

# UNVEILING VALLEY AND TOPOLOGICAL PROPERTIES OF QUANTUM MATERIALS USING FIRST-PRINCIPLES SIMULATIONS

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DEPARTMENT OF PHYSICS  
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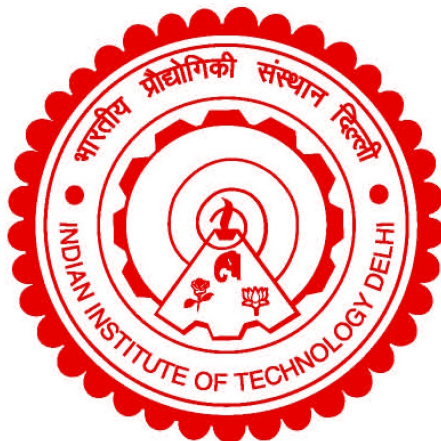
by

**ANKITA**

**Department of Physics**

Submitted

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



**INDIAN INSTITUTE OF TECHNOLOGY DELHI  
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*Dedicated to my beloved family*

## Certificate

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This is to certify that the thesis entitled “**Unveiling Valley and Topological Properties of Quantum Materials Using First-Principles Simulations**” being submitted by **Ankita**, 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 her under my supervision and guidance. She 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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Date:.....

Place: New Delhi

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**Ankita**

# Abstract

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The fields of valleytronics and topological insulators have witnessed explosive growth in recent years, driven by the quest for novel electronic and spintronic functionalities. This thesis contributes to this emerging area by exploring novel valleytronic and topological phenomena across a diverse range of material systems, employing state-of-the-art first-principles computational methodologies. The search for two-dimensional materials with exotic valley-dependent properties has gained considerable momentum, driven both by their fundamental scientific significance and their potential for applications in nanoscale devices. Therefore, we firstly present the identification of promising intrinsic valley-related switchable Hall effects in  $\text{Cr}_2\text{CSF}$ .  $\text{Cr}_2\text{CSF}$ , characterized by high out-of-plane magnetic anisotropy, is identified as a ferrovalley semiconductor with spontaneously polarized valleys, exhibiting a valley polarization of 27.1 meV in the conduction band. This facilitates the observation of an intrinsic anomalous valley Hall (AVH) effect, which can be manipulated by an in-plane electric field. We elucidate the underlying physics of spontaneous valley polarization using the SOC Hamiltonian model. Furthermore, by applying unidirectional compressive strain, we transition  $\text{Cr}_2\text{CSF}$  from the AVH phase to a long sought quasi-half valley metal state. In this state, only the electrons are valley polarized, enabling the separation of hole and electron carriers under an in-plane electric field. Our study contributes to the expanding array of materials with valley-related Hall effects, providing a platform for exploring the interplay between valleytronics and spintronics.

Further, we explore the antiferromagnetic (AFM) materials, which are distinguished by their zero net magnetic moment, high resistance to external magnetic disturbances, and ultra-fast dynamic responses. To advance the application of AFM materials in valleytronics, we focus on achieving spontaneous valley polarization and the AVH effect. We predict an A-type AFM monolayer  $\text{Fe}_2\text{C}(\text{OH})_2$ , which exhibits a significant spontaneous valley polarization of 157 meV. In  $\text{Fe}_2\text{C}(\text{OH})_2$ , the spatial inversion symmetry ( $P$ ) and the time-reversal symmetry ( $T$ ) are individually broken, while the combined  $PT$  symmetry is preserved. This symmetry

conservation leads to spin degeneracy, resulting in zero Berry curvature in the momentum space and the absence of AVH effect. However, a layer-locked hidden Berry curvature is produced, leading to the observation of valley layer-spin Hall effect. We further demonstrate that an external out-of-plane electric field can induce spin splitting by introducing a layer-dependent electrostatic potential, enabling the layer-locked AVH effect. Additionally, the introduction of a built-in electric field, achieved through a Janus structure in monolayer  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ , also induces spin splitting due to the electric-potential-difference-AFM mechanism. The high out-of-plane magnetic anisotropy and realization of AVH effect in these materials offer promising opportunities for the development of next-generation valleytronic technologies.

Herein, we propose a general scheme enabling nonvolatile electrical control of the AVH effect through the utilization of multiferroic van der Waals heterostructures. Effective external control over the AVH effect is paramount for the practical realization of valleytronic devices, however, current approaches frequently suffer from limitations of irreversibility or volatility. Employing first-principles density functional theory calculations, we demonstrate the feasibility of this design principle via a system comprising ferromagnetic monolayer VSSe stacked upon ferroelectric monolayer  $\text{Al}_2\text{S}_3$ . Our findings indicate that the reversible switching of the AVH effect can be precisely manipulated by reversing the ferroelectric polarization of  $\text{Al}_2\text{S}_3$  via an applied electric field. Crucially, the regulated AVH state of VSSe remains stably preserved due to the intrinsic ferroelectric nonvolatility of  $\text{Al}_2\text{S}_3$ . Furthermore, the sign of the valley polarization can be simultaneously inverted through this same ferroelectric polarization reversal. These results not only lay the foundation for developing intrinsically ferroelectricity-controlled ferrovalley materials but also identify an exceptional candidate for realizing advanced bidirectional and nonvolatile switching valleytronic devices.

Furthermore, we shift our focus on the prediction of three-dimensional topological insulators (TIs), leveraging density functional theory (DFT) and many-body perturbation theory ( $G_0W_0$ ) combined with spin-orbit coupling (SOC) effects. We begin with the well-established 3D TI,  $\text{TlBiSe}_2$ , and systematically perform complete isostructural substitutions at various atomic sites. This approach aims to identify if the resulting materials maintain or exhibit novel topological properties. Subsequently, we conduct a meticulous screening of these materials, focusing on the SOC-induced parity inversion at time-reversal invariant momenta. To confirm the topological nature of selected materials, we generate surface state plots and compute  $Z_2$  topological invariants. Our findings reveal that  $\text{GaBiSe}_2$  emerges as a strong TI. Additionally,

we identify six weak TIs:  $\text{PbBiSe}_2$ ,  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$ , and  $\text{PbSbSe}_2$ . Furthermore, we demonstrate the dynamical stability of all reported TIs by analyzing their phonon dispersion, confirming the presence of all real phonon modes of vibration.

Finally, we examine the strain-induced topological phase transitions in centrosymmetric and non-centrosymmetric halide perovskites. We observe that centrosymmetric perovskites undergo a continuous phase transition from a trivial to a TI state at a critical strain value. Conversely, non-centrosymmetric halide perovskites exhibit a discontinuous phase transition. This discontinuity is attributed to the absence of a stable gapless state, which is destabilized by the lack of centrosymmetry. To understand the evolution of band topology under compressive strain, we employ DFT and Slater-Koster formalism-based tight-binding Hamiltonian studies. Our analysis indicates that both cubic and pseudocubic  $\text{FAPbI}_3$  undergo a Pb s-p band inversion at critical strain values. Notably, the pseudocubic structure exhibits two conducting states around the M point, a feature absent in the cubic counterpart. We attribute this difference to the Pb-Pb second nearest neighbor interactions. Moreover, we model mixed cation halide perovskites  $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ) to investigate their topological properties. We also perform structural stability analyses of various strained configurations to enhance the experimental relevance of our findings.



हाल के वर्षों में वैलीट्रॉनिक्स और टोपोलॉजिकल इंसुलेटर के क्षेत्रों में जबरदस्त प्रगति हुई है, जिसका मुख्य कारण नए इलेक्ट्रॉनिक और स्पिनट्रॉनिक कार्यों की खोज है। यह शोध प्रबंध अत्याधुनिक प्रथम-सिद्धांतों वाली कम्प्यूटेशनल पद्धतियों का उपयोग करके, विभिन्न प्रकार के मटेरियल सिस्टम में नवीन वैलीट्रॉनिक और टोपोलॉजिकल घटनाओं की खोज करके इस उभरते क्षेत्र में योगदान देता है। विशिष्ट वैली-आधारित गुणों वाले टू-डायमेंशनल सामग्रियों की खोज ने काफी गति पकड़ी है, जो उनके मौलिक वैज्ञानिक महत्व और नैनोस्केल उपकरणों में अनुप्रयोगों की संभावनाओं से प्रेरित है।

इसलिए, हम सबसे पहले  $\text{Cr}_2\text{CSF}$  में आंतरिक वैली संबंधित स्विच करने योग्य हॉल प्रभावों की पहचान प्रस्तुत करते हैं। उच्च आउट-ऑफ-प्लेन मैग्नेटिक अनिसोट्रॉपी वाला  $\text{Cr}_2\text{CSF}$ , स्वतःस्फूर्त ध्रुवीकृत वैली वाले एक फेरोवैली सेमीकंडक्टर के रूप में पहचाना गया है, जो कंडक्शन बैंड में 27.1 meV का वैली ध्रुवीकरण प्रदर्शित करता है। यह एक आंतरिक एनोमलस वैली हॉल प्रभाव के अवलोकन की सुविधा प्रदान करता है, जिसे इन-प्लेन इलेक्ट्रिक फील्ड द्वारा नियंत्रित किया जा सकता है। हम SOC हैमिल्टनियन मॉडल का उपयोग करके स्वतःस्फूर्त वैली ध्रुवीकरण के अंतर्निहित भौतिकी को स्पष्ट करते हैं। इसके अलावा, यूनिडायरेक्शनल कंप्रेसिव स्ट्रेन लागू करके, हम  $\text{Cr}_2\text{CSF}$  को एनोमलस वैली हॉल चरण से लंबे समय से प्रतीक्षित क्रासी-हाफ वैली मेटल अवस्था में परिवर्तित करते हैं। इस अवस्था में, केवल इलेक्ट्रॉन ही वैली ध्रुवीकृत होते हैं, जिससे इन-प्लेन इलेक्ट्रिक फील्ड के तहत होल और इलेक्ट्रॉन कैरियर्स को अलग करना संभव हो जाता है। हमारा अध्ययन वैली संबंधित हॉल प्रभावों वाली सामग्रियों की बढ़ती श्रृंखला में योगदान देता है, जो वैलीट्रॉनिक्स और स्पिनट्रॉनिक्स के बीच परस्पर क्रिया की खोज के लिए एक मंच प्रदान करता है।

आगे, हम एंटीफेरोमैग्नेटिक (AFM) सामग्रियों का अन्वेषण करते हैं, जो अपने शून्य शुद्ध चुंबकीय क्षण, बाहरी चुंबकीय विक्षोभों के प्रति उच्च प्रतिरोध और अति-तीव्र गतिशील प्रतिक्रियाओं के लिए विशिष्ट हैं। वैलीट्रॉनिक्स में एंटीफेरोमैग्नेटिक सामग्रियों के अनुप्रयोग को आगे बढ़ाने के लिए, हम स्वतःस्फूर्त वैली ध्रुवीकरण और एनोमलस वैली हॉल प्रभाव को प्राप्त करने पर ध्यान केंद्रित करते हैं। हम एक ए-प्रकार के एंटीफेरोमैग्नेटिक मोनोलेयर  $\text{Fe}_2\text{C}(\text{OH})_2$  की भविष्यवाणी करते हैं, जो 157 meV का महत्वपूर्ण स्वतःस्फूर्त वैली ध्रुवीकरण प्रदर्शित करता है।  $\text{Fe}_2\text{C}(\text{OH})_2$  में, स्थानिक व्युत्क्रमण समरूपता और समय-व्युत्क्रमण समरूपता व्यक्तिगत रूप से टूट जाती हैं, जबकि संयुक्त पीटी समरूपता संरक्षित रहती है। यह समरूपता संरक्षण स्पिन डिजेनरेसी की ओर ले जाता है, जिसके परिणामस्वरूप मोमेंटम स्पेस में शून्य बेरी कर्वचर प्राप्त होता है और एनोमलस वैली हॉल (AVH) प्रभाव अनुपस्थित रहता है। हालांकि, एक लेयर-लॉक्ड हिडन बेरी कर्वचर उत्पन्न होता है, जिससे वैली लेयर-स्पिन हॉल प्रभाव का अवलोकन होता है। हम आगे यह प्रदर्शित करते हैं कि एक बाहरी आउट-ऑफ-प्लेन इलेक्ट्रिक फील्ड, लेयर-आधारित इलेक्ट्रोस्टैटिक पोटेंशियल पेश करके स्पिन स्प्लिटिंग को प्रेरित कर सकता है, जिससे लेयर-लॉक्ड AVH

