed. Detailed information on these methods can be found in the Wannier90 Package documentation. The results agree with the symmetry analysis (see inset in Fig. 5.14(b)). The transition is exclusively coupled to a specific circular polarization at the valley center for zero strain. After introducing strain, the $\eta(k)$ at the K point decreases due to the continuous reduction of the group of wavevector from C_{3h} to C_{2h} . The unequal rates of electron and hole valley drifts soften the valley-selective optical selection rules arising from the C_3 symmetry operation due to changes in its optical matrix elements ($\langle v(k) | P_{\pm} | c(k) \rangle$). The $\eta(k)$ reduces up to 0.99 and 0.98 for 10% uniaxially strained MoSi₂N₄ along AC and ZZ directions, respectively (see Fig. 5.14(b)). Therefore, uniaxial strain makes monolayer MoSi₂N₄ less valley selective, and effects are more prominent along the ZZ direction.

Finally, we emphasize that the analysis presented here can also be manifested in other septuple-layered MA₂Z₄ (M=Cr, Mo, W, V; A=Si, Ge; Z=N, P, As) materials [47]. However, the strength of effects can be different. In addition, there are no states other than K/K' near the Fermi level in monolayer MA₂P₄ and MA₂As₄ [48, 53]. Therefore, interference from the different parts of BZ will be minimal, providing an additional advantage over the monolayer MoSi₂N₄. Furthermore, geometric properties of Bloch states other than Berry curvature can also be modified with the uniaxial strain. For example, orbital magnetic moments (m_{nk}) are normal to the plane for 2D materials and have opposite nature for the K and K' valleys. Orbital moments tuning allows control over valley polarization by a vertical magnetic field [316].

5.4 Summary and outlook

We have revealed that different stacking patterns of Si-Z, Z-W-Z and Ge-Z generate the dynamically stable structures. The most stable structure for monolayer WSiGeN₄ is H-BB, whereas for monolayer WSiGeP₄ and WSiGeAs₄ is H-AA. These materials show valley contrasting circular dichroism, spin-valley coupling, and Berry curvature. Additionally, the out-of-plane asymmetry in them leads to Rashba effect around the center of the BZ. The stacking pattern greatly modifies the spintronics and valleytronics properties. The highest Rashba SOC around the Γ point is observed for the H-BA phase having the highest out-of-plane electric dipole moment. Whereas, the Berry curvature is strongest at valleys for H-BB phase with the highest contribution coming from d_{xy} and $d_{x^2-y^2}$ orbitals. Additionally, valleys observed in WSiGeP₄ and WSiGeAs₄ monolayers at K and K' points have multiple folds. Furthermore, we have found that the band gap type and valleys can be tuned with an EEF and biaxial strain. Under large strain and high electric field, monolayer WSiGeP₄ and WSiGeAs₄ show semiconductor to metal transition. We have found the strong anisotropy in carrier mobilities along the armchair and zigzag directions. Rashba spin splitting and valley polarization can facilitate the manipulation of electron spin and valley. The regulation of spin direction of separated valley carriers by controlling symmetry can be realized better in septuple-atomic-layer materials compared to TMDs.

In addition, We have reported valley drifts in uniaxially strained monolayer MoSi₂N₄ for the first time. By taking strain along AC, IM, and ZZ directions, we confirmed the stronger strain-valley coupling along the ZZ direction due to pronounced geometric deformation. Additionally, electron valleys show a faster response (nearly 1.7 times) to the strain than hole valleys owing to contribution coming from out-of-plane d_{z^2} orbitals. The observed rates of valley drifts are up to $3.89 \times 10^{-3} (\frac{2\pi}{a'})/\%$. These effects noticeably affect the valley's selective optical excitation. The reduction of three-fold rotation symmetry leads to a substantial drop in the degree of circular polarization to ~ 0.98 . Besides, valley drifts influence the Berry curvature profile around the K/K' point, where an increase in the flux along with drift can induce the valley current in monolayer MoSi₂N₄. This strong valley asymmetry between valley carriers directly results from changing geometric and orbital effects under directional lattice strain that reduces the lattice symmetry.

Valley drifts lead to the pure electrical generation of valley magnetization in 2D materials

through magnetoelectric effect, and its direct imaging by Kerr rotation microscopy [308]. The strength and direction of uniaxial strain can be controlled using stretchable van der Waals heterostructures [281]. The valley drift observed in monolayer MoSi_2N_4 are larger than graphene ($\sim 0.6 \times 10^{-3} (\frac{2\pi}{a})/\%$) [317] and similar to monolayer MoS_2 ($\sim 4.5 \times 10^{-3} (\frac{2\pi}{a})/\%$) [318, 284]. In addition, high-carrier mobility ($\sim 2.29 \times 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [303]) and excellent ambient stability [47] make strained monolayer MoSi_2N_4 a suitable candidate to observe the Berry curvature dipole induced nonlinear Hall effect [306, 307]. Moreover, the drop in degree of circular polarization in monolayer MoSi_2N_4 is smaller than monolayer MoS_2 (~ 0.95 [319]) under similar strain, making valley polarization by optical pumping more robust to the strain. Our theoretical finding in this work may trigger valley-based electronic and optoelectronic applications in MoSi_2N_4 monolayers under in-plane lattice strain.

Nonrelativistic spin splittings from 2D $\mathcal{PT}$ -symmetric antiferromagnets

6.1 Introduction

Antiferromagnetic (AFM) materials have emerged as viable substitutes for nonmagnetic and FM materials, benefiting from resilience towards stray fields, ultrafast dynamics, magnetotransport effects, and lack of susceptibility to magnetic perturbations [320, 321, 322, 323, 71]. In addition, the coupling of spin to lattice DOF via an inhomogeneous intrinsic magnetic field is analogous to SOC, leading to spin splitting even without SOC [64]. Numerous efforts have been undertaken to investigate spin splittings in AFM materials by breaking combined $\hat{P}\hat{T}\hat{\tau}$ and/or $\hat{U}\hat{\tau}$ symmetries, where $\hat{U}$ and $\hat{\tau}$ are spinor and translation symmetry, respectively [77, 78, 79, 2, 80, 81, 75]. Nevertheless, the majority of AFM spin splittings are limited to bulk materials (e.g., MnF_2 [324, 78], LaMnO_3 , and MnTiO_3 [2]), require SOC (e.g., MnS_2 [2] and ZnV_2O_4 [325]), or external perturbation (e.g., bilayer MnPSe_3 [82], bilayer MnSe [90], Fe_2TeO_6 , and $\text{SrFe}_2\text{S}_2\text{O}$ [84]).

However, antiferromagnetism-induced spin splitting has yet to be explored in two-dimensional (2D) van der Waals (vdW) AFM materials. Ever since the experimental revelation of 2D magnetic ordering, 2D magnetic materials have garnered significant attention in scientific research, emerging as promising contenders for future information technology. Interestingly, two recent works focus on spin splitting in FM NiCl_2 [74] and FeBr_2 (although “*hidden*”) [326] monolayers vdW stacked antiferromagnetically. In contrast, spin splitting among materials with AFM order within each layer is not achieved. Despite being abundant in nature, this impedes practical applications of 2D centrosymmetric AFM materials [327, 328, 329, 330].

Here, we will establish two design principles to obtain SOC-independent spin splittings

in centrosymmetric (i.e., $\hat{P}\hat{T}$ -symmetric) antiferromagnets. Note that SOC-independent spin splitting means its origin is completely nonrelativistic. It can arise from other mechanisms, like exchange interactions in magnetic materials with broken specific symmetries. In bilayer MnSe, the origin of *hidden* Zeeman spin splitting (HZSS) is *local* PT -asymmetry due to unusual out-of-plane magnetic ordering (or simply local ferromagnetism). Whereas, spin splitting in twisted bilayers originates from altermagnetic ordering where net magnetization is zero. However, opposite spin sublattices are connected through rotation symmetry and *not* inversion symmetry.

6.2 Hidden Zeeman-type spin splittings

This section examines the hidden Zeeman-type spin splitting (HZSS) in $\hat{P}\hat{T}$ -symmetric AFM 2D materials originating from specific local sites asymmetries. We perform symmetry analysis and DFT calculations on prototypical layered MnSe to show that doubly degenerate states with opposite spin polarization are segregated on different sublayers connected through $\hat{P}\hat{T}$ symmetry. The specific states from a single layer are locally Zeeman-split, exhibiting a unique spin-sublayer locking effect. In addition, the mirror plane ($\hat{M}_x$) enforces the spins to be $\mathbf{k}$ -independent. Strikingly, a tiny electric field splits the otherwise doubly degenerate bands, preserving the spin configurations. Switching the electric field can reverse the electronic spin magnetization connected to the energy level splitting.

6.2.1 Monolayer MnSe

The MnSe monolayer consists of two buckled honeycomb sublayers of MnSe, interconnected by Mn-Se bonds [see Fig. 6.1(a)]. Within the monolayer, the upper Mn/Se atoms are positioned alternately on top of the lower Se/Mn atoms. Each unit cell of monolayer contains two Mn and two Se atoms, with a lattice constant of 4.28 Å, belonging to the space group $P\bar{3}m1$ with P symmetry (ignoring spin configurations). Considering different possible magnetic configurations, we find that the upper and lower sublayers are coupled antiferromagnetically through Néel-type antiferromagnetism. The robust Néel-type AFM state is more stable than the FM state by 0.38 eV per unit cell. Additionally, the magnetic anisotropic energy (MAE) calculations reveal that the monolayer MnSe prefers in-plane magnetization over out-of-plane magnetization, with an energy difference of 0.37 meV/u.c. These results are consistent with the previous experimental [329] and theoretical reports [329, 330, 331].