प्रभाव सक्षम हो जाता है। इसके अतिरिक्त, मोनोलेयर  $\text{Fe}_2\text{C}(\text{OH})_2$  में जेनस संरचना के माध्यम से प्राप्त बिल्ट-इन इलेक्ट्रिक फील्ड, इलेक्ट्रिक-पोटेंशियल-डिफरेंस-AFM मैकेनिज्म के कारण स्पिन स्प्लिटिंग को भी प्रेरित करता है। इन सामग्रियों में उच्च आउट-ऑफ-प्लेन मैग्नेटिक अनिसोट्रॉपी और AVH प्रभाव का अहसास अगली पीढ़ी की वैलीट्रॉनिक प्रौद्योगिकियों के विकास के लिए आशाजनक अवसर प्रदान करता है।

इसके बाद, हम मल्टीफेरोइक वैन डेर वाल्स हेटरोस्ट्रक्चर के उपयोग के माध्यम से AVH प्रभाव के नॉन-वोलेटाइल इलेक्ट्रिकल कंट्रोल को सक्षम करने वाली एक सामान्य योजना प्रस्तावित करते हैं। वैलीट्रॉनिक उपकरणों के व्यावहारिक अहसास के लिए AVH प्रभाव पर प्रभावी बाहरी नियंत्रण सर्वोपरि है, हालांकि, वर्तमान दृष्टिकोण अक्सर अपरिवर्तनीयता या अस्थिरता की सीमाओं से ग्रस्त हैं। प्रथम-सिद्धांतों वाली डेंसिटी फंक्शनल थ्योरी गणनाओं का उपयोग करते हुए, हम फेरोइलेक्ट्रिक मोनोलेयर  $\text{Al}_2\text{S}_3$  पर रखे गए फेरोमैग्नेटिक मोनोलेयर VSSe वाले सिस्टम के माध्यम से इस डिज़ाइन सिद्धांत की व्यवहार्यता प्रदर्शित करते हैं। हमारे निष्कर्ष बताते हैं कि AVH प्रभाव के प्रतिवर्ती स्विचिंग को लागू इलेक्ट्रिक फील्ड के माध्यम से  $\text{Al}_2\text{S}_3$  के फेरोइलेक्ट्रिक पोलराइजेशन को उलट कर सटीक रूप से नियंत्रित किया जा सकता है। महत्वपूर्ण बात यह है कि VSSe की विनियमित AVH अवस्था  $\text{Al}_2\text{S}_3$  की अंतर्निहित फेरोइलेक्ट्रिक नॉन-वोलेटिलिटी के कारण स्थिर रूप से बनी रहती है। इसके अलावा, वैली ध्रुवीकरण के चिह्न को इसी फेरोइलेक्ट्रिक पोलराइजेशन रिवर्सल के माध्यम से एक साथ बदला जा सकता है। ये परिणाम न केवल अंतर्निहित फेरोइलेक्ट्रिसिटी-नियंत्रित फेरोवैली सामग्रियों को विकसित करने के लिए आधार तैयार करते हैं, बल्कि उन्नत बिडायरेक्शनल और नॉन-वोलेटाइल स्विचिंग वैलीट्रॉनिक उपकरणों को साकार करने के लिए एक असाधारण उम्मीदवार की पहचान भी करते हैं।

इसके अतिरिक्त, हम डेंसिटी फंक्शनल थ्योरी और मैनी-बॉडी पर्टर्बेशन थ्योरी ( $G_0W_0$ ) के साथ स्पिन-ऑर्बिट कपलिंग (SOC) प्रभावों का लाभ उठाते हुए, थ्री-डायमेंशनल टोपोलॉजिकल इंसुलेटर (3D TIs) की भविष्यवाणी पर ध्यान केंद्रित करते हैं। हम अच्छी तरह से स्थापित 3D TI,  $\text{TlBiSe}_2$ , के साथ शुरुआत करते हैं और विभिन्न परमाणु स्थानों पर व्यवस्थित रूप से पूर्ण आइसोस्ट्रक्चरल सब्स्टीट्यूशन करते हैं। इस दृष्टिकोण का उद्देश्य यह पहचानना है कि क्या परिणामी सामग्रियां अपने टोपोलॉजिकल गुणों को बनाए रखती हैं या नए गुण प्रदर्शित करती हैं। इसके बाद, हम इन सामग्रियों की सावधानीपूर्वक स्क्रीनिंग करते हैं, जो टाइम-रिवर्सल इनवेरिएंट मोमेंटम पर SOC-प्रेरित पैरिटी इन्वर्जन पर केंद्रित है। चयनित सामग्रियों की टोपोलॉजिकल प्रकृति की पुष्टि करने के लिए, हम सरफेस स्टेट प्लॉट्स उत्पन्न करते हैं और  $Z_2$  टोपोलॉजिकल इनवेरिएंट्स की गणना करते हैं। हमारे निष्कर्षों से पता चलता है कि  $\text{GaBiSe}_2$  एक स्ट्रांग TI के रूप में उभरता है। इसके अलावा, हम छह वीक TIs की पहचान करते हैं:  $\text{-PbBiSe}_2$ ,  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$  तथा  $\text{PbSbSe}_2$ । इसके अतिरिक्त, हम उनके फोनोन डिस्पर्सन का विश्लेषण करके सभी रिपोर्ट किए गए TIs की गतिशील स्थिरता का प्रदर्शन करते हैं, जो कंपन के सभी वास्तविक फोनोन मोड्स की उपस्थिति की पुष्टि करता है।

अंत में, हम केंद्रसममित और गैर-केंद्रसममित हैलाइड पेरोव्स्काइट्स में तनाव-प्रेरित टोपोलॉजिकल चरण संक्रमणों की जांच करते हैं। हम देखते हैं कि केंद्रसममित पेरोव्स्काइट्स एक महत्वपूर्ण तनाव मूल्य पर एक तुच्छ से टोपोलॉजिकल इंसुलेटर राज्य में एक सतत चरण संक्रमण से गुजरते हैं। इसके विपरीत, गैर-केंद्रसममित हैलाइड पेरोव्स्काइट्स एक असंतत चरण संक्रमण प्रदर्शित करते हैं। यह असंततता एक स्थिर गैपलेस राज्य की अनुपस्थिति के कारण होती है, जो केंद्रसममिति की कमी से अस्थिर हो जाती है। संपीड़ित तनाव के तहत बैंड टोपोलॉजी के विकास को समझने के लिए, हम DFT और स्लेटर-कोस्टर औपचारिकता-आधारित टाइट-बाइंडिंग हैमिल्टनियन अध्ययन का उपयोग करते हैं। हमारा विश्लेषण इंगित करता है कि घन और स्यूडोकुबिक  $\text{FAPbI}_3$  दोनों महत्वपूर्ण तनाव मूल्यों पर Pb s-p बैंड व्युत्क्रमण से गुजरते हैं। विशेष रूप से, स्यूडोकुबिक संरचना M बिंदु के आसपास दो संचालन राज्य प्रदर्शित करती है, जो घन समकक्ष में अनुपस्थित एक विशेषता है। हम इस अंतर को Pb-Pb दूसरे निकटतम पड़ोसी अंतःक्रियाओं के लिए जिम्मेदार ठहराते हैं। इसके अलावा, हम मिश्रित धनायन हैलाइड पेरोव्स्काइट्स  $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$  ( $x = 0.25, 0.50$  और  $0.75$ ) को उनके टोपोलॉजिकल गुणों की जांच के लिए मॉडल करते हैं। हम विभिन्न तनावग्रस्त विन्यासों के संरचनात्मक स्थिरता विश्लेषण भी करते हैं ताकि हमारे निष्कर्षों की प्रायोगिक प्रासंगिकता को बढ़ाया जा सके।

## List of Publications

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1. **Ankita Phutela**, and Saswata Bhattacharya, “Reversible switching of anomalous valley hall effect to quasi-half-valley metal state in 2D magnetic MXenes: A case study of  $\text{Cr}_2\text{CSF}$ ”, *Physical Review Materials* **9**, 054002 (2025).
2. **Ankita Phutela**, and Saswata Bhattacharya, “Inducing Spin Splitting and Anomalous Valley Hall Effect in A-Type AFM  $\text{Fe}_2\text{C}(\text{OH})_2$  through Electric Field and Janus Engineering”, *Physical Review Materials (Letter)* **9**, L081001 (2025).
3. **Ankita Phutela** and Saswata Bhattacharya, “Unlocking reversible and nonvolatile anomalous valley Hall control through multiferroic van der Waals heterostructures”, (arXiv:2508.13614 (2025)).
4. **Ankita Phutela**, Preeti Bhumla, Manjari Jain, and Saswata Bhattacharya. “Exploring strong and weak topological states on isostructural substitutions in  $\text{TlBiSe}_2$ ”, *Scientific Reports* **12**, 21970 (2022).
5. **Ankita Phutela**, Sajjan Sheoran, Deepika Gill, and Saswata Bhattacharya, “Strain-driven topological quantum phase transition in (pseudo) cubic (mixed)-Cs/MA/FA halide perovskites”, *Journal of Materials Chemistry C* **12**, 2165 (2023).
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- MoS<sub>2</sub> nanocomposites by transition metal doping: Experimental and first-principles studies”, *International Journal of Hydrogen Energy* **79**, 826 (2024).
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  11. Arindam Modak, **Ankita Phutela**, Aniruddha Kundu, Srijib Das, Vidha Bhasin, Dibyendu Bhattacharyya, and Saswata Bhattacharya, “Hyper-Cross-Linked Polymer-Derived Carbon-Coated Fe-Ni Alloy/CNT as a Bifunctional Electrocatalyst for Rechargeable Zinc-Air Batteries”, *The Journal of Physical Chemistry Letters* **16**, 1051 (2025).

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## Introduction

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### 1.1 The dawn of quantum materials: beyond conventional electronics

Conventional silicon-based electronics, while undeniably successful, face inherent limitations that hinder the further progress of the field. These include power consumption due to Joule heating, size constraints as devices approach atomic scales, speed limitations caused by electron scattering, susceptibility to external factors like noise and interference, and limited functional integration. While electrons possess both charge and spin degrees of freedom, traditional electronics primarily focuses on manipulating the charge, ignoring the spin. This oversight represents a significant missed opportunity, as spin offers a lot of possibilities for information processing and storage.

This realization has accelerated the growth of spintronics, a multidisciplinary field aiming to control the spin degree of freedom in solid state systems [8, 9]. Spin is either intrinsic property of a single electron, which can be detected through its magnetic moment, or the average spin of many electrons in a material, known as magnetization. Spin manipulation refers to controlling the population of spins i.e., how many spins point in a particular direction, and how their quantum phases change. This control can be achieved in system of large collections of electrons and also in systems with only one or a few spins. The main aim of spintronics is to understand how electron spin interacts with the crystal environment and to use this knowledge to build new types of devices. Spintronics includes a wide range of research areas. On one side, researchers work on controlling individual spins at specific atomic locations, such as nitrogen-vacancy centers in diamond or semiconductor quantum dots. These systems are important for solid-state quantum computing. On the other side, scientists study how spin moves and evolves in larger materials, focusing on the relationship between spin transport and spin dynamics.

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Beyond spintronics, the exploration of another electronic degree of freedom, i.e., valley, is also underway. In certain materials, like transition metal dichalcogenides (TMDs) and graphene, electrons can occupy multiple valleys in the electronic band structure. These valleys, residing at different points in momentum space, can be selectively populated and manipulated, offering a new degree of freedom analogous to spin [10]. Electrons in different valleys possess distinct properties, such as different effective masses and Berry curvature, leading to unique responses to external fields. Valleytronics aims to control these valley degrees of freedom for novel device functionalities, including valley-based transistors, logic gates, and sensors. The manipulation of valley degrees of freedom offers the potential for highly efficient and versatile electronic devices.

Furthermore, a new and powerful approach has emerged from the study of topological materials, which have attracted significant attention in condensed matter physics over the past few years [11, 12, 13, 14]. These materials exhibit remarkable properties, especially at their boundaries, where they support unidirectional and dissipationless energy transport that is robust against backscattering. Such features make them highly attractive for applications in spintronics and quantum information science. In recent years, the concept of topological materials has also been extended beyond electronic systems to other areas, including acoustics [16, 17, 18, 19, 20, 21], photonics [15], optics [15] and mechanics [22, 23]. This expansion has opened novel possibilities for manipulating and engineering advanced devices, poised to revolutionize contemporary electronics.

## 1.2 Valleytronics

When individual atoms combine to form a crystalline solid, interactions among their electrons and ionic cores lead to the formation of energy bands that govern the electronic behavior of the

material. In semiconductors, the electrons participating in chemical bonding fully occupy the valence band, while the conduction band lies at higher energy and is typically empty. These two bands are separated by an energy region devoid of electronic states, known as the band gap. In many semiconductors, regions of minimum energy can form within the conduction band, with the only distinction being the orientation of the crystal axes. When carriers are excited across the band gap and occupy these energy minima in the conduction band, they will have the same energy but different crystal momenta, depending on the crystal axis. These energy minima are referred to as "valleys".

The concept of valleytronics arises from exploiting these valleys as carriers of information. Devices that utilize electrons, holes, or excitons confined to specific valleys are known as valleytronic devices. A central requirement for such applications is the ability to selectively populate one valley over others, a condition known as valley polarization. The term valleytronics was introduced by analogy with spintronics. In spintronic systems, information is stored and processed using the electron's spin degree of freedom. In a similar spirit, valleytronics encodes information using discrete valley indices associated with different extrema in the electronic band structure. In this framework, binary information can be assigned to different valleys, effectively using crystal momentum states as logical bits. This additional degree of freedom is often described as the valley pseudospin, which complements the real spin of the particle. Although energy-degenerate valleys are common in many crystalline materials, controlling the valley degree of freedom remains challenging. The primary difficulty lies in the weak interaction between valley indices and external fields. Unlike electron spin, which can be manipulated using magnetic fields or through spin-orbit coupling, valley states generally couple only weakly to external perturbations [10]. This limited controllability has so far restricted the practical realization of valleytronic devices in most materials.

For valleytronics to be useful, it is essential that the particles populating a specific valley remain there for long enough to perform their desired function. Some materials exhibit anisotropy in the particle mass along different crystal orientations, leading to valley polarization under an applied field. In these materials, preferential scattering between valleys can occur, as demonstrated in diamond, aluminum arsenide, silicon, and bismuth at cryogenic temperatures. However, these materials lack strong enough coupling between the valley index and external fields, preventing selective manipulation of particles in a particular valley. As a result, such materials are not considered viable for valleytronic applications.

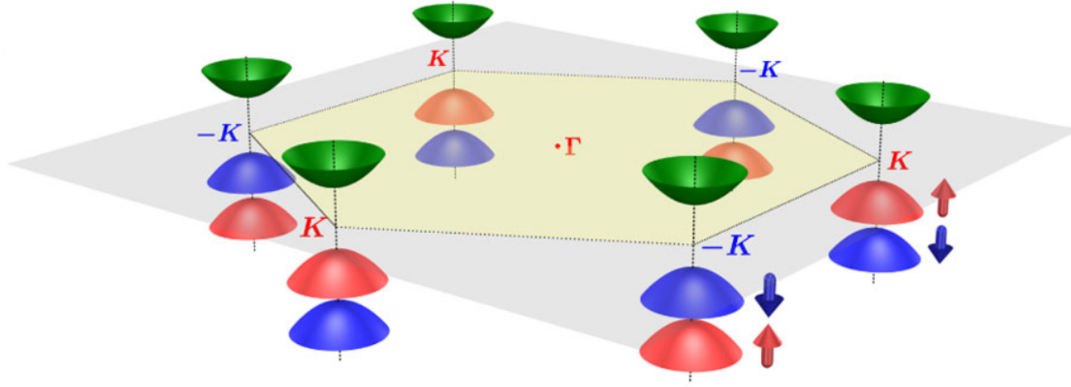


Figure 1.1: Schematic depiction of spin-valley coupling in hexagonal 2D materials with opposite spin polarization at the  $K$  and  $K'$  points. This Figure is taken from Ref. [1].

However, a class of materials does exist where valley pseudospins can be more readily addressed. Unlike other materials, 2D materials such as graphene [24, 25, 26] and monolayer molybdenum disulfide [27, 28] exhibit valleys at inequivalent  $K$  and  $K'$  points in the Brillouin zone, which have strong valley selective interactions with applied electric and magnetic fields (see Fig. 1.1). The isolation and investigation of these 2D materials were key milestones in the field of valleytronics. The publication history in this field shows a significant boost in research after the isolation of graphene in 2004, but it was the exploration of the optical properties of transition metal dichalcogenide monolayers that truly ignited the valleytronic research explosion [29, 30, 31, 32, 33, 34, 35].

To enable selective control over different valley degrees of freedom, it is necessary to identify physical quantities that can distinguish between inequivalent valleys. A key quantity in this context is the Berry curvature, which encodes the geometric properties of electronic bands and plays a central role in phenomena associated with band topology. Within the semiclassical description of electron dynamics in crystalline solids, charge carriers are treated as Bloch wave packets whose group velocity is primarily determined by the gradient of the band energy. The effects of lattice periodicity are incorporated through the Bloch form of the electronic wavefunction, while external electric and magnetic fields govern the carrier dynamics.

In addition to the conventional band velocity, an extra contribution known as the anomalous velocity arises, which is directly proportional to the Berry curvature of the electronic band. This anomalous velocity is generally transverse to the applied electric field and can give rise to valley-dependent transverse transport in systems with nonzero Berry curvature. Such behavior forms the foundation of valleytronic phenomena, as it enables the generation, manipulation,

and control of valley-polarized currents.

The orbital magnetic moment serves as another physical quantity to differentiate valley states, conceptually arising from the self-rotation of an electron wavepacket. It is particularly valuable as it allows for valley state discrimination akin to experiments utilizing the spin magnetic moment of charge carriers (e.g., distinguishing spin-up and spin-down states with a magnetic field). However, the Berry curvature and orbital magnetic moment, and their utility in distinguishing valley states, can vanish if both time-reversal symmetry and inversion symmetry are simultaneously present in a crystal. Time-reversal symmetry describes a system's symmetry under time sign reversal, while spatial inversion symmetry denotes symmetry under coordinate axes direction reversal. These symmetries have significant implications. Pseudovectors, like the Berry curvature and orbital magnetic moment, do not change sign under spatial inversion. Consequently, they cannot differentiate valleys when both symmetries are present, as they become identically zero. The  $K$  and  $K'$  points in hexagonal 2D materials are time-reversed images, making physical quantities with odd parity under time reversal suitable candidates for valley state distinction. If the Berry curvature and orbital magnetic moment are non-equivalent at the  $K$  and  $K'$  points, electric and magnetic fields, respectively, can be employed to distinguish between the valleys. The semiclassical equations of motion for Bloch electrons under the influence of applied electric and magnetic fields, with nonvanishing Berry curvature, are given by:

$$\mathbf{r}_k = \frac{\partial \mathbf{k}}{\partial t} - \nabla_k \times \boldsymbol{\Omega}_k, \quad (1.1)$$

$$\mathbf{E}_k = -e(\mathbf{E} + \mathbf{v}_k \times \mathbf{B}), \quad (1.2)$$

where  $\boldsymbol{\Omega}_k$  can be expressed in terms of the Bloch functions as:

$$\boldsymbol{\Omega}_k = \nabla_k \times \mathbf{A}_n(k), \quad (1.3)$$

with

$$\mathbf{A}_n(k) = \langle u_n(k) | \nabla_k | u_n(k) \rangle. \quad (1.4)$$

Here,  $\mathbf{A}_n(k)$  is the Berry connection, and  $u_n(k)$  represents the periodic part of the Bloch electron wavefunction in the  $n$ -th energy band.

We can also write Berry curvature as:

$$\Omega_k = \frac{2i\hbar}{\Omega} \sum_{n \neq m} \frac{\langle u_n(k) | \nabla_k | u_m(k) \rangle \times \langle u_m(k) | \nabla_k | u_n(k) \rangle}{(E_n(k) - E_m(k))^2}, \quad (1.5)$$

where  $E_n(k)$  is the energy dispersion of the  $n$ -th band, and  $P_{n,m}(k) = \langle u_n(k) | v | u_m(k) \rangle$  represents the matrix element of the velocity operator.

By demanding that the equation of motion remains invariant under the system's symmetries, it can be shown that:

- With time-reversal symmetry,  $\Omega_n(k) = -\Omega_n(-k)$ ,
- With inversion symmetry,  $\Omega_n(k) = \Omega_n(-k)$ .

Consequently, valley-contrasting effects can arise only in systems where inversion symmetry is broken. The semiclassical equations of motion further show that, in a two-dimensional crystal, the application of an in-plane electric field generates an anomalous velocity due to the Berry curvature. This velocity is directed perpendicular to the applied field and possesses opposite signs for charge carriers residing in time-reversal related valleys.

The broken inversion symmetry also allows the existence of an orbital magnetic moment. Imagine electrons in a material as tiny spinning tops. Sometimes, these spinning electrons create tiny magnetic fields, like little magnets. This is related to something called orbital magnetic moment. Now, in some special materials, the way these electrons move and spin is linked to their energy. Think of it like different lanes for electrons with slightly different energies. These lanes are called valleys. If a material has a special kind of asymmetry, it can happen that electrons in different valleys have different magnetic moments (they act like little magnets with different strengths or orientations). This difference in magnetic moment between valleys is a key ingredient for valleytronics. One consequence of this difference is that light can interact differently with electrons in different valleys. It is like some electrons prefer to absorb light that is spinning clockwise, while others prefer light spinning in counterclockwise direction. This is called optical circular dichroism. It means the material interacts differently with right and left-handed circularly polarized light. Another consequence is that if you apply a magnetic field, electrons in different valleys will behave differently. They might move in slightly different ways or have different energies. This difference in behavior can be used to control the electrons in the different valleys, kind of like how you might steer cars in different lanes on a highway. All of these methods of control of the valley state are illustrated in Fig. 1.2.

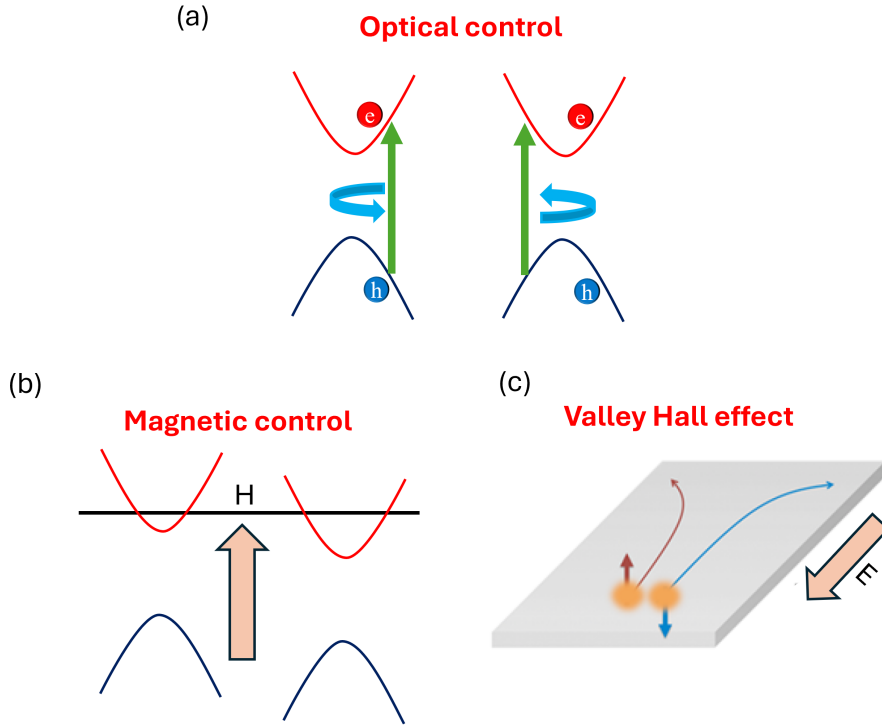


Figure 1.2: Three methods of control of the valley state: (a) optical, (b) electrostatic, and (c) magnetic[2, 3]

This valleytronics is interesting because it offers a new way to control electrons and potentially build new types of electronic devices. It exploits the valley degree of freedom of electrons, in addition to their charge and spin. The lack of mirror symmetry in the material is crucial for making all of this happen. Certain materials, like 2D transition metal dichalcogenides, have this built-in asymmetry, making them promising candidates for valleytronic applications.