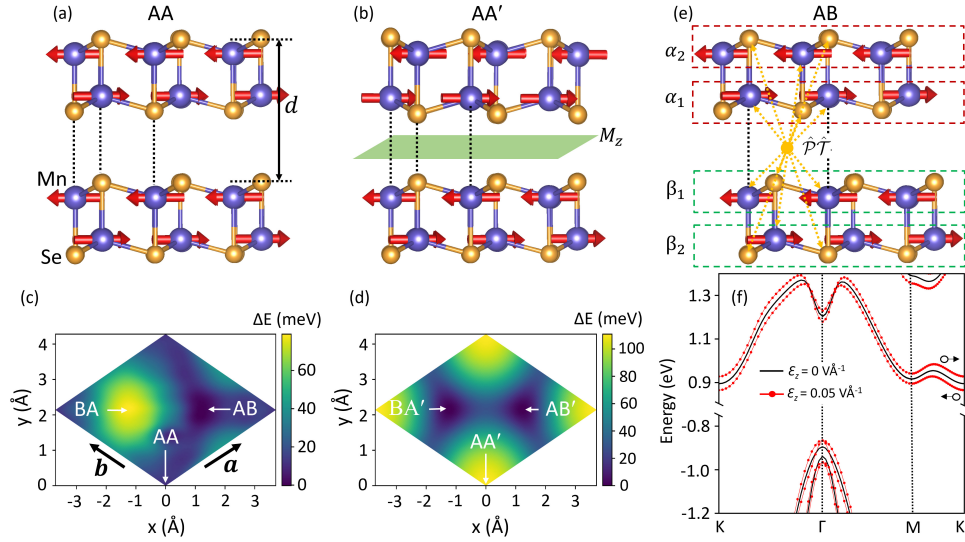


Figure 6.1: Geometric structures of bilayer MnSe with high-symmetry stackings (a) AA and (b) AA'. The upper layer in AA and AA' is obtained by the translation ($d\hat{z}$) and mirror reflection (M_z) of the lower layer, respectively. The energy distribution of different translations between layers for the (c) AA and (d) AA' stacking. The energy surfaces are interpolated using 10 steps in $\mathbf{a}$ and $\mathbf{b}$ directions such that all possible high-symmetry stackings are included. (e) Structure of the global ground state with AB stacking having magnetization $M\uparrow\downarrow\uparrow\downarrow$. The sublayers α_i and β_i ($i = 1, 2$) are connected by $\hat{P}\hat{T}$ -center with orange dashed lines. (f) Energy band dispersion of monolayer MnSe without (solid black lines) and with an electric field (red dashed lines) of $0.05 \text{ V}\text{\AA}^{-1}$ along z -direction.

6.2.2 Bilayer stackings

Determination of stacking orders in multilayers is challenging, especially for more complex structures. Firstly, we have created bilayer MnSe by taking the upper layer as translation (by $d\hat{z}$) and mirror reflection ($\hat{M}_z$) of the lower layer, as shown in Figs. 6.1(a) and 6.1(b). We name these stacking AA (obtained through $d\hat{z}$) and AA' (obtained through $\hat{M}_z$), following the nomenclature used in Ref. [332]. After that, we transformed these stackings into other possible high-symmetry stacking by translation sliding of one of the basal planes in the unit cell: going to AB and BA state from AA, and going to AB' and BA' from AA'. Further, DFT calculations were conducted to ascertain the lowest energy states for various stacking arrangements. As shown in Fig. 6.1(c), translating the top layer in AA by $\frac{2}{3}\mathbf{a} + \frac{1}{3}\mathbf{b}$ results in AB stacking with nondegenerate global energy minimum. In comparison, BA stacking is energetically unfavorable. On the other hand, shifting the top layer from AA' leads to doubly degenerate energy

minima AB' and BA' [Fig. 6.1(d)]. AB stacking is energetically most favorable, having lower energy than AB'/BA' by 14 meV per unit cell. Bilayer MnSe can be divided into sublayers α_i and β_i ($i = 1, 2$), each sublayer containing a single Mn atom. Note that we have taken four nondegenerate magnetic configurations $M\uparrow\uparrow\uparrow\uparrow$, $M\uparrow\downarrow\uparrow\downarrow$, $M\uparrow\downarrow\downarrow\uparrow$, and $M\uparrow\uparrow\downarrow\downarrow$ (here, up and down arrows represent the magnetic moment direction of sublayers along $+x$ and $-x$ direction, respectively, in the order of β_2 , β_1 , α_1 , and α_2 [Fig. 6.1(e)]). Given that the easy axis of magnetization lies in the x - y plane with MAE of 0.9 meV/u.c., we have chosen the x -direction as the axis for magnetization. Our DFT calculations discover that Néel-type AFM configuration $M\uparrow\downarrow\uparrow\downarrow$ has the lowest energy. Therefore, our calculation assumes that the bilayer MnSe exhibits AB stacking with $M\uparrow\downarrow\uparrow\downarrow$ configuration unless otherwise specified.

6.2.3 Symmetry analysis

$\hat{P}\hat{T}$ symmetry flips the spin but retains the k invariance, i.e., $\hat{P}\hat{T}E(\mathbf{k}, \boldsymbol{\sigma}) = \hat{P}E(-\mathbf{k}, -\boldsymbol{\sigma}) = E(\mathbf{k}, -\boldsymbol{\sigma})$, enforcing the spin degeneracy. Therefore, energy bands are doubly degenerate without spin polarization locally or globally if all atomic sites are $\hat{P}\hat{T}$ -symmetric [Fig. 6.2(a)]. Broken $\hat{P}\hat{T}$ symmetry, i.e., in ferromagnetic or noncentrosymmetric AFM materials, leads to the Zeeman spin splittings [Fig. 6.2(b)] [2]. The magnetic point group (MPG) for bilayer MnSe with AB stacking is $2'/m$, having symmetry operations $\hat{M}_x$, $\hat{C}_{2x}\hat{T}$, and $\hat{P}\hat{T}$ besides trivial identity operation ($\hat{I}$). Here, $\hat{M}_x$ and $\hat{C}_{2x}$ are mirror reflection in the y - z plane and two-fold rotation around the x -axis, respectively. Bilayer MnSe is globally centrosymmetric (D_{3d}). However, the atomic site symmetries of Mn (C_{3v}) and Se (C_{3v}) are noncentrosymmetric. MPG of each sublayer (α_i , β_i) contains $\hat{I}$ and $\hat{M}_x$. While the total spin polarization is prohibited by global $\hat{P}\hat{T}$ symmetry, the $\hat{P}\hat{T}$ -asymmetric nature of sublayers allows the observation of spin polarization locally dubbed hidden spin polarization. α_i sublayer is connected to the β_i sublayer through $\hat{P}\hat{T}$ symmetry, making bilayer MnSe global $\hat{P}\hat{T}$ -symmetric [Fig. 6.1(e)]. Therefore, we say that α_i is the inversion partner of β_i . As a consequence, the state localized on the α_i sublayer $|\psi_{\mathbf{k},\uparrow}^{\alpha_i}\rangle$ and the state localized on β_i sublayer $|\psi_{\mathbf{k},\downarrow}^{\beta_i}\rangle$ are energy degenerate ($E_{\mathbf{k},\uparrow}^{\alpha_i} = E_{\mathbf{k},\downarrow}^{\beta_i}$). More importantly, the two components of doubly degenerate bands have opposite spin polarization ($S_{\mathbf{k}}^{\alpha_i} = -S_{\mathbf{k}}^{\beta_i}$), each spatially localized on one of the two separate sublayers forming the inversion partners called spin-sublayer locking effect [Fig. 6.2(c)]. When examining a specific layer (say α) [see Ref. [333] for experimental procedure] that consists of sublayers α_1 and α_2 , the states localized on α_1 and α_2 have non-degenerate energy. Consequently, the states $|\psi_{\mathbf{k},\uparrow}^{\alpha_1}\rangle$ and

$|\psi_{\mathbf{k},\downarrow}^{\alpha_2}\rangle$ create a Zeeman pair. Similarly, β_1 and β_2 states also make a Zeeman Pair. Moreover, the anticommutation relationship between $\hat{M}_x$ and $\hat{\sigma}_{y,z}$ in spin space (where $\hat{\sigma}_{x,y,z}$ represents the Pauli matrices) imposes a condition on the general energy eigenstate $|\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}\rangle$. Specifically, $\langle\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}|\hat{M}_x^{-1}\hat{\sigma}_{y,z}\hat{M}_x|\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}\rangle = -\langle\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}|\hat{\sigma}_{y,z}|\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}\rangle$, which implies that $\langle\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}|\hat{\sigma}_{y,z}|\psi_{\mathbf{k},\uparrow/\downarrow}^{\alpha_i/\beta_i}\rangle = 0$. Consequently, the spin orientations are independent of $\mathbf{k}$ and aligned parallel or antiparallel to x direction. That leads to the HZSS with persistent spin textures [Fig. 6.2(c)], and energy relationship can be expressed as

$$E_{\mathbf{k},\uparrow}^{\alpha_i} = E_{\mathbf{k},\downarrow}^{\beta_i}; i = 1, 2 \quad \text{and} \quad E_{\mathbf{k},\uparrow}^{s_1} \neq E_{\mathbf{k},\downarrow}^{s_2}; s = \alpha, \beta. \quad (6.1)$$

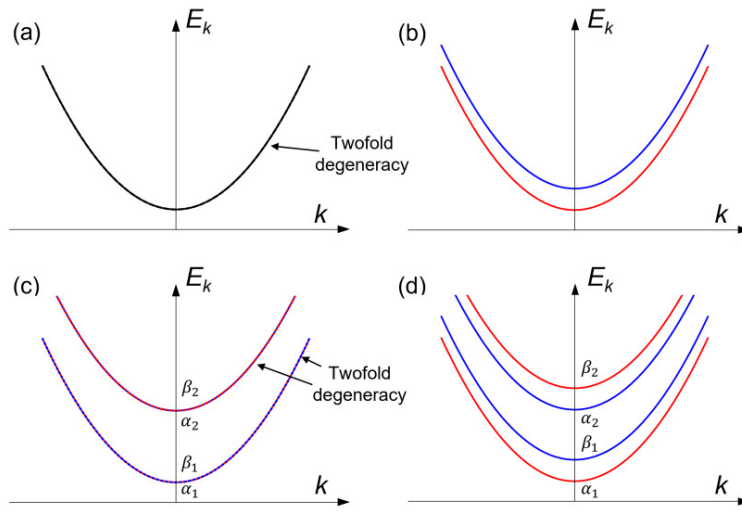


Figure 6.2: Schematic illustration of band structures with (a) null spin splitting and (b) Zeeman spin splitting. (c) Sketches of twofold degenerate bands in the presence of $\hat{P}\hat{T}$ symmetry with hidden spin polarization, where each band is segregated on different sublayers. (d) The lifting of band degeneracy when an electric field along the z -direction is applied. The energy levels with positive and negative spin magnetization are sketched in the red and blue curves, respectively.