### 1.3 Hall effect and its analogues

The Hall effect, discovered by Edwin Hall in 1879, is a fundamental transport phenomenon observed when a magnetic field is applied perpendicular to the current in a conductor. It results in a transverse voltage due to the Lorentz force acting on charge carriers. For a current density  $\mathbf{J}$  flowing in the  $x$ -direction and a magnetic field  $\mathbf{B}$  applied along the  $z$ -direction, the transverse Hall electric field  $E_y$  satisfies:

$$E_y = \frac{1}{ne} J_x B_z, \quad (1.6)$$



where  $n$  is the carrier density and  $e$  is the elementary charge. The proportionality constant defines the classical Hall conductivity:

$$\sigma_{xy}^{\text{Hall}} = \frac{ne}{B_z}. \quad (1.7)$$

### 1.3.1 Anomalous Hall effect

In ferromagnetic materials and systems with significant spin-orbit coupling, a transverse voltage can arise even in the absence of an external magnetic field, leading to the Anomalous Hall Effect (AHE). The intrinsic contribution to AHE originates from the Berry curvature of the electronic bands. In the semiclassical formalism, the anomalous velocity of a Bloch electron in band  $n$  is:

$$\mathbf{v}_n^{\text{an}} = -\frac{e}{\hbar} \mathbf{E} \times \boldsymbol{\Omega}_n(\mathbf{k}), \quad (1.8)$$

where  $\boldsymbol{\Omega}_n(\mathbf{k})$  is the Berry curvature of band  $n$  at momentum  $\mathbf{k}$ . The anomalous Hall conductivity is then given by:

$$\sigma_{xy}^{\text{AHE}} = -\frac{e^2}{\hbar} \sum_n \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} f_n(\mathbf{k}) \Omega_n^z(\mathbf{k}), \quad (1.9)$$

where  $f_n(\mathbf{k})$  is the Fermi-Dirac distribution function.

### 1.3.2 Valley Hall Effect

The Valley Hall Effect (VHE) emerges in materials with multiple inequivalent valleys (e.g.,  $K$  and  $K'$  points in the Brillouin zone), where the Berry curvature has opposite signs in different valleys. Although the total Hall conductivity cancels out in the absence of a magnetic field (due to time-reversal symmetry), carriers from different valleys experience opposite transverse deflections, resulting in a net valley current:

$$\mathbf{J}_v = \frac{e^2}{\hbar} \sum_{\tau=\pm 1} \tau \int \frac{d^2k}{(2\pi)^2} f_{\tau}(\mathbf{k}) \boldsymbol{\Omega}_{\tau}(\mathbf{k}), \quad (1.10)$$

where  $\tau$  is the valley index. This effect is particularly strong in two-dimensional materials like transition metal dichalcogenides (TMDs), where inversion symmetry breaking and spin-valley locking make electrical manipulation of valley degrees of freedom feasible.

These Hall effects-classical, anomalous, and valley, form the foundation for a range of emergent quantum phenomena in modern condensed matter physics and are central to the development of topological electronics and valleytronic devices.

## 1.4 The Berry curvature

For a two-dimensional electronic system, the Hall conductivity  $\sigma_{xy}$  may be formulated in terms of the system's Bloch wave functions [36, 37] as follows:

$$\sigma_{xy} = \frac{e^2}{h} \nu = \frac{e^2}{h} \int_{BZ} \frac{i}{2\pi} \sum_{\text{occupied}} \left( \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_x} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_y} \right\rangle - \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_y} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_x} \right\rangle \right) dk_x dk_y \quad (1.11)$$

In this expression, the integration is performed over the full Brillouin zone, and the summation runs over all occupied electronic bands. Although the form of the equation may appear complex, it conveys important insights. The result is determined solely by the Bloch wave functions and does not depend explicitly on the energy eigenvalues, the role of energy here is limited to selecting which bands are occupied. A key consequence of this formulation is that the Brillouin zone integral always evaluates to an integer, which requires the topological invariant  $\nu$  to take integer values when all occupied bands are fully filled. This quantization guarantees that  $\nu$  is robust against small changes in system parameters, as long as the energy gap remains open and the number of occupied bands does not change, which is characteristic of an insulating phase.

Although the equation (1.11) establishes the formal connection between the Hall conductance and the Bloch wave functions, it does not directly clarify the origin of the integer-valued invariant  $\nu$ . To gain insight into this quantization, the concept of the Berry phase [36] has been introduced. Within this framework, the Berry connection  $\mathbf{A}$  and the Berry phase  $\phi$  are defined as:

$$\mathbf{A}(\mathbf{k}) = \sum_{\text{occupied}} \langle u_{n\mathbf{k}} | i \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle \quad (1.12)$$

$$\phi = \oint_{\gamma} \mathbf{A} \cdot d\mathbf{k} \quad (1.13)$$

The Berry connection  $\mathbf{A}(\mathbf{k})$  is defined in terms of the Bloch wave functions and gives rise to the Berry phase  $\phi$  when integrated along a closed path  $\gamma$  in momentum space. Due to the inherent phase freedom of quantum states, the Bloch functions  $u_{n\mathbf{k}}$  are not uniquely defined, which renders the Berry connection gauge dependent and, in general, not globally single-valued over the Brillouin zone. In many physical systems, it is not possible to choose a smooth gauge throughout momentum space, and the Berry connection must therefore be

defined locally in different regions. Under a gauge transformation of the form  $u_{n\mathbf{k}} \rightarrow e^{i\theta(\mathbf{k})}u_{n\mathbf{k}}$ , the Berry connection transforms as  $\mathbf{A} \rightarrow \mathbf{A} - \nabla_{\mathbf{k}}\theta(\mathbf{k})$ , resulting in a corresponding shift of the Berry phase. Although the phase function  $\theta(\mathbf{k})$  itself may be multi-valued, physical consistency requires the quantity  $e^{i\theta(\mathbf{k})}$  to remain single-valued. Consequently, while the Berry phase  $\phi$  depends on the chosen gauge, the quantity  $e^{i\phi}$  is gauge invariant and depends only on the topology of the closed loop  $\gamma$  in momentum space.

Analogous to the electromagnetic vector potential, we can define the Berry curvature:

$$\mathbf{\Omega}_n(\mathbf{k}) = \nabla_{\mathbf{k}} \times \mathbf{A} \quad (1.14)$$

With this, Eq. (1.11) becomes:

$$\nu = \frac{1}{2\pi} \int_{BZ} \mathbf{\Omega} \cdot d^2\mathbf{k} \quad (1.15)$$

The geometric description of Bloch electrons reveals a strong analogy with classical electromagnetism. In this framework, the Berry connection  $\mathbf{A}$  plays a role similar to the electromagnetic vector potential, while the Berry curvature  $\mathbf{\Omega}$  corresponds to the magnetic field  $\mathbf{B}$  and is therefore gauge invariant. Just as a magnetic field deflects an electron in real space, the Berry curvature can be viewed as causing a transverse deflection of electrons in momentum space. The Berry phase acquired by an electron when its crystal momentum traces a closed loop in the Brillouin zone is analogous to the Aharonov-Bohm phase accumulated along a closed path in real space. Furthermore, the quantization of magnetic flux in electromagnetism has a direct counterpart in the quantization of the Hall conductivity, which is determined by an integer topological invariant known as the Chern number. Within this analogy, the Chern number plays a role similar to that of a magnetic monopole charge, reflecting the topological nature of the underlying field.

## 1.5 The quantum Hall effect

The quantum Hall effect represents one of the earliest and most striking manifestations of topology in condensed matter systems. It occurs in two-dimensional electron gases subjected to strong perpendicular magnetic fields and cooled to sufficiently low temperatures. The experimental discovery of this phenomenon by von Klitzing in 1980 [38] revealed that the Hall

conductance assumes highly precise, quantized values that are insensitive to material imperfections, disorder, or sample geometry. This unexpected robustness marked a fundamental departure from conventional transport theory and laid the groundwork for the modern understanding of topological phases of matter.

Experimentally, the QHE is observed as a series of plateaus in the Hall resistance as the magnetic field is varied, accompanied by a vanishing longitudinal resistance (Fig. 1.3). The Hall conductance takes the universal form

$$\sigma = \nu \frac{e^2}{h}, \quad (1.16)$$

where  $e$  is the elementary charge,  $h$  is Planck's constant, and  $\nu$  is an integer known as the filling factor. The striking accuracy of this quantization, maintained across a wide range of experimental conditions, immediately suggested that its origin must be rooted in a fundamental principle beyond microscopic details.

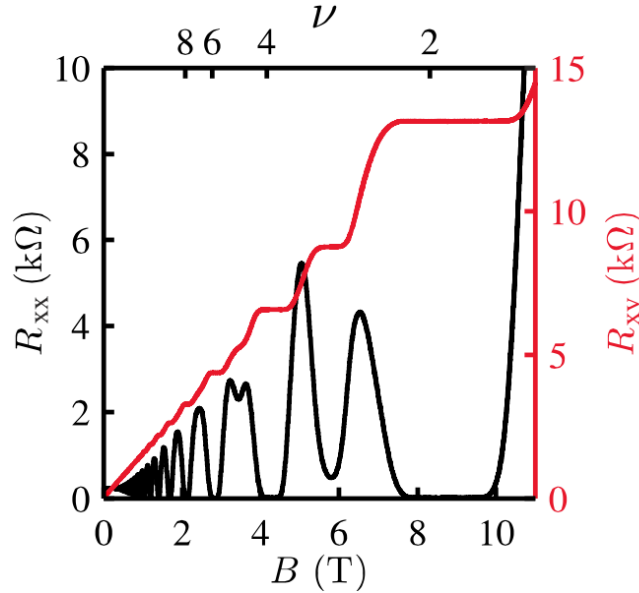


Figure 1.3: A plot of Hall resistance versus perpendicular magnetic field, illustrating the quantized Hall effect. The distinct plateaus represent precise values of Hall resistance. The source of this Figure is [4].

In the presence of a magnetic field, the kinetic energy of electrons is discretized into highly degenerate Landau levels,

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_c, \quad (1.17)$$

where  $\omega_c$  is the cyclotron frequency and  $n$  is a non-negative integer. When an integer number of Landau levels are completely filled, the Fermi energy lies within a gap separating occupied and unoccupied states. As a result, electronic transport through the bulk becomes suppressed,

while current is carried by chiral edge states localized at the boundaries of the sample. These edge modes are immune to backscattering, ensuring dissipationless transport and contributing directly to the quantized Hall response.

The deeper theoretical understanding of why the Hall conductance is quantized with such precision was provided by Thouless et al. [39, 40]. They demonstrated that the Hall conductivity, when expressed using linear response theory, is governed by a topological invariant of the electronic band structure rather than by local material properties. This invariant is known as the Chern number.

For a Bloch Hamiltonian  $H(\mathbf{k})$  with energy bands  $E_n(\mathbf{k})$ , the Chern number associated with the  $n$ -th band is defined as

$$C_n = \frac{1}{2\pi} \int_{BZ} d^2\mathbf{k} \Omega_n(\mathbf{k}), \quad (1.18)$$

where the integration extends over the entire Brillouin zone and  $\Omega_n(\mathbf{k})$  denotes the Berry curvature of the band. The Berry curvature is obtained from the Berry connection  $\mathbf{A}_n(\mathbf{k})$  according to

$$\Omega_n(\mathbf{k}) = \frac{\partial A_{n,2}}{\partial k_1} - \frac{\partial A_{n,1}}{\partial k_2}, \quad (1.19)$$

with

$$\mathbf{A}_n(\mathbf{k}) = -i\hbar \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle, \quad (1.20)$$

where  $|u_{n\mathbf{k}}\rangle$  is the periodic part of the Bloch wave function.

The total Hall conductance is determined by summing the Chern numbers of all occupied bands, such that the filling factor  $\nu$  in Eq. (1.16) equals the net Chern number of the system. Since the Chern number is an integer valued topological quantity, it remains unchanged under continuous deformations of the Hamiltonian as long as the energy gap does not close. This topological protection explains the extraordinary stability of the quantized Hall plateaus observed experimentally.

From a geometrical viewpoint, the Chern number plays a role analogous to global invariants in topology, such as the genus of a surface. Just as the number of holes in a surface cannot change without tearing it, the Chern number cannot vary unless the electronic band gap vanishes. In this way, the quantum Hall effect provides a direct physical realization of topological invariants, establishing a profound connection between geometry, topology, and electronic transport.

## 1.6 The quantum spin Hall effect

The discovery of the quantum Hall effect naturally led to a fundamental question that if it is possible to realize quantized edge transport without applying an external magnetic field. Also, can such a phenomenon be protected solely by intrinsic properties of the material? These questions motivated the search for time-reversal-invariant analogues of the quantum Hall effect and ultimately led to the prediction of the quantum spin Hall effect. Unlike the conventional quantum Hall effect, which relies on strong magnetic fields to break time-reversal symmetry, the quantum spin Hall effect emerges in two-dimensional systems with strong intrinsic spin-orbit coupling while preserving time-reversal invariance. In such systems, the electronic edge structure differs qualitatively from that of the quantum Hall effect. Instead of a single chiral edge mode, each boundary hosts pairs of counter propagating states with opposite spin orientations. These edge modes are referred to as helical states, reflecting the locking between an electron's spin and its momentum. The theoretical foundation of the quantum spin Hall effect was established independently by Kane and Mele [5, 41, 42] and by Bernevig, Hughes, and Zhang [43], who demonstrated that strong spin-orbit coupling can drive a two-dimensional system into a topologically non-trivial insulating phase.

In an effective one-dimensional description, a spinful system possesses four fundamental edge channels, forward and backward moving states for both spin-up and spin-down electrons. In the quantum spin Hall effect phase, these channels are spatially organized such that, for a given edge, a forward moving electron carries one spin projection while the backward moving electron carries the opposite spin. The remaining pair appears on the opposite edge, leading to a characteristic separation summarized schematically as  $4 = 2 + 2$  [44] (see Fig. 1.4). This spatial and spin separation distinguishes the quantum spin Hall effect from both ordinary one-dimensional conductors and the integer quantum Hall effect. A defining feature of the quantum spin Hall effect is the robustness of its edge transport. Although forward and backward movers coexist on the same edge, elastic backscattering is strongly suppressed in the presence of non-magnetic disorder. Any backscattering process necessarily involves a simultaneous reversal of both momentum and spin. However, as long as time-reversal symmetry is preserved, such processes are forbidden. Consequently, electrons propagate along the edges without dissipation, despite the absence of an external magnetic field. Unlike the quantum Hall effect, which is characterized by an integer Chern number, the quantum spin Hall effect is classified by a binary

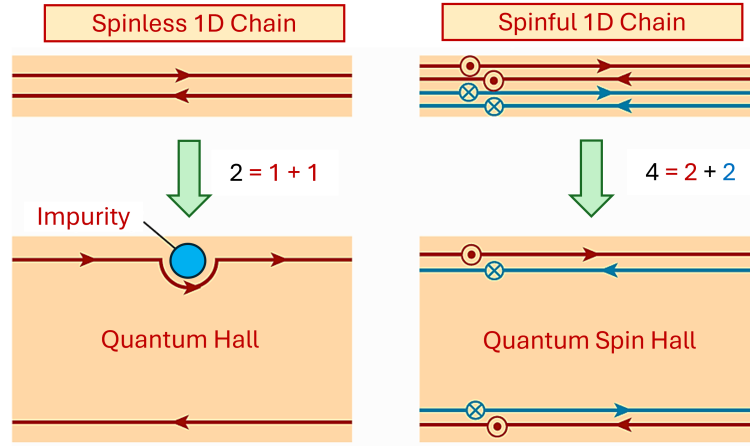


Figure 1.4: (a) In an effectively spinless one-dimensional system, transport involves a forward and a backward moving mode. In the quantum Hall regime, these two modes are spatially separated, with the forward moving state localized on one edge and the backward moving state on the opposite edge, as indicated schematically by the relation " $2 = 1 + 1$ ". These edge states are robust and can bypass impurities without backscattering. (b) In a spinful one-dimensional system, four transport channels are present. In the quantum spin Hall phase, these channels are arranged such that each edge hosts a pair of counter propagating modes with opposite spin orientations, while the corresponding pair appears on the opposite edge. This helical organization is illustrated by the relation " $4 = 2 + 2$ ".

topological invariant known as the  $\mathbb{Z}_2$  index. A non-trivial  $\mathbb{Z}_2$  invariant guarantees the presence of an odd number of helical edge state pairs, which is essential for the stability of the quantum spin Hall effect. If the number of such pairs were even, scattering between channels could occur without violating time-reversal symmetry, leading to dissipative transport. The quantum spin Hall effect represents a major conceptual extension of the quantum Hall paradigm, demonstrating that topologically protected edge transport can arise solely from spin-orbit coupling and time-reversal symmetry. By enabling dissipationless, spin resolved transport without magnetic fields, the quantum spin Hall effect provides a natural bridge between topology and spintronics. Furthermore, it forms the foundation for higher-dimensional topological phases, including three-dimensional topological insulators, and continues to play a central role in the development of spin-based quantum materials and devices.

## 1.7 Topology

The advent of quantum mechanics in the 1920s provided a robust framework for understanding the physical properties of matter at the atomic, molecular, and solid-state levels. Shortly thereafter, Bloch's work on metallic behavior and electrical resistance [45] laid the foundation for our understanding of solid-state materials. His model, which considers electrons moving within a periodic crystal potential, introduced the concept of electronic bands, which explains many of the physical properties we observe in everyday crystalline materials. However, Bloch's framework proved insufficient to explain phenomena observed in lower-dimensional systems at low temperatures.

To address these limitations, the mathematical concept of topology was introduced. Topology is concerned with the properties of geometric objects that are preserved under continuous deformations, such as stretching, twisting, crumpling, and bending, but not tearing or gluing. As developed by Thouless and Kosterlitz in the early 1970s, topology revealed that certain systems exhibit ordering robust against thermal fluctuations [46]. This ordering arises from the presence of topological defects, like vortices, which are topologically distinct and cannot be removed without fundamentally altering the system. A common analogy to visualize this distinction is the difference between a sphere and a doughnut. They are topologically distinct because of the number of holes; one would have to drill a hole into the sphere to make it topologically equivalent to the doughnut. As seen in Fig. 1.5, a mug with one hole can be converted to a donut using continuous transformations without drilling a hole. Therefore, they belong to the same topological class [47]. Generally, the objects belonging to same topological class can be continuously deformed into one another. This characteristic can be expressed through topological invariants, quantities that remain unchanged under these continuous transformations.

This concept of topologically distinct phases extends to solid-state systems, where the topology can be related to the electronic band structure of a crystal. The phase of the Bloch wave functions can give rise to different topological classifications in materials. A crucial quantity defining the topology of an electronic band structure is topologically protected, meaning it remains invariant unless the band gap closes. This topological invariant is a robust property of the band structure. Connecting two materials with different topologies necessitates a crossover state to bridge this topological disparity. Such a crossover state arises naturally from topological considerations and often leads to intriguing physical phenomena.



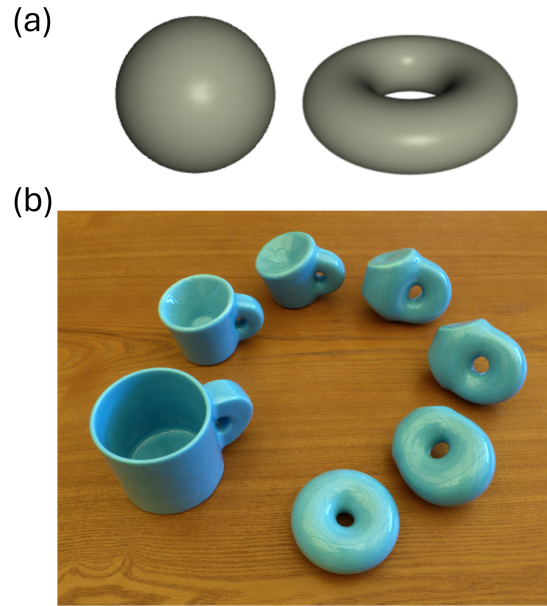


Figure 1.5: Topological transformations: (a) Discontinuous change from a sphere (genus ( $g$ ) = 0) to a torus ( $g$  = 1) by adding a hole. (b) Continuous deformation of a mug into a torus ( $g$  = 1), illustrating their topological equivalence.

## 1.8 Bulk boundary correspondence

A central insight of topological band theory is the principle known as the bulk boundary correspondence, which establishes a rigorous link between the topological properties of a material's bulk electronic structure and the appearance of conducting states at its boundaries. In systems described by gapped band structures, bulk phases can be classified by discrete topological invariants, such as the Chern number or  $\mathbb{Z}_2$  index. While these quantities characterize the interior of the material, their physical consequences are most strikingly revealed at edges or interfaces [43].

When two regions with distinct bulk topological invariants meet such as a topological phase adjoining a trivial insulator or vacuum, the system cannot evolve smoothly from one phase to the other without a fundamental change in its electronic structure. In particular, the bulk energy gap must close at the interface, since topological invariants are ill-defined in gapless regions. As a result, electronic states necessarily emerge at the boundary, with energies crossing the bulk gap (see for Figure 1.6 for visualization of these states). These states are therefore gapless and spatially confined near the interface, providing a direct manifestation of the underlying bulk topology.