Next, we apply an electric field ($\mathcal{E}$) to break $\hat{P}\hat{T}$ symmetry. The electric field creates a net charge polarization ($\mathbf{P} \propto \mathcal{E}$) [334]. Induced polarization generates a net magnetization ($M_i \propto P_j$) through the magnetoelectric effect [334], lifting the $\hat{P}\hat{T}$ symmetry between inversion partners. The occurrence of magnetization induces an effective magnetic field ($\mathbf{B}^{eff} \propto \mathbf{P}$) that couples with the spin DOF, yielding a Zeeman-like Hamiltonian $\sum_{i,j} \lambda_{i,j} P_i \hat{\sigma}_j$. Tensor $\lambda_{i,j}$ determines the strength of the magnetoelectric coupling. Some components of $\lambda_{i,j}$ are never non-zero and vanish due to the symmetry. We determine the symmetry-allowed terms λ_{ij} using

the method of invariants [223] ($\hat{H} = \hat{O}^\dagger \hat{H} \hat{O}$, where $\hat{O}$ is the symmetry operation belonging to the MPG $2'/m$), generally used to determine the $\mathbf{k}, \mathbf{p}$ Hamiltonian in nonmagnetic materials [19, 54]. The Zeeman Hamiltonian ($\hat{H}_Z$), following the transformation rules of P_i and $\hat{\sigma}_j$ listed in Table 6.1, is given by

$$\hat{H}_Z = \lambda_{x,y} P_x \hat{\sigma}_y + \lambda_{x,z} P_x \hat{\sigma}_z + \lambda_{y,x} P_y \hat{\sigma}_x + \lambda_{z,x} P_z \hat{\sigma}_x. \quad (6.2)$$

$\hat{H}_Z$ breaks the $\hat{P}\hat{T}$ symmetry and lifts the energy degeneracy between states localized on inversion partners [Fig. 6.2(d)] and thus forming additional Zeeman-like pairs

$$E_{\mathbf{k},\uparrow}^{\alpha_i} \neq E_{\mathbf{k},\downarrow}^{\beta_i}; i = 1, 2 \quad \text{and} \quad E_{\mathbf{k},\uparrow}^{s_1} \neq E_{\mathbf{k},\downarrow}^{s_2}; s = \alpha, \beta. \quad (6.3)$$

It should be noted that $\hat{H}_Z$ is determined assuming that the magnetization axis aligns with the x -direction. However, the Hamiltonian can be adapted for any in-plane direction by rotating it accordingly.

Table 6.1: The transformation rules of electric polarization (P_x, P_y, P_z) and Pauli spin matrices ($\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$) with respect to operation ($\hat{O}$) belonging to MPG $2'/m$.

$\hat{O}$	(P_x, P_y, P_z)	$(\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$	Invariants
$\hat{I}$	(P_x, P_y, P_z)	$(\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$	$P_i \hat{\sigma}_j (i, j=x, y, z)$
$\hat{M}_x$	$(-P_x, P_y, P_z)$	$(\hat{\sigma}_x, -\hat{\sigma}_y, -\hat{\sigma}_z)$	$P_x \hat{\sigma}_{y/z}, P_{y/z} \hat{\sigma}_x$
$\hat{C}_{2x} \hat{T}$	$(P_x, -P_y, -P_z)$	$(-\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$	$P_x \hat{\sigma}_{y/z}, P_{y/z} \hat{\sigma}_x$
$\hat{P}\hat{T}$	$(-P_x, -P_y, -P_z)$	$(-\hat{\sigma}_x, -\hat{\sigma}_y, -\hat{\sigma}_z)$	$P_i \hat{\sigma}_j (i, j=x, y, z)$

6.2.4 DFT analysis

According to symmetry analysis, there are two conditions to observe HZSS: (i) global $\hat{P}\hat{T}$ symmetry and (ii) the states segregated on the local $\hat{P}\hat{T}$ -asymmetric sites. Condition (i) is already fulfilled, and to check condition (ii), we plot the orbital-projected band structure of bilayer MnSe considering SOC [Fig. 6.3(a)]. Under C_{3v} site symmetry, the Mn- d orbitals split into three categories d_{z^2} , $(d_{x^2-y^2}, d_{xy})$, and (d_{xz}, d_{yz}) . The Se- p orbitals are split into two categories p_z and (p_x, p_y) . The Mn- d orbitals form CB states, while Se- p orbitals mainly contribute to VB states. Compared to the band structure of monolayer MnSe [Fig. 6.1(f)], interlayer interaction between inversion partners α_1 and α_2 results in increased separation between the nested bands

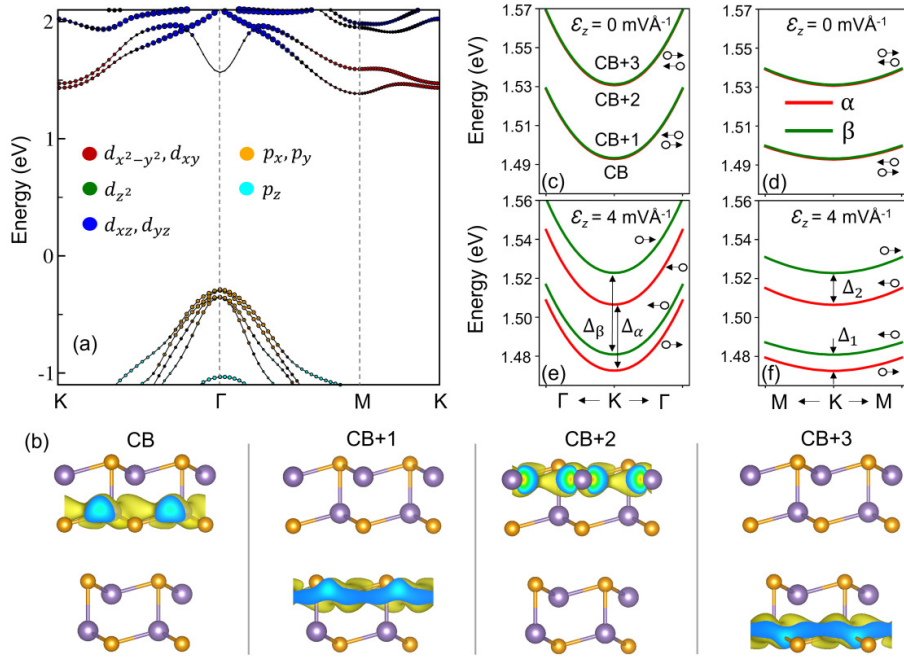


Figure 6.3: (a) Orbital-projected band dispersion curves of bilayer MnSe with AB stacking. (b) $|\psi_{n\mathbf{k}}(\mathbf{r})|^2$ for the states CB, CB+1, CB+2, and CB+3 at K point. Layer-projected CBs of bilayer MnSe around the K point along the (c) K- Γ and (d) K-M. (e)-(f) counterparts of (c)-(d) in the presence of a small electric field of 4 mVÅ $^{-1}$ along the z -direction.

and spin mixture from another sublayer. Compared to the in-plane orbitals ($d_{x^2-y^2}, d_{xy}, p_x, p_y$), the out-of-plane orbitals ($d_{xz}, d_{yz}, d_{z^2}, p_z$) exhibit significant interlayer and intersublayer interaction. Observing HZSS is not ideal with the CB states around the M and Γ points and the VB states around the K and M points. That is because these states have contribution from the hybridization of out-of-plane orbitals between different sublayers, and thus their wavefunctions are not segregated. The CB states near the K point are predominantly contributed by ($d_{x^2-y^2}, d_{xy}$) and VB states around the Γ point are composed of mainly (p_x, p_y). Therefore states arising from the in-plane orbitals, i.e., the CBs near the K point and the VBs near the Γ point, have weak communication between different sublayers, leading to minimal separation between nested bands and spin mixture from neighboring layers. Consequently, each wavefunction is localized within the sublayer for the CBs near the K point and the VBs near the Γ point, forming the ideal choice to observe spin-sublayer locking effect and HZSS [Fig. 6.3(b)].