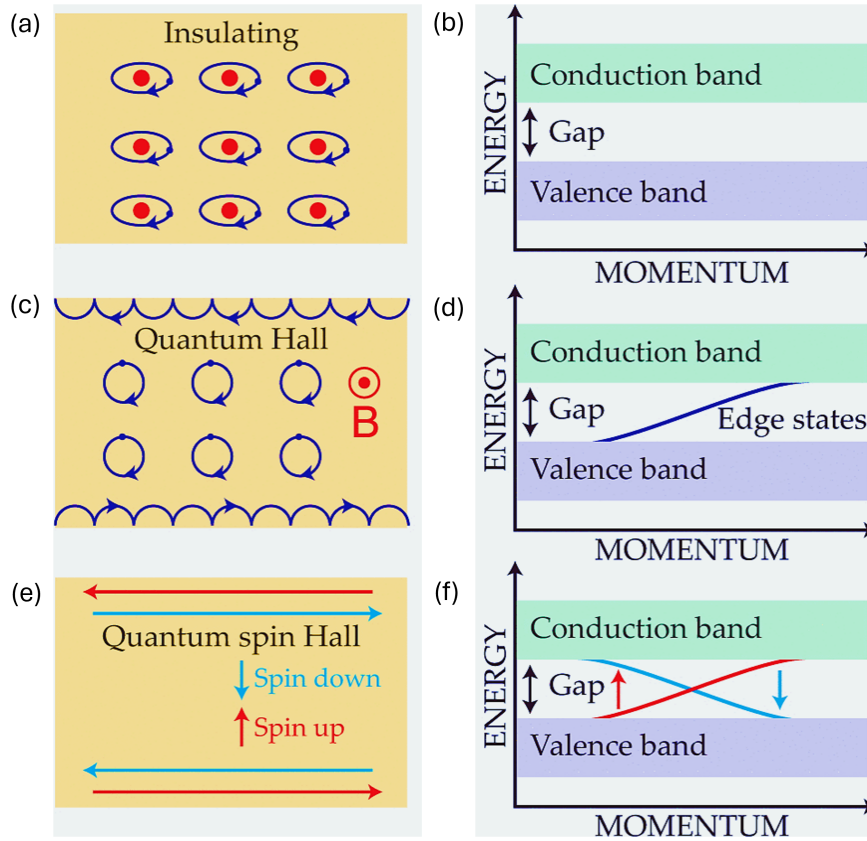


Figure 1.6: (a) Conventional insulators feature valence electrons tightly bound to atoms, resulting in a continuous energy gap across all momentum values. (b) In contrast, the quantum Hall effect, induced by a magnetic field, creates an energy gap and supports current-carrying edge states within that gap. (c) The quantum spin Hall system also exhibits a persistent bulk energy gap, but its edge states are unique due to counter-propagating currents carried by spin-up and spin-down electrons. These three states are topologically distinct, meaning a transition between them requires a significant perturbation capable of closing and reopening the bulk energy gap.

The integer quantum Hall effect offers a paradigmatic realization of this correspondence. Although the bulk of the system is insulating due to Landau level quantization, the boundary hosts conducting modes that propagate along the edge. These modes are chiral, meaning that their direction of motion is fixed by the magnetic field and the bulk Chern number. The absence of counter propagating states at a given edge suppresses elastic backscattering, rendering the edge transport exceptionally robust against disorder. This robustness is not accidental but follows directly from the non-trivial topology of the bulk quantum Hall state. More generally, the number and character of boundary modes are determined by changes in the bulk topological invariant across an interface. While microscopic details near the boundary can modify the

dispersion of edge states introducing curvature or additional crossings of the Fermi level, the net imbalance between right-moving and left-moving modes remains fixed. This imbalance is a topological quantity and cannot be altered unless the bulk gap closes. In this sense, boundary transport properties are protected by global features of the bulk band structure rather than by local symmetries alone.

The bulk boundary correspondence thus provides a unifying framework for understanding why topological phases, despite being defined through bulk quantities, exhibit their most distinctive experimental signatures at edges and surfaces. It explains the inevitable emergence of protected boundary states and highlights the deep connection between abstract topological classification and measurable electronic transport phenomena.

## 1.9 Topological Insulators

The identification of topological phases of matter has fundamentally reshaped our understanding of quantum materials. Established by Thouless, Kosterlitz, and Haldane demonstrated that phases of matter can be classified not only by symmetry and local order parameters, but also by global topological properties that remain invariant under continuous deformations of the system. These breakthroughs, which revealed entirely new mechanisms underlying phase transitions and electronic transport, were recognized by the award of the Nobel Prize in Physics in 2016 [48]. Beyond their profound conceptual importance, topological phases have opened new directions for material design, promising robust functionalities that are intrinsically protected against disorder and perturbations.

The central idea governing these systems is rooted in topology, a branch of mathematics as discussed earlier. In condensed matter physics, two quantum states are said to be topologically equivalent if their many-body wave functions can be continuously deformed into one another without closing the energy gap. For most conventional solids, the electronic wave function can be adiabatically connected to a collection of localized atomic orbitals, leading to a topologically trivial insulating phase often referred to as the atomic limit. In contrast, if such a deformation is impossible without a gap closing, the system is classified as topologically non-trivial. This distinction provides a natural framework for understanding why certain materials host robust boundary states despite being insulating in the bulk.

The quantum Hall effect represents the earliest and most striking realization of a topolog-

ically non-trivial electronic phase. Its discovery established that electronic transport can be governed by topological invariants, rather than microscopic material details, thereby initiating extensive research into topological quantum states. Subsequent advances generalized these ideas beyond strong magnetic fields, leading to the discovery of a broad family of topological phases, including the quantum spin Hall effect, quantum anomalous Hall effect, topological insulators, and topological semimetals, each exhibiting distinct yet related manifestations of band topology.

A major milestone in this progression was the theoretical prediction of the quantum spin Hall state by Kane and Mele in 2005 [5]. By analyzing the influence of intrinsic spin-orbit coupling on graphene, a two-dimensional honeycomb lattice of carbon atoms, they demonstrated that spin-orbit interactions can open a bulk energy gap while preserving time-reversal symmetry. Unlike ordinary band insulators, this gapped state possesses a non-trivial topological character arising from spin-dependent band inversion at the inequivalent  $K$  and  $K'$  points of the Brillouin zone. Importantly, the nature of this inversion is opposite for opposite spin channels, leading to a fundamentally new insulating phase. A direct consequence of this band

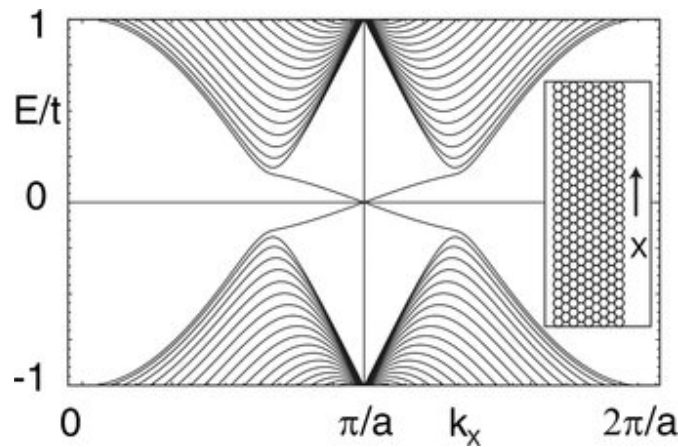


Figure 1.7: Electronic band structure of a graphene nanoribbon calculated along the longitudinal momentum direction  $k_x$  (schematic inset). The bulk bands exhibit an energy gap, within which spin-resolved edge states appear. These gap-crossing states are localized at the ribbon boundaries and correspond to oppositely propagating modes with opposite spin polarization. The presence of such edge states within the bulk gap is a hallmark of a non-trivial topological phase. The source of this Fig. is [5].

topology is the emergence of one-dimensional conducting edge states within the bulk energy gap. These edge modes consist of counter-propagating electrons with opposite spin orientations, forming helical channels rather than the chiral modes characteristic of the quantum Hall effect. Although electrons can propagate in both directions along a given edge, elastic backscat-

tering is strongly suppressed due to spin polarization and time-reversal symmetry. The paired edge states constitute Kramers doublets, which remain degenerate and protected against non-magnetic perturbations as long as time-reversal symmetry is preserved. When this symmetry is broken, for instance by applying a magnetic field, the protection is lifted and a gap can open in the edge-state spectrum.

The quantum spin Hall phase therefore represents a new type of insulating state that is distinguished from conventional insulators by its topological order rather than symmetry breaking. Recognizing this distinction, Kane and Mele subsequently introduced a topological invariant adapted to time-reversal symmetric systems, providing a rigorous theoretical foundation for classifying such phases [41]. This framework led naturally to the broader concept of topological insulators, a class of materials that are insulating in the bulk but support symmetry-protected conducting states at their boundaries (see Fig. 1.7).

From a practical perspective, the quantum spin Hall effect is particularly appealing because it enables dissipationless edge transport without the need for an external magnetic field. The one-dimensional nature of the edge channels leads to quantized conductance, making them attractive for applications in spin injection, spin detection, and low-power electronic devices. More broadly, the discovery of the quantum spin Hall state established time-reversal invariant topological insulators as a fertile platform for exploring robust quantum phenomena with potential relevance to future spintronic and quantum technologies.

### 1.9.1 2D Topological Insulators

The experimental observation of the quantum spin Hall effect in graphene is strongly limited by the very small magnitude of its intrinsic spin-orbit coupling. As a consequence, the predicted bulk energy gap is only a few mill-electron volts, which means that edge-dominated transport would be observable only at extremely low temperatures and in nearly defect-free samples. These stringent conditions make graphene an impractical platform for the experimental realization of robust quantum spin Hall states.

To overcome these limitations, alternative material systems with stronger spin-orbit coupling were proposed shortly after the theoretical work of Kane and Mele. A major breakthrough came with the prediction of the quantum spin Hall state in HgTe/CdTe quantum wells by Bernevig, Hughes, and Zhang [43]. In this heterostructure, a thin layer of HgTe is confined between two CdTe layers. CdTe behaves as a conventional semiconductor with a normal band

ordering and a large energy gap near the Brillouin zone center. In contrast, HgTe exhibits strong spin-orbit coupling, which reverses the usual ordering of conduction and valence bands at the  $\Gamma$  point.

When HgTe is grown as a quantum well, the reduced dimensionality lifts the degeneracy of the bulk bands and opens a finite energy gap. For quantum well thicknesses below a critical value, the band structure remains topologically trivial and no protected edge states appear. However, when the thickness exceeds this critical value, the inverted band ordering is restored, driving a topological phase transition. In this regime, the system supports helical edge states, where electrons with opposite spins propagate in opposite directions along the sample boundary. These edge states are protected by time-reversal symmetry and give rise to the quantum spin Hall effect. Experimental confirmation of this prediction established HgTe quantum wells as the first realized two-dimensional topological insulators [49]. In addition to HgTe-based systems, other material platforms have been identified as two-dimensional topological insulators. A notable example is the GaSb/InAs heterostructure, where the topological phase arises from an unusual band alignment rather than strong spin-orbit coupling alone [50]. In this system, the conduction band minimum of InAs lies below the valence band maximum of GaSb, resulting in an inverted band structure at the interface. This inversion enables the formation of topologically protected edge states, further demonstrating that two-dimensional topological insulating phases can emerge from different physical mechanisms.

### 1.9.2 $\mathbb{Z}_2$ classification of topological insulator

Topological phases protected by time-reversal symmetry constitute a distinct class of quantum matter that cannot be characterized within the integer Chern number framework underlying the quantum Hall effect. The origin of this distinction lies in the constraints imposed by time-reversal invariance, which require the Berry curvature to appear in pairs of opposite sign at momenta related by time reversal. As a consequence, the total Chern number of a time-reversal symmetric insulator must vanish, even when the band structure itself remains topologically non-trivial. This observation necessitates a classification scheme beyond integer-valued topological invariants. A concrete realization of a time-reversal invariant topological phase was introduced by Kane and Mele through a graphene-based model incorporating intrinsic spin-orbit coupling [5]. In this construction, spin-orbit interactions open a bulk energy gap without breaking time-reversal symmetry. The electronic bands naturally separate into spin-resolved sectors,

each characterized by a finite Chern number of opposite sign. While these contributions cancel in the total charge Hall response, the system supports a quantized spin Hall conductivity, giving rise to the quantum spin Hall phase [41]. This mechanism established a viable route to dissipationless spin transport and stimulated broad interest in applications ranging from spintronics [51] to thermoelectric and photovoltaic technologies [52].

Because time-reversal symmetry enforces a vanishing total Chern number, such insulators are instead classified by a discrete topological index known as the  $\mathbb{Z}_2$  invariant. This invariant distinguishes between topologically trivial and non-trivial insulating phases and captures the robustness of their boundary states. The defining symmetry condition for time-reversal invariant systems is

$$\mathcal{T}H(\mathbf{k})\mathcal{T}^{-1} = H(-\mathbf{k}), \quad (1.21)$$

where  $\mathcal{T} = i\sigma_y K$  denotes the time-reversal operator,  $\sigma_y$  is a Pauli matrix, and  $K$  represents complex conjugation. A direct consequence of this symmetry is Kramers degeneracy: for every eigenstate at momentum  $\mathbf{k}$ , there exists a degenerate partner at  $-\mathbf{k}$  with opposite spin.