Next, we plot layer-projected dispersion curves for low CBs in the vicinity of K point for bilayer MnSe [Figs. 6.3(c) and 6.3(d)]. The four lowest CBs form two two-fold degenerate pairs [see Eq. 6.1]. Despite having the same energy, these states are localized on distinct sub-

layers and can be probed using $\mathbf{r}$ -resolved spectroscopy techniques [243, 335]. For instance, the degenerate states CB and CB+1 segregate on inversion partners α_1 and β_1 , respectively [Fig. 6.3(b)]. Both inversion partners possess finite and opposite $\mathbf{k}$ -independent spin orientations, either parallel or antiparallel to the x direction, ensuring zero net spin polarization respecting the $\hat{P}\hat{T}$ symmetry requirement (see Fig. 6.4). The k -independent persistent spin textures overcome spin dephasing and provide non-dissipative spin transport [21, 129, 87]. α_1 sublayer has a magnetization of magnitude $4.38 \mu_B$ along $+x$ direction and compensated by the opposite magnetization of inversion partner β_1 . A similar analysis also applies to the upper degenerate pair CB+2 and CB+3, where wavefunctions corresponding to the CB+2 and CB+3 have segregated on α_2 and β_2 sublayers, respectively. If we focus locally on each layer, $(|\psi_{K,\uparrow}^{\alpha_1}\rangle, |\psi_{K,\downarrow}^{\alpha_2}\rangle)$ and $(|\psi_{K,\downarrow}^{\beta_1}\rangle, |\psi_{K,\uparrow}^{\beta_2}\rangle)$ form two Zeeman pair with energy splitting $\Delta_\alpha, \Delta_\beta$, respectively [Figs. 6.3(c) and 6.3(d)]. As a consequence of $\hat{P}\hat{T}$ symmetry, the strength of the Zeeman spin splitting is the same for each layer ($\Delta_\alpha = \Delta_\beta$) to satisfy the Kramers' degeneracy. We have observed Zeeman spin splitting of order ~ 39.5 meV. Observed Zeeman splitting in our case (without external fields) is comparable to bulk AFM semiconductors Fe_2TeO_6 (55 meV) and $\text{SrFe}_2\text{S}_2\text{O}$ (33 meV) under the external electric field of strength $60 \text{ mV}\text{\AA}^{-1}$ [84]. However, it is still smaller than nonmagnetic transition metal dichalcogenides, i.e., MoS_2 (150 meV) [37]. HZSS is also observed for the VB states near the Γ point, where both α and β bands are Zeeman split ($\Delta_\alpha, \Delta_\beta$) by ~ 70 meV.

The $\hat{H}_Z$ expressed in Eq. 6.2 shows that two-fold degeneracy will be lifted by including polarization along an arbitrary direction (P_x, P_y, P_z). We include P_z through the application of an electric field along the z direction ($\mathcal{E}_z$), and our model in Eq. 6.2 can readily be generalized to

$$\hat{H}_Z = \gamma_{z,x} \mathcal{E}_z \hat{\sigma}_x \quad (6.4)$$

where $\gamma_{z,x}$ determines the strength of splitting. We plot the CBs in a tiny $\mathcal{E}_z$ of $4 \text{ mV}\text{\AA}^{-1}$ [Figs. 6.3(e) and 6.3(f)]. The $\mathcal{E}_z$ creates an asymmetric potential on the inversion partners sublayers, resulting in global $\hat{P}\hat{T}$ symmetry breaking. Each degenerate pair splits into two levels $E_+ = \gamma_{z,x} \mathcal{E}_z$ (eigenstate being $|+\rangle$) and $E_- = -\gamma_{z,x} \mathcal{E}_z$ (eigenstate being $|-\rangle$), where $\hat{\sigma}_x|+\rangle = +|+\rangle$ and $\hat{\sigma}_x|-\rangle = -|-\rangle$. Therefore, two degenerate pairs in bilayer MnSe splits into four energy levels, as represented by the Δ_1 and Δ_2 in Fig. 6.3(f). Here Δ_1 (Δ_2) represents the energy difference between the state localized on the α_1 (α_2), and the state localized on β_1 (β_2). Upon initial observation, it is evident that $\Delta_1 < \Delta_2$ due to the smaller real space separation

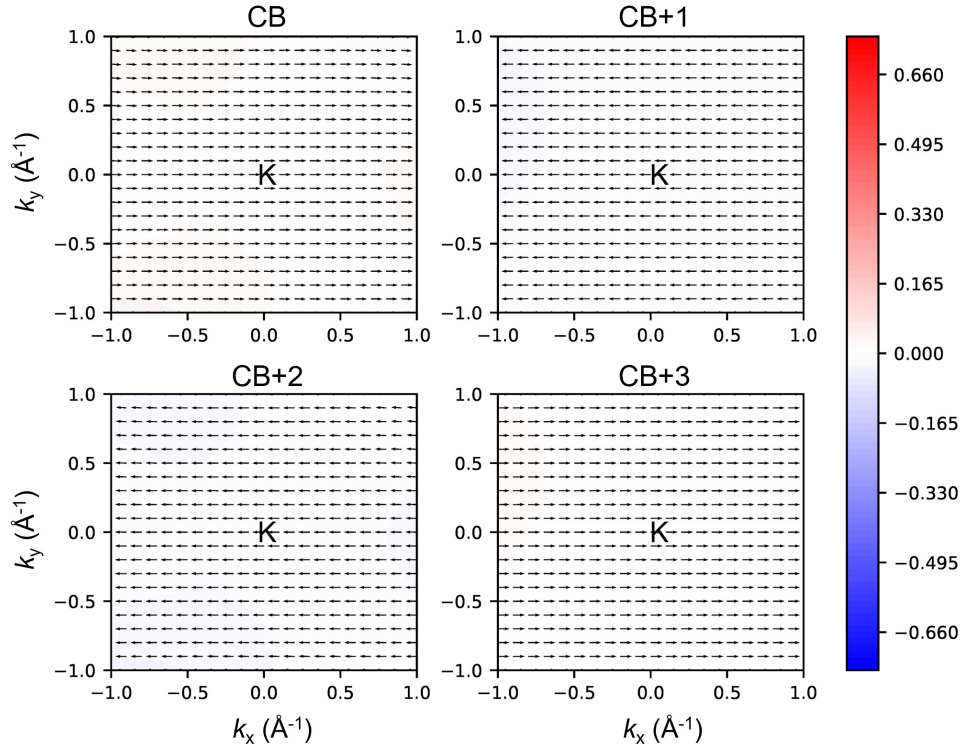


Figure 6.4: Spin textures of four lowermost conduction bands CB, CB+1, CB+2, and CB+3 around the K point.

between α_1 and β_1 compared to that between α_2 and β_2 . Consequently, this results in a lesser potential difference between α_1 and β_1 , leading to a smaller energy splitting Δ_1 compared to Δ_2 .

After that, we plot energy splittings (Δ_1 , Δ_2 , Δ_α , and Δ_β) as a function of the $\mathcal{E}_z$ [Figs. 6.5(a) and 6.5(b)]. We notice that the energy splittings show a linear dependence on the $\mathcal{E}_z$ in the range of 0 to 10 mVÅ⁻¹. Maximum Δ_1 and Δ_2 are observed to be 20.0 and 39.9 meV, respectively, with the $\mathcal{E}_z$ of strength 10 mVÅ⁻¹. The $\mathcal{E}_z$ breaks the equality between Δ_α and Δ_β , where Δ_α decreases and Δ_β increases with increasing strength of the $\mathcal{E}_z$. The observed strength of Δ_α and Δ_β are 28.0 and 47.8 meV, respectively, under the influence of 10 mVÅ⁻¹ $\mathcal{E}_z$. For electric field along $+z$ direction the energy levels split in each degenerate pair splits into two levels $E_+ = \gamma_{z,x}\mathcal{E}_z$ (eigenstate being $|+\rangle$) and $E_- = -\gamma_{z,x}\mathcal{E}_z$ (eigenstate being $|-\rangle$), where $\hat{\sigma}_x|+\rangle = +|+\rangle$ and $\hat{\sigma}_x|-\rangle = -|-\rangle$. For electric field along $-z$ direction, two split energy levels are $E_+ = -\gamma_{z,x}\mathcal{E}_z$ (eigenstate being $|+\rangle$) and $E_- = \gamma_{z,x}\mathcal{E}_z$ (eigenstate being $|-\rangle$), where $\hat{\sigma}_x|+\rangle = +|+\rangle$ and $\hat{\sigma}_x|-\rangle = -|-\rangle$. Therefore, the reversal of the electric field from $\mathcal{E}_z$ to $-\mathcal{E}_z$ will reverse the spin magnetization S_x to $-S_x$ (see Fig 6.6). Under an electric field of the same magnitude along the $+z$ or $-z$ direction, the strength of splittings $|\Delta_1|$ and $|\Delta_2|$ is independent

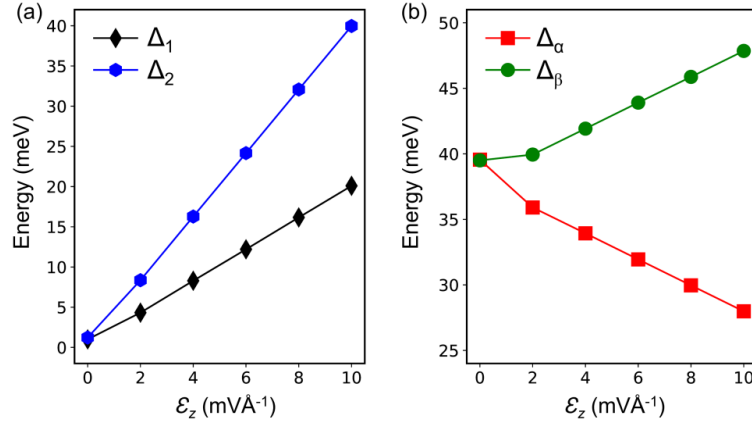


Figure 6.5: The Zeeman spin splittings for the CBs (a) Δ_1 , Δ_2 and (b) Δ_α , Δ_β in bilayer MnSe as a function of electric field $\mathcal{E}_z$.

of the electric field direction. However, Δ_1 and Δ_2 will flip their sign under electric field reversal. These results are in qualitative agreement with our model Hamiltonian $\hat{H}_z$ in Eq. 6.4. If we compare the effect of the electric field on bilayer MnSe with monolayer MnSe [Fig. 6.1(f)], we find that a large electric field is required in monolayer MnSe to obtain the Zeeman splitting of the same order. More specifically, Zeeman split pair of 50.9 meV is observed with $\mathcal{E}_z$ of strength 50 mVÅ⁻¹. Also, Zeeman splitting without any external field in bilayer MnSe is an additional advantage over monolayer MnSe.