A central role in this classification is played by time-reversal invariant momenta (TRIM), which are special points in the Brillouin zone satisfying

$$\mathbf{k}_i = -\mathbf{k}_i + \mathbf{G}, \quad (1.22)$$

where  $\mathbf{G}$  is a reciprocal lattice vector. At these points, Bloch states must form degenerate Kramers pairs. The global topology of the band structure is encoded in how the occupied bands evolve and connect between these symmetry-protected momenta.

The physical implications of the  $\mathbb{Z}_2$  invariant become particularly transparent through the bulk-boundary correspondence. In two-dimensional time-reversal invariant insulators, a non-trivial phase is characterized by an odd number of Kramers pairs crossing the Fermi energy between any two TRIM in the edge Brillouin zone, whereas a trivial insulator exhibits an even number of such crossings. This parity distinction is robust against continuous deformations of the Hamiltonian that preserve the bulk energy gap and time-reversal symmetry.

Additional insight into the stability of boundary states is obtained by considering the combined role of time-reversal and inversion symmetries. In the bulk of a three-dimensional crystal, time-reversal symmetry enforces

$$E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \downarrow), \quad (1.23)$$



while inversion symmetry implies

$$E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \uparrow). \quad (1.24)$$

When both symmetries are present, the energy bands become spin degenerate at the same crystal momentum,

$$E(\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow). \quad (1.25)$$

Such degeneracies occur precisely at TRIM points. On a two-dimensional surface Brillouin zone, four TRIM typically appear at  $(0, 0)$ ,  $(\pi, 0)$ ,  $(0, \pi)$ , and  $(\pi, \pi)$ . When surface bands close the bulk gap, the resulting crossings between conduction and valence bands necessarily occur at these points. As long as time-reversal symmetry is preserved, these crossings are protected against non-magnetic perturbations, whereas breaking time-reversal symmetry allows a gap to open.

The distinction between trivial and topological insulating phases is formalized by the  $\mathbb{Z}_2$  index

$$\nu = N_k \bmod 2, \quad (1.26)$$

where  $N_k$  denotes the number of Kramers pairs of edge or surface states crossing the Fermi energy. An even value of  $N_k$  corresponds to a trivial insulator ( $\nu = 0$ ), while an odd value identifies a topological insulator ( $\nu = 1$ ). Since the invariant admits only two possible values, it is naturally described by the  $\mathbb{Z}_2$  group, the simplest non-trivial topological classification. This invariant lies at the heart of modern topological insulator theory and provides a unified explanation for the exceptional stability of their boundary states.

### 1.9.3 3D Topological insulators

The extension of topological band theory from two to three dimensions led to the identification of a new class of quantum materials known as three-dimensional topological insulators. Unlike their two-dimensional counterparts, these systems are insulating throughout the bulk while supporting metallic electronic states confined to their two-dimensional surfaces. The existence of such surface states has been confirmed experimentally through angle-resolved photoemission spectroscopy (ARPES) and transport measurements in several material systems [53, 54, 55]. A defining feature of the surface electronic structure of three-dimensional topological insulators is the presence of Dirac-like states with a linear dispersion relation. While the energy momentum relationship resembles that of graphene, an important distinction lies in the absence of spin



degeneracy: each surface Dirac cone is non-degenerate and exhibits spin-momentum locking, such that the electron spin orientation is rigidly tied to its crystal momentum [53, 54]. As a consequence, the surface hosts a single Dirac cone rather than multiple spin-degenerate cones. The emergence of the three-dimensional topological insulating phase is closely linked to strong spin-orbit coupling, which profoundly alters the ordering of electronic bands. Materials composed of heavy elements are therefore natural candidates, as their large atomic numbers give rise to strong relativistic effects. For a topological phase to develop, the spin-orbit coupling energy scale must be comparable to or larger than the bulk band gap, enabling band inversion at high-symmetry points in the Brillouin zone.

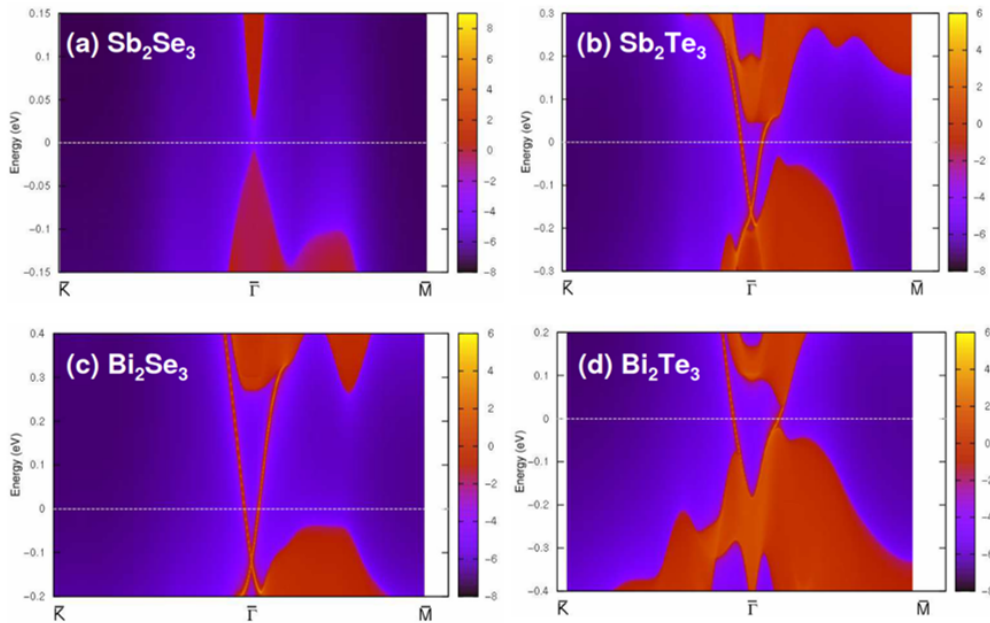


Figure 1.8: First-principles derived surface electronic dispersions along the (111) surface for (a)  $\text{Sb}_2\text{Se}_3$ , (b)  $\text{Sb}_2\text{Te}_3$ , (c)  $\text{Bi}_2\text{Se}_3$ , and (d)  $\text{Bi}_2\text{Te}_3$ . The projected bulk continuum is shown in red, whereas the bulk band gap is highlighted in blue. The source of this Figure is [6].

The first material system in which three-dimensional topological insulating behavior was experimentally established was the  $\text{Bi}_x\text{Sb}_{1-x}$  alloy [53, 54, 55]. Shortly thereafter, a simpler and more experimentally accessible family of compounds was identified, consisting of  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ , and  $\text{Sb}_2\text{Te}_3$ , all crystallizing in the rhombohedral  $R\bar{3}m$  space group [56, 57, 58]. Compared to  $\text{Bi}_x\text{Sb}_{1-x}$ , these materials possess larger bulk band gaps and cleaner surface electronic structures, making them particularly attractive for both fundamental studies and potential applications. Among these compounds,  $\text{Bi}_2\text{Se}_3$  stands out due to its relatively large bulk band gap of approximately 0.3 eV, which significantly exceeds thermal energies at room tempera-

ture. First-principles calculations indicate that the topological character of  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ , and  $\text{Sb}_2\text{Te}_3$  originates from spin-orbit coupling driven band inversion at the  $\Gamma$  point [53]. In contrast,  $\text{Sb}_2\text{Se}_3$  does not undergo such an inversion owing to the weaker spin-orbit coupling of antimony and therefore remains topologically trivial. The calculated surface band structures for these materials are shown in Fig. 1.8, where gapless surface states bridging the bulk band gap are clearly visible in the topologically non-trivial compounds.

On the surface of a three-dimensional topological insulator, the Fermi surface typically consists of a single contour enclosing the Dirac point, with the electron spin rotating tangentially around it. This helical spin texture suppresses certain scattering processes and leads to unusual transport phenomena. While surface disorder and non-magnetic impurities can induce scattering, the metallic surface states cannot be removed without closing the bulk energy gap or breaking time-reversal symmetry. This protection reflects the topological origin of the surface states and distinguishes them from ordinary surface states arising from band bending or structural defects. It is important to note that, unlike one-dimensional edge channels in two-dimensional topological insulators, surface states in three-dimensional systems do not completely forbid backscattering. Electrons with the same helical chirality may still scatter in the presence of disorder. Nevertheless, the surface remains metallic as long as the underlying bulk topology is preserved. This robustness, together with spin-momentum locking, positions three-dimensional topological insulators as promising platforms for spin-based electronics and for exploring novel quantum phenomena at surfaces and interfaces. From a broader perspective, three-dimensional topological insulators redefine the traditional classification of solids. Rather than being distinguished solely by whether they conduct electricity, these materials are characterized by global properties of their electronic wave functions. Their insulating bulk and symmetry-protected metallic surfaces exemplify how topology governs observable electronic behavior, establishing three-dimensional topological insulators as a cornerstone of modern condensed matter physics.

## 1.10 A short overview

- **Chapter 2 :** This chapter describes the theoretical methods used in this work. It presents a brief overview of first-principles based density functional theory (DFT) along with the tight-binding formalism and the construction of maximally localized Wannier functions for effective low-energy modeling.

- **Chapter 3** : The search for two-dimensional materials with exotic valley-dependent properties has attracted rapid attention as they are fundamentally intriguing and practically appealing for nanoscale device applications. Here, using first-principles calculations, we report the identification of promising intrinsic valley-related switchable Hall effects in  $\text{Cr}_2\text{CSF}$ . With a high out-of-plane magnetic anisotropy,  $\text{Cr}_2\text{CSF}$  is a ferrovalley semiconductor with spontaneously polarized valleys having a valley polarization of 27.1 meV in the conduction band. This facilitates the observation of an intrinsic anomalous valley Hall (AVH) effect that is manipulated under an in-plane electric field. The underlying physics of spontaneous valley polarization is also discussed based on the SOC Hamiltonian model. Furthermore, on application of unidirectional compressive strain,  $\text{Cr}_2\text{CSF}$  is transitioned from the AVH phase to a long-sought quasi-half valley metal state. Here, only the electrons are valley polarized such that holes and electrons carriers are separated under the in-plane electric field. Our work enriches materials with the valley-related Hall effects and provides a platform for interplay among valleytronics and spintronics.
- **Chapter 4** : The antiferromagnetic (AFM) materials are distinguished by zero net magnetic moment, high resistance to external magnetic disturbances, and ultrafast dynamic responses. For advancing AFM materials in spintronic and valleytronic applications, achieving spontaneous valley polarization and the anomalous valley Hall effect (AVHE) is pivotal. We predict an A-type AFM monolayer  $\text{Fe}_2\text{C}(\text{OH})_2$ , which shows a significant spontaneous valley polarization of 157 meV. In  $\text{Fe}_2\text{C}(\text{OH})_2$ , spatial inversion symmetry ( $P$ ) and time-reversal symmetry ( $T$ ) are individually broken, yet the combined  $PT$  symmetry is preserved. This symmetry conservation leads to spin degeneracy, resulting in zero Berry curvature in the momentum space and absence of AVHE. However, a layer-locked hidden Berry curvature is produced, leading to the observation of the valley layer-spin Hall effect. Further, an external out-of-plane electric field can induce spin splitting by introducing layer-dependent electrostatic potential, enabling the layer-locked AVHE. Additionally, the introduction of a built-in electric field caused by the Janus structure also induces spin splitting in monolayer  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  due to the electric-potential-difference-AFM mechanism. The high out-of-plane magnetic anisotropy and realization of AVHE, offer promising opportunities for next-generation spintronic technologies.
- **Chapter 5** : This study proposes a multiferroic heterostructure combining monolayer  $\text{VSSe}$ ,

a ferrovalley material, with 2D  $\text{Al}_2\text{S}_3$ , a ferroelectric substrate, to achieve electrically tunable valley polarization for next-generation valleytronic devices. Traditionally, tuning valley polarization relies on magnetic fields or magnetic proximity effects. However, these approaches are energy-intensive and less suitable for practical, low-power devices. This motivates the search for an alternative method that offers reversible, nonvolatile, and energy-efficient control over valley polarization. Ferroelectric  $\text{Al}_2\text{S}_3$  possesses two stable out-of-plane polarization states ( $P_{up}$  and  $P_{dn}$ ) that can be switched by an external electric field and maintained without continuous power. In the  $P_{up}$  state, valley polarization ( $\Delta E_c = 35$  meV) appears in the conduction band minimum (CBM), while in the  $P_{dn}$  state, significant valley polarization ( $\Delta E_v = 77$  meV) emerges in the valence band maximum (VBM). Berry curvature maps reveal opposite signs at  $+K$  and  $-K$  valleys, and flipping the substrate's polarization reverses the Berry curvature sign, effectively switching the AVH effect. A prototype valleytronic memory device based on this heterostructure is proposed. In the  $P_{up}$  state, spin-up electrons accumulate at one side of the VSSe monolayer, generating a measurable transverse Hall voltage corresponding to the “0” memory state. When the polarization switches to  $P_{dn}$ , spin-up holes dominate, leading to a distinct Hall voltage that represents the “1” state. The electrically switchable AVH effect demonstrates a promising strategy for developing low-power, high-efficiency valleytronic memory and logic devices.