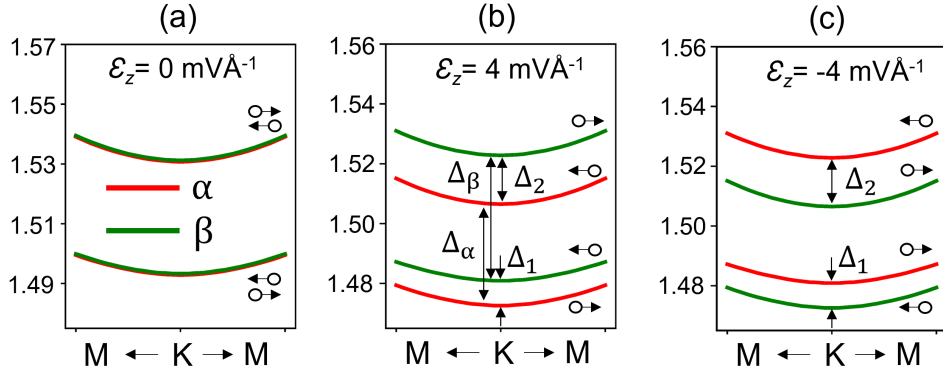


Figure 6.6: Layer-projected CBs around K point in bilayer MnSe (a) without and with $\mathcal{E}_z$ of strength 4 mVÅ⁻¹ along (b) $+z$ and (c) $-z$ direction, respectively. Here α and β represent upper and lower layer, respectively.

It is interesting to note that $\hat{P}\hat{T}$ symmetry remains intact with increasing layer thickness. Therefore, effects similar to bilayer MnSe are also achieved in trilayer and tetralayer MnSe, where every band is doubly degenerate, and degenerate pair of bands are localized on different sublayers connected through $\hat{P}\hat{T}$ symmetry. Thus, experimental realization of HZSS can be

easily achieved in layered MnSe with arbitrary thickness.

6.3 Spin splittings in twisted bilayers

This section aims to generate nonrelativistic spin splitting (NRSS) from $\hat{P}\hat{T}$ -symmetric AFM monolayers vdW stacked with a twist angle between the layers. We extensively performed first-principles DFT simulations on twisted bilayer (tb-) MnPSe₃ and MnSe as prototypical candidates. Further calculation demonstrated that Rashba-Dresselhaus (RD) and Zeeman-like momentum-dependent spin splittings arise along certain crystallographic $\mathbf{k}$ -paths. Based on the symmetry analysis, we find that the strengths of RD and Zeeman-like spin splittings are comparable to the conventional SOC-induced counterparts. Moreover, external perturbations (i.e., electric and strain fields) provide exceptional tunability to NRSS in tb-MnPSe₃ and tb-MnSe.

6.3.1 Monolayer MnSe and MnPSe₃

MnPSe₃ and MnSe (space group #162, $P\bar{3}1m$) represent two distinct classes of vdW materials that possess exceptional exfoliation properties [327, 336, 328, 329, 330]. Unlike the majority of other 2D magnetic materials, they exhibit an AFM arrangement, conforming to the conventional collinear Néel order on the honeycomb lattice [Figs. 6.7(a),(c)]. This in-plane antiferromagnetism is different from the A-type antiferromagnetism observed in various other 2D vdW compounds, i.e., MnBi₂Te₄ [337], CrI₃ [338], and CrSBr [339], where individual layers exhibit FM order but stack antiferromagnetically. The antiferromagnetism of MnPSe₃ is “truly” in-plane and differs from that of MnSe, where Mn ions with opposite magnetic moments form unusual out-of-plane ordering within the individual layer.

The magnetic space group (MSG) of single-layer MnPSe₃ and MnSe is $C2'/m$ (type-III Shubnikov MSG), containing $\hat{P}\hat{T}$, $\hat{T}\hat{C}_{2a}$, and $\hat{M}_a$ symmetry operations (calculated using FINDSYM [133] and MAGNDATA [340]). Here, the $\hat{P}\hat{T}$ symmetry transforms energy eigenstate $E(\mathbf{k}, \sigma)$ as $\hat{P}\hat{T}E(\mathbf{k}, \sigma) = PE(-\mathbf{k}, -\sigma) = E(\mathbf{k}, -\sigma)$, leading to spin degeneracy throughout the BZ. We have verified that through DFT+U calculations performed on the projector augmented wave method [124] based VASP [106] code. DFT simulated energy bands for MnPSe₃ and MnSe monolayer and untwisted bilayer are double degenerate. The semiconducting MnPSe₃ and MnSe have a magnetic moment of $\sim 4.5\mu_B/\text{Mn}$ with weak interlayer coupling.

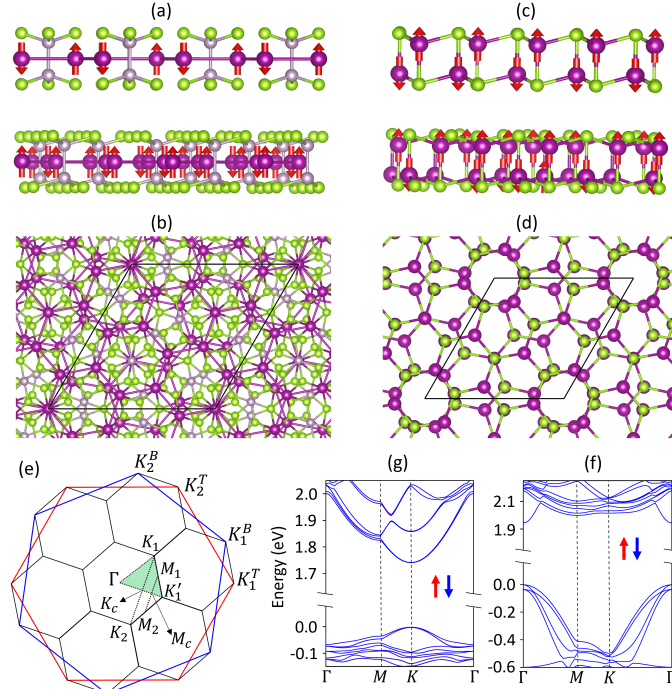


Figure 6.7: The Moiré superlattices formed by twisting bilayer of MnPSe3 [(a),(b)] and MnSe [(c),(d)] by 21.79° . Violet, brown, and green atoms represent Mn, P, and Se, respectively. The ground-state magnetic structures are also highlighted in (a) and (c). The structures are illustrated using VESTA [3]. (e) The Moiré BZ construction uses BZs of the top and bottom layers. The large red and blue hexagons are the first BZ of the top and bottom layers, respectively, and black hexagons represent the BZ corresponding to the Moiré superlattice. Spin-polarized band structure of (f) tb-MnPSe3 and (g) tb-MnSe at the PBE level.

The Mn atoms with opposite on-site magnetic moments are connected through $\hat{P}\hat{T}$ symmetry. Since 2D systems have only in-plane components of momentum k , nonrelativistic Hamiltonian for 2D systems may have symmetries other than $\hat{P}\hat{T}$ enforcing spin degeneracy. Overall, $\hat{U}$, $\hat{P}\hat{T}$, $\hat{M}_{xy}\hat{U}$, $\hat{M}_{xy}\hat{P}\hat{T}$, $\hat{P}\hat{T}\hat{\tau}$, $\hat{U}\hat{\tau}$, $\hat{M}_{xy}\hat{U}\hat{\tau}$, $\hat{M}_{xy}\hat{P}\hat{T}\hat{\tau}$, where $\hat{U} : \hat{U}E(\mathbf{k}, \sigma) = E(\mathbf{k}, -\sigma)$ is spinor, $\hat{M}_{xy} : \hat{M}_{xy}E(\mathbf{k}, \sigma) = E(\mathbf{k}, \sigma)$ is planer mirror reflection, and $\hat{\tau} : \hat{\tau}E(\mathbf{k}, \sigma) = E(\mathbf{k}, \sigma)$ is translation, can enforce spin-degeneracy for the 2D systems. That makes achieving SOC-unrelated spin splitting difficult, especially for 2D cases [2, 74, 5]. In the case of MnPSe3 and MnSe monolayers, M_{xy} is broken due to nonmagnetic ligands (P_2Se_6 and Se_3 , respectively) [Figs. 6.7(a),(c)], whereas MSG type-III ensures $\hat{U}\hat{\tau}$ symmetry breaking owing to the absence of screw axis, glide plane, and centering (body- or face-centering) [5]. The only symmetry preserving spin degeneracy is $\hat{P}\hat{T}$ symmetry in monolayers and untwisted bilayers of MnPSe3 and MnSe.