- **Chapter 6 :** In this chapter, we have explored 3D topological insulators. Topological Insulators (TIs) are unique materials where insulating bulk hosts linearly dispersing surface states protected by the Time-Reversal Symmetry. These states lead to dissipationless current flow, which makes this class of materials highly promising for spintronic applications. Here, we predict TIs by employing state-of-the-art first-principles based methodologies, viz., Density Functional Theory (DFT) and many-body perturbation theory ( $G_0W_0$ ) combined with Spin-Orbit Coupling (SOC) effects. For this, we take a well-known 3D TI,  $\text{TlBiSe}_2$  and perform complete substitution with suitable materials at different sites to check if the obtained isostructural materials exhibit topological properties. Subsequently, we scan these materials based on SOC-induced parity inversion at Time-Reversal Invariant Momenta. Later, to confirm the topological nature of selected materials, we plot their surface states along with calculation of  $Z_2$  invariants. Our results show that  $\text{GaBiSe}_2$  is a strong Topological Insulator, besides, we report six weak

Topological Insulators, viz.,  $\text{PbBiSe}_2$ ,  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$  and  $\text{PbSbSe}_2$ . We have further verified that all the reported TIs are dynamically stable, showing all real phonon modes of vibration.

- **Chapter 7 :** The centrosymmetric halide perovskites undergo a continuous phase transition from trivial to topological insulator at the critical value of strain. Contrarily, in non-centrosymmetric halide perovskites, this phase transition is discontinuous. The noncentrosymmetry does not stabilize the gapless state, causing a discontinuity in the bandgap. We have employed density functional theory and Slater-Koster formalism-based tight-binding Hamiltonian studies to understand the evolution of band topology under the compressive strain. Our study shows that both cubic and pseudocubic  $\text{FAPbI}_3$  undergo a Pb  $s$ - $p$  band inversion at  $\gamma (V/V_0) = 0.76$  and  $0.73$ , respectively. The pseudocubic structure shows two conducting states around  $\bar{M}$ , unlike the cubic counterpart. The Pb-Pb second nearest neighbor interactions determine this topological phase transition. Alongside, we have modeled mixed cation halide perovskites  $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$  ( $x = 0.25, 0.50$  and  $0.75$ ) to study their topological properties. In addition, structural stability of different strained configurations strengthens the experimental relevance.

- **Chapter 8 : Conclusion**

This chapter concludes the thesis and present some future directions to be explored.

## Theoretical methodology

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### 2.1 Computer simulation

Computational simulation has become an important pillar of modern scientific inquiry, extending its reach across a vast spectrum of disciplines. It serves as a bridge between the theoretical models and is often expressed through complex mathematical equations, and the real-world experiments. By exploiting the power of computers, simulations create virtual representations of complex systems, enabling researchers to probe their behavior in ways that would be impractical, dangerous, or even impossible through traditional experimental methods. This virtual laboratory allows us the exploration of a multitude of scenarios, the testing of hypotheses under controlled conditions, and the generation of insights that illuminate the underlying mechanisms driving system dynamics. The credibility of a computational simulation relies on its ability to accurately reflect the real world phenomena. This is achieved through a rigorous process of validation, where simulation predictions are compared against empirical observations. Discrepancies between simulated and observed behavior cause iterative refinements of the model, leading to accurate and reliable representations of the system (Figure 2.1).

Computational simulations have a wide-ranging impact across both fundamental and applied sciences. They are extensively used in disciplines such as physics, chemistry, and biology, as well as in applied areas including engineering, economics, and healthcare. In physics, simulations enable the study of systems across vastly different scales, from subatomic particle interactions to the large-scale evolution of galaxies, and they play a key role in understanding the behavior of complex materials. In chemistry, computational methods assist in analyzing chemical reactions, designing new molecules, and predicting material properties. Biological systems, which involve highly complex and interconnected processes, also benefit significantly from simulations, allowing investigations into phenomena such as protein folding, cellular dy-

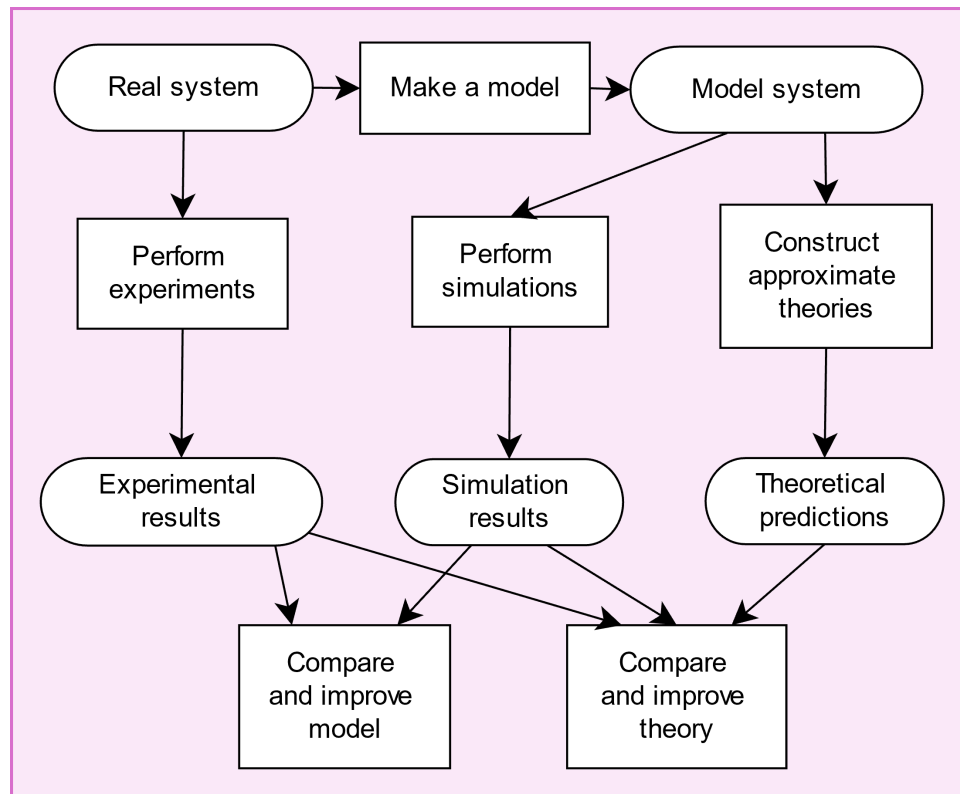


Figure 2.1: Steps involved in creating a computer model and interaction between theory, simulation, and experiment.

namics, and ecosystem behavior. Furthermore, simulations play a crucial role in engineering, enabling the design and optimization of everything from aircraft and bridges to microchips and medical devices. In economics and healthcare, simulations can model market behavior, predict the spread of diseases, and evaluate the effectiveness of different treatment strategies. These applications highlight the versatility and practical importance of computational modeling in addressing real-world problems.

Advances in computing power and the development of efficient numerical algorithms have made computational simulations an essential component of modern research. High-performance parallel computing systems now allow scientists to study problems across multiple length and time scales, from atomic-scale processes to macroscopic phenomena. This multiscale capability enables the investigation of complex systems over time spans ranging from picoseconds to years and over length scales extending from individual atoms to bulk materials. In materials science, for instance, simulations can predict material properties by explicitly modeling atomic interactions. Different computational approaches are employed depending on the scale of interest. Atomistic methods, such as Molecular Dynamics and Monte Carlo simulations, describe behavior at the atomic level, while mesoscale techniques, including Phase Field and Dislocation

Dynamics methods, capture microstructural evolution. At larger scales, continuum-based approaches such as Finite Element and Finite Difference methods are used to model macroscopic behavior (see Fig. 2.2). These methods are complementary, with insights from one scale informing simulations at others. By enabling the study of systems that are difficult or impossible to access experimentally, computational simulations play a crucial role in advancing scientific understanding and supporting technological innovation.

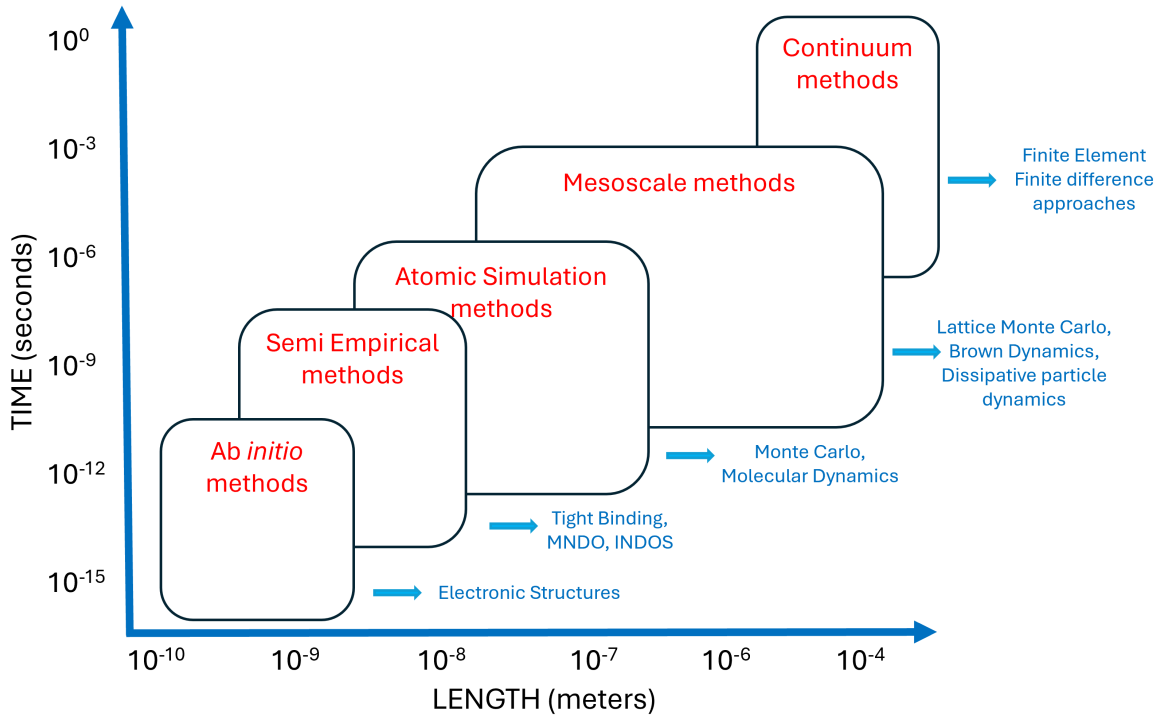


Figure 2.2: Multi-scale simulation in various length and time scales.

In this thesis, we discuss the frameworks corroborating the atomistic simulations. The first-principles based approaches have been employed to understand spintronic