6.3.2 Twisted bilayer MnSe and MnPSe₃

Commensurate twisted bilayers are obtained using coincidence lattice theory [341] by taking the AA bilayer (all atoms on top of each other) as the untwisted limit to break $\hat{P}\hat{T}$ symmetry. A periodic lattice structure, including Moiré superlattice, can form with special twist angle θ , $\cos \theta = \frac{n^2+4mn+m^2}{2(m^2+mn+n^2)}$, where m, n are whole numbers [342]. We only considered twist angles that resulted in reasonably sized commensurate supercells with the number of atoms in unit-cell fewer than 350. Figures 6.7(a)-6.7(d) show relaxed crystal structures and Moiré patterns in $\theta = 21.79^\circ$ tb-MnPSe₃ and tb-MnSe [see Moiré BZ in Fig. 6.7(e)]. Note that the orientation of on-site magnetic moments with respect to the lattice only matters if SOC is included. The absence of SOC decouples the spin and lattice DOF, and therefore, without loss of generality, the z -axis is chosen to align or antialign the local magnetization. Different possible interlayer and intralayer magnetic couplings $\uparrow\uparrow\uparrow\uparrow$, $\uparrow\downarrow\uparrow\downarrow$, $\uparrow\downarrow\downarrow\uparrow$, and $\uparrow\uparrow\downarrow\downarrow$ were considered to determine the preferred magnetic ordering [here, up and down arrows represent the relative magnetic moment direction on Mn atoms]. The most stable magnetic structure is $\uparrow\downarrow\uparrow\downarrow$, where magnetic order is intralayer and interlayer AFM [Figs. 6.7(a), 6.7(c)]. Twist angle leads to variation in the magnitude of local magnetic moments from 4.441 to 4.448 μ_B/Mn in tb-MnSe. However, the net magnetic moment in tb-MnSe and tb-MnPSe₃ is strictly zero. In addition to Mn atoms, nonmagnetic ligands also contribute to $\hat{P}\hat{T}$ symmetry breaking in tb-MnPSe₃ and tb-MnSe.

Firstly, we compute the spin-polarized band structures of tb-MnPSe₃ and tb-MnSe along the high-symmetry paths (HSPs) [Figs. 6.7(f),(g)]. The bands are spin degenerate along HSPs due to special symmetries arising at arbitrary k -point on HSP. For instance, $\hat{T}\hat{C}_{2a}$ transforms spin-up to spin-down state along the Γ - K path, enforcing degeneracy between them [74, 87]. However, this is not the case for any generic k -point. No symmetry transform transform spin-up to spin-down at generic k -point, leading to the lifting of Kramers degeneracy. Therefore, the full BZ analysis of spin splitting is required. We plot spin splitting energy $\delta E [=E_{\uparrow}(\mathbf{k}) - E_{\downarrow}(\mathbf{k})]$ of VBs in tb-MnSe as a function of k [Fig. 6.8(a)]. The δE shows the 6-fold symmetry, which is different from the 3-fold symmetry of δE observed in well-known monolayer MoS₂, including SOC [343]. The higher-fold symmetry is attributed to the presence of additional symmetries (particularly $\hat{T}$) other than 3-fold symmetry along Γ - K and Γ - M paths, which make $K_{1/2}$ ($M_{1/2}$) and $K'_{1/2}$ ($M'_{1/2}$) equivalent. Similar patterns are also observed for δE of CB in tb-MnSe and VB in tb-MnPSe₃. The maximum NRSS is observed at the orthocenter (H/H') of

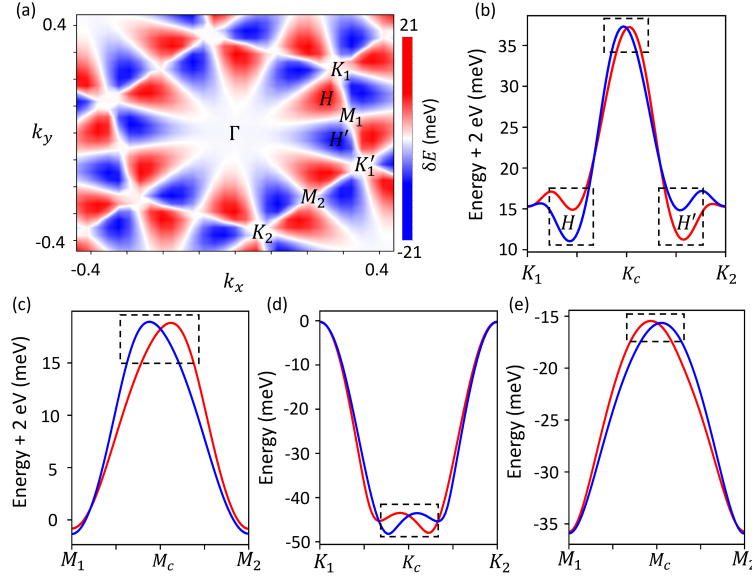


Figure 6.8: (a) Spin splitting energy [$\delta E = E_{\uparrow}(\mathbf{k}) - E_{\downarrow}(\mathbf{k})$] distribution of VB in 21.79° tb-MnSe. The units of k_x and k_y are $\text{\AA}^{-1}$. CBs of tb-MnSe along the (b) K_1 - K_c - K_2 and (c) M_1 - M_c - M_2 paths [see Fig. 6.7(e) for paths]. VBs of tb-MnPSe₃ along the (d) K_1 - K_c - K_2 and (e) M_1 - M_c - M_2 paths. Black dashed squares represent prominent spin splittings.

the triangle formed by Γ , M , and K_1/K'_1 points. Maximum splitting observed is 20.4, 4.2, and 5.1 meV for VB of tb-MnSe, CB of tb-MnSe, and VB of tb-MnPSe₃, respectively. Maximum δE is smaller than well-known bulk antiferromagnets, i.e., MnF₂ [78], Fe₂TeO₆ [84], and LaMnO₃ [2], however, is still sizable ($\sim k_B T$) for room temperature applications. The δE observed in CB of tb-MnPSe₃ is negligible and beyond the accuracy of our calculations.

6.3.3 Nonrelativistic Rashba-Dresselhaus-like spin splittings

To understand the nature of NRSS, we plot band structures along both K_1 - K_c - K_2 and M_1 - M_c - M_2 directions [Figs. 6.8(b)-(e)]. Interestingly, linear Rashba-Dresselhaus-like spin splitting is observed around K_c and M_c for VB and CB of tb-MnSe and VB of tb-MnPSe₃. Whereas splitting occurred around the H/H' point predominantly of Zeeman-type in CB of tb-MnSe [Fig. 6.8(b)]. The spin splittings exhibit contrasting characteristics at the H and H' points, featuring distinct valleys, suggesting the potential for valleytronics applications in twisted bilayers of antiferromagnets. Note that the spin splittings around the Γ point, along the Γ - H/H' direction, exhibit cubic characteristics, which result in their being relatively small and, as such, are excluded from the current discussion [129]. The magnitude of δE also depends upon the

dispersiveness of energy bands, where δE increases with increasing band dispersion. Similar effects were also investigated for other twist angles, including 9.43° , 13.17° , 27.79° , 32.20° , 38.21° , and 42.10° . In addition, the strength of splitting is the same for twist angles θ and $60^\circ - \theta$.

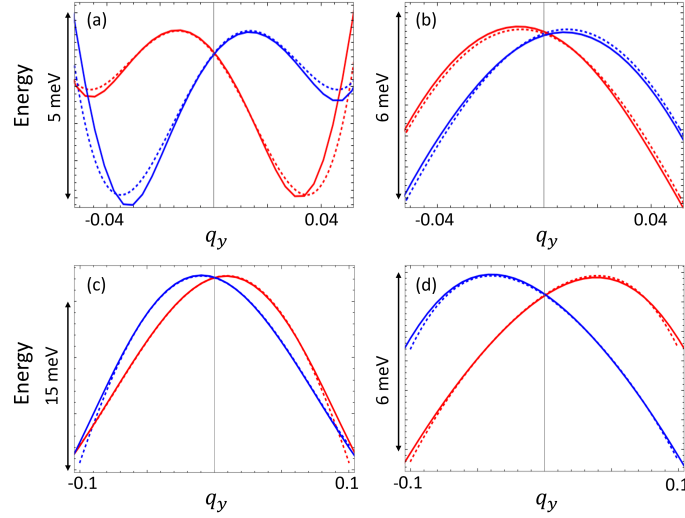


Figure 6.9: Band structures of tb-MnPSe₃ around (a) K_c and (b) M_c along q_y direction. (c) and (d) are counterparts of (a) and (b), respectively, obtained for tb-MnSe. The solid and dotted lines are band structures obtained by DFT and the model described by Eq. 6.5, respectively.

Spin splittings around M_c and K_c points are further analyzed using the symmetry-based model Hamiltonian, deduced using the “*method of invariants*” [21, 129]. The symmetry elements of M_c and K_c points are identity ($\hat{E}$) and $\hat{T}\hat{C}_{2a}$, and symmetry invariant terms include $q_y\sigma_z$, $q_z\sigma_y$, $q_yq_i^3\sigma_z$, and $q_zq_i^3\sigma_y$ ($i = x, y, z$), where $q = k - M_c/K_c$ are the momenta measured from M_c/K_c . Therefore, spin splitting is anisotropic in nature. Splitting is absent along the q_x ($K_c-K'_1$ and $M_c-K'_1$) direction, whereas it is present along the q_y direction ($K_c-K_{1/2}$ and $M_c-M_{1/2}$). To understand the spin splitting along the q_y direction, it is possible to write an effective Hamiltonian (H_{eff}), up to third-order in k :

$$H_{eff} = \alpha q_y \sigma_z + \eta q_y^3 \sigma_z \quad (6.5)$$

where α and η are the constants determining the strength of spin splitting. The primary linear term in Eq. 6.5 can be regarded as analogous to the mixture of linear Rashba $\alpha_R(q_y\sigma_z - q_z\sigma_y)$ and linear Dresselhaus $\alpha_D(q_y\sigma_z + q_z\sigma_y)$ with equal strength ($\alpha_R = \alpha_D = \alpha/2$). In that way, α is the nonrelativistic counterpart of α_R and α_D . We fit the energy levels around M_c and K_c along the q_y direction to obtain spin-splitting parameters. The fits are obtained by minimization

Table 6.2: Classification of 2D materials based on the MSG type, magnetic order and their impact on the nonrelativistic spin splitting. Here, $\hat{P}$, $\hat{T}$, $\hat{M}_{xy}$, $\hat{U}$, and $\hat{\tau}$ represent inversion, time-reversal, planar mirror, spinor, and translation symmetry, respectively. The relevant symmetry is also indicated in the case of spin-degeneracy at generic k .

Spin splitting prototype	Monolayer			Twisted bilayer	Examples
	Magnetic ordering	MSG type	NRSS at generic k	NRSS at generic k	
SST-1	NM	II	$\chi(\hat{U})$	$\chi(\hat{U})$	MoS ₂ [344], PtSe ₂ [345]
SST-2	FM	I/III	✓	✓	NiCl ₂ , CrI ₃ , CrN, CrSBr [74]
SST-3	AFM	III	$\chi(\hat{P}\hat{T})$	✓	MnPSe ₃ , MnSe [This work]
SST-4	AFM	I/III	✓	-	
SST-5	AFM	IV	$\chi(\hat{U}\hat{\tau})$	-	

of the summation

$$S = \sum_{i=1}^2 \sum_q f(q) |\text{Det}[H_{eff}(q) - E^i(q)I]|^2 \quad (6.6)$$

over the i^{th} energy eigenvalues $[E^i(q)]$ as training sets. We have also included a weight function $f(q)$ with normal distribution to get a better fit near the spin-degenerate point and avoid overfitting. The obtained fits to the DFT energy levels of tb-MnPSe₃ and tb-MnSe are shown in Figs. 6.9(a)-6.9(d). The Hamiltonian in Eq 6.1 with $\alpha=58.6$ meVÅ and $\eta=34.2$ eVÅ³ provide the best fit to the VBs of tb-MnPSe₃ around the K_c point [Fig. 6.9(a)]. Whereas $\alpha=39.8$ meVÅ and $\eta=3.5$ eVÅ³ are observed for VBs of tb-MnPSe₃ around the M_c point, respectively [Fig. 6.9(b)]. Similarly, linear splitting strength of 35.4 and 60.7 meVÅ is observed in CBs of tb-MnSe around the K_c and M_c points, respectively [Figs. 6.9(c)-3(d)]. The nonrelativistic spin splitting is comparable to those experimentally reported in the literature (e.g., 10 meVÅ for KTaO₃ [346], 4.3 meVÅ for LaAlO₃/SrTiO₃ interface [347], ~ 70 meVÅ in InGaAs/InAlAs interface [348], and 77 meVÅ for MoSSe monolayer [236]). The growing field of twistrionics makes NRSS observed in tb-MnPSe₃ and tb-MnSe experimentally accessible.

6.3.4 Materials classification

The 2D magnetic materials can be classified into five spin-splitting prototypes (SST) depending on the magnetic order, MSG, and whether NRSS is absent or present in a monolayer [Ta-

ble 6.2]. Spin degeneracy in nonmagnetic materials (SST-1) is enforced by $\hat{U}$ and remains preserved under twisting operations. In contrast, FM materials (SST-2) show spin splitting in both monolayer limits and two layers stacked antiferromagnetically with a twist [74]. AFM materials exhibit a wide range of spin-splitting prototypes depending on the symmetries present in MSG. MSG type-IV always has AFM order with $\hat{U}\hat{\tau}$ symmetry (SST-5) and necessitates SOC to induce spin splitting [2]. AFM materials with MSG type-III containing $\hat{P}\hat{T}$ symmetry (SST-3) are unique, as spin degeneracy is present in the monolayer and lifted in two layers with a relative twist. Therefore, the twisting operation generates splittings in SST-3 type materials, the most common magnetic ordering (AFM) found in nature.

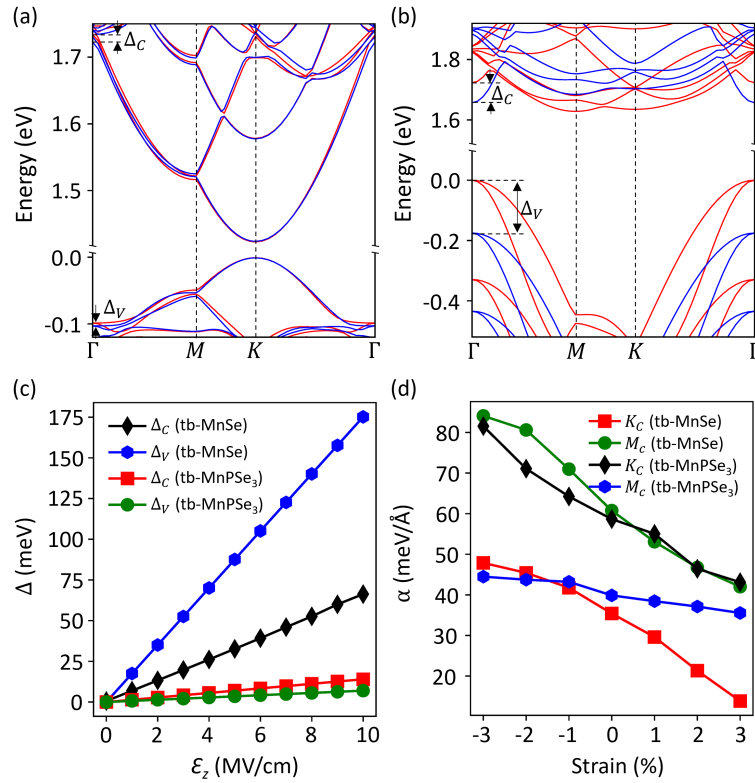


Figure 6.10: Band structures of 21.79° (a) tb-MnPSe_3 and (b) tb-MnSe in the presence of the out-of-plane electric field ($\mathcal{E}_z$) of strength 10 MV/cm. (c) The Zeeman spin splittings in the CB (Δ_C) and VB (Δ_V) of 21.79° tb-MnPSe_3 and tb-MnSe at Γ point as a function of $\mathcal{E}_z$. (d) The variation in α (see Eq. 6.5) as a function of biaxial strain for 21.79° tb-MnPSe_3 and tb-MnSe .

6.3.5 Effect of external electric field and biaxial strain

Although controlling crystal symmetries in bulk materials is challenging, it has been shown that gating can effectively break the symmetries in 2D materials, including twisted bilay-

ers [349, 350, 54]. In the following, we apply an out-of-plane electric field to the tb-MnPSe₃ and tb-MnSe using the approach introduced by Neugebauer and Scheffler [351]. The electric field creates not only polarization but also magnetization through the magnetoelectric effect [334], yielding a Zeeman-like Hamiltonian $\sum_{i,j=x,y,z} \epsilon_{ij} \mathcal{E}_i \sigma_j$. The symmetry-allowed couplings associated with the $C2'/m$ MSG are given by [84]

$$\hat{H}_Z = \epsilon_{xy} \mathcal{E}_x \sigma_y + \epsilon_{xz} \mathcal{E}_x \sigma_z + \epsilon_{yx} \mathcal{E}_y \sigma_x + \epsilon_{zx} \mathcal{E}_z \sigma_x, \quad (6.7)$$

where ϵ_{ij} are coefficients determining coupling strengths. In the presence of $\mathcal{E}_Z$, the spin degenerate levels at the high symmetry points (Γ , M , and K) and along HSPs will be split into two sublevels, $E_+ = \epsilon_{zx} \mathcal{E}_z$ and $E_- = -\epsilon_{zx} \mathcal{E}_z$ [Figs. 6.10(a)-6.10(c)]. We observe that the splitting induced by $\mathcal{E}_z$ in tb-MnPSe₃ and tb-MnSe exhibits markedly distinct characteristics. Specifically, an electric field $\mathcal{E}_z$ with a strength of 10 MV/cm results in nearly negligible splitting at the Γ point for tb-MnPSe₃, suggesting a small coupling coefficient ϵ_{zx} as described in Eq. 6.7 [Figs. 6.10(a), 6.10(c)]. In contrast, for tb-MnSe, the Γ point experiences a significantly larger Zeeman-type splitting (~ 175 meV) induced by an electric field $\mathcal{E}_z$ of 10 MV/cm [Figs. 6.10(b), 6.10(c)]. This disparity can be explained through structural analysis: in tb-MnPSe₃, Mn atoms with opposite magnetic moments lie within the same z -plane, while in tb-MnSe, they are situated in different z -planes, thus supporting magnetoelectric coupling when an electric field is applied along the z -direction. On the contrary, when we compare the Zeeman splittings induced in the CB and VB of tb-MnSe at the Γ point [Fig. 6.10(b)], it becomes evident that the splitting in the VB is significantly greater in magnitude compared to that in the CB. This pronounced splitting in the VB of tb-MnSe can be attributed to the in-plane orbitals, which have wavefunctions segregated on different z -planes and, as a result, are more susceptible to the $\mathcal{E}_z$. In addition, tunability in electronic states can be achieved by the strain engineering of 2D materials [352]. The in-plane biaxial strain preserves the crystal symmetry, thus creating no additional splittings. However, the strength of nonrelativistic Rashba splittings (α) around K_c/M_c for twisted bilayers are modified under biaxial in-plane strain [Fig. 6.10(d)]. α increases with compressive strain and increases with tensile strain, providing exceptional tunability. Note that the models in Eqs. 6.5 and 6.7 include only spin DOF, thus revealing spin splitting qualitatively. For quantitative analysis, other DOF (i.e., orbital and sublattice) through first-principles or multiband tight-binding model calculations need to be included.

6.4 Summary and outlook

We have shown the existence of HZSS in bilayer MnSe, combining first-principles calculations and symmetry analysis. The stacking characteristic study shows that AB with $\hat{P}\hat{T}$ symmetry is the lowest energy stacking. The doubly degenerate states arising due to $\hat{P}\hat{T}$ symmetry are segregated into different sublayers forming inversion partners. Then, we identified the local Zeeman splitting as large as ~ 70 meV in bilayer MnSe, where states forming Zeeman pair with opposite spin orientation segregate on different sublayers within a single layer. Interestingly, a tiny out-of-plane electric field yields additional Zeeman pairs through breaking two-fold degeneracy. Mirror symmetry ($\hat{M}_x$) enforced persistence spin textures remain preserved under an out-of-plane electric field and are known for nondissipative spin transport. Moreover, the fact that our results are independent of the layer number adds credibility to the possibility of experimental observation. Zeeman splittings with hidden spin polarization in centrosymmetric antiferromagnets form another prospective aspect in developing semiconductor spintronics devices [353].

In addition, we have also shown that SOC-independent spin splittings can be induced in type-III $\hat{P}\hat{T}$ -symmetric antiferromagnets by taking bilayers with a relative twist. By first-principles calculations and symmetry analysis, we further predict spin-moment coupling in 21.79° tb-MnPSe₃ and tb-MnSe that accommodate Rashba-Dresselhaus-type spin splittings as large as ~ 90 meVÅ. The lateral electric field split otherwise spin degenerate bands along the HSPs through magnetoelectric coupling, with more prominent effects in tb-MnSe. In addition, NRSSs are tunable using the biaxial strain. The measurement of these spin splittings can be conducted through well-established optical [82] and electrical transport [354] techniques commonly used in the field of spintronics. Employing antiferromagnets featuring spin-split bands as described in the present study may obviate the necessity for a heavy-metal layer, given that the current AFM mechanism yields a substantial magnitude of spin-moment splitting, even with lighter elements. Moreover, the low-Z antiferromagnets with even larger NRSSs can be predicted by the inverse design approach with desired functionality [355]. In addition, NRSS in Moiré-induced flat bands ($\theta \lesssim 3^\circ$) can be an interesting avenue to prospect. We aspire to broaden the pool of available materials and enrich the field of AFM semiconductor spintronics [8, 9].

Epilogue and outlook

This thesis mainly focuses on the electronic and magnetic structures of materials, thereby explaining various spin splitting mechanisms of bulk and 2D materials. Our study opens a plethora of future research, which are discussed below.

In Chapter 3, we discussed SOC-related effects in perovskites. However, performing non-collinear DFT calculations requires a significant computational cost. Therefore, training machine learning algorithms (data-driven science paradigm) to reverse-design perovskites with high SOC will be an ideal avenue to explore. It is worth mentioning that the atomic number (Z) is a necessary but not sufficient descriptor of SOC. In particular, Crystal Graph Neural Networks (CGNNs) are a type of neural network specifically designed for analyzing crystal structures. They have gained attention in materials science for predicting various material properties, and spin-orbit coupling is one such property that researchers may be interested in. It will be interesting to pursue a more universal and generalized model, including spin, orbital, sublattice, and layer degrees of freedom spanning a variety of spin textures. Moreover, the spin transport in these materials can be modeled using atomistic spin dynamics and time-dependent DFT.

In Chapter 4, we discussed full-plane and full-space spin textures in the bulk and 2D materials, respectively. Therefore, experimental investigations using angle-resolved photoemission spectroscopy (ARPES) and transport measurements of these effects will benefit spintronics. High-throughput simulations on full-space persistent spin textured materials with large spin splittings will be ideal to obtain the effects of these materials under room temperature applications. Moreover, k^3 splitting terms give rise to a larger spin-Hall conductivity and therefore provide unique advantage in spin transport.

In Chapter 5, we show the effect of the symmetry-breaking strain field on the spin-valley physics on the MoSi_2N_4 monolayer. We considered strain uniform along the armchair, inter-

mediate, and zigzag directions. In general, the strain obtained in experiments is not uniform, and therefore, it is also interesting to explore the effect of a non-uniform strain field. In addition, understanding the effect of strain on orbital moments and orbital currents, which can be magnitudes larger than spin-Hall-induced spin current, will be of great interest.

In Chapter 6, we obtained nonrelativistic spin splittings in centrosymmetric antiferromagnetic materials using the local asymmetry and twisting the bilayer, breaking global symmetry. Note that we have used large twist angles ($\theta_{\text{twist}} > 9^\circ$) with smaller commensurate unit cells to limit the computational cost required by the DFT simulations. However, the smaller twist angles ($\theta_{\text{twist}} \lesssim 3^\circ$) lead to moiré reconstruction and flat bands. Therefore, nonrelativistic spin splittings in moiré flat bands will be of prime interest. In addition, high throughput screening of centrosymmetric antiferromagnetic materials with sizable spin splittings ($> k_B T$) will make them suitable for room temperature applications.

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BASIC DETAILS

Birth date : 25/03/1996
Gender : Male
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Researcher Profiles : [ResearchGate](#), [Google Scholar](#), [ORCID](#)

RESEARCH EXPERIENCE

📅 2022/01–present **Senior Research fellow**
Department of Physics, Indian Institute of Technology Delhi, India
📅 2020/01–2021/12 **Junior Research fellow**
Department of Physics, Indian Institute of Technology Delhi, India

EDUCATION

📅 2020/01–present **Ph.D. in Physics**
Department of Physics, Indian Institute of Technology Delhi, India
Thesis title: *Theoretical Insights to Symmetry-Induced Spin Splittings and Textures in (Non)-Magnetic Materials.*
Thesis supervisor: Prof. Saswata Bhattacharya
Ph.D. coursework CGPA: 9.00/10.0
📅 2017/07–2019/07 **M.Sc. in Physics**
Department of Physics, Indian Institute of Technology Gandhinagar, India
CGPA: 8.57/10.0 (*Institute Rank: 2*)
M.Sc. Project: *Local Hidden Variables and Nonclassicality in System of Spin-1/2 Particles.*
Project Supervisor: Prof. Ravinder R. Puri
📅 2014/07–2017/07 **B.Sc.(H) in Physics**
Deen Dayal Upadhyaya College, University of Delhi, India
Percentage: 80.03

EXPERTISE & TECHNICAL SKILLS

- ✓ **Methods:** Ground state electronic structure calculations: DFT and beyond DFT, tight-binding methods, $k.p$ perturbation theory; excited-state calculations: GW, BSE, model-BSE; Density functional perturbation theory, ab initio atomistic thermodynamics, machine learning, molecular dynamics.
- ✓ **Programming:** Python, Mathematica, MATLAB, Bash Shell Scripting.
- ✓ **Codes:** VASP, Quantum ESPRESSO, FHI-aims, Wannier90, WannierTools, Phono3py, PythTB, TBPLaS, PyProcar, Scikit, CASTEP, DMol3.
- ✓ **OS:** Various Linux distributions, Windows.
- ✓ **Tools:** Gnuplot, Xmgrace, Materials Studio, P4vasp, Jmol, Vesta, VMD, XCrySDen, GIMP, LaTeX.

RESEARCH INTERESTS

My research interests focus on investigating electronic, magnetic, ferroelectric, magnetoelectric, and geometric properties of quantum materials ranging from bulk to 2D materials. My applications of interest range from spin-orbital coupling and magnetic order-driven band splittings, persistent spin textures, valley pseudospin, and various “hidden” orders in quantum materials. I use *ab initio* first-principles approaches and model Hamiltonian-based analytical and numerical techniques to understand physical phenomena. During doctoral thesis, I understood the role of symmetries in determining spin splittings and persistent spin textures in wider regions of the Brillouin zone. In addition, I demonstrated the two paradigms to harness nonrelativistic spin splittings in $\hat{P}\hat{T}$ -symmetric antiferromagnetic using local site asymmetries and twisting bilayers. I am also experienced in collaborating with experimentalists to offer theoretical insights into fundamental and technologically relevant aspects of materials.

PUBLICATIONS

See “List of Publications” on Page VII.

AWARDS & ACADEMIC RECOGNITIONS

- **Best Poster Award** by ACS at international conference **IUMRS-ICA 2022** held at IIT Jodhpur.
- **CSIR Travel Grant** by CSIR, India in 2022 to participate in PSI-K conference, held at EPFL, Laussane, Switzerland.
- **Reviewer in Scientific Journals:** Nature Communications, Physical Review B, Applied Physics Letters, Scientific Reports, Physical Chemistry Chemical Physics.
- Awarded **Institute’s Silver Medal** for securing second highest CPI among M.Sc. students at IIT Gandhinagar.
- Qualified **CSIR-NET JRF** with all India Rank **34** in June-2018.
- Awarded **Merit-cum-Means** scholarship for excellent performance at IIT Gandhinagar.
- Qualified **JEST** with all India Rank 90 in 2019.
- Received cost-free education, grades 6-12, under ‘**Jawahar Navodaya Vidyalaya scheme,**’ through JNVST entrance test admission.

CONFERENCES ATTENDED

- 14th annual international conference on “Recent Progress in Graphene and 2D materials Research (**RPGR**)”, November 20-23, 2023, at Bengaluru, India.
- 6th International Conference on Molecular Simulation (**ICMS 2023**), October 6-9, 2023, at National Taiwan University, Taipei.
- **Machine Learning for Materials Bootcamp** organized by Dept. of Materials Science & Engineering, UW- Madison, August 15 - 17, 2023, at virtual platform.
- Workshop on “New Approaches and Machine learning Methods for Ab initio calculations (**NAMMA**)” organized by **PSI-K** network, IISc, and JNCASR Bengaluru, at Bengaluru, India from July 24-28, 2023.
- **IUMRS-ICA 2022** organized by “International Union of Materials Research Societies (IUMRS)”, December 19-23, 2022, at IIT Jodhpur, Jodhpur, India.
- **PSI-K conference**, August 22–25, 2022, at EPFL, Lausanne, Switzerland.
- Young Investigator Meet on Quantum Condensed Matter Theory (**YIMQCMT-2020**), December 15-18, 2020, at virtual platform.

- DAE Symposium on Current Trends in Theoretical Chemistry (**CTTC-2020**), September 23-25, 2021, at virtual platform.

LANGUAGES

Hindi (native), English (fluent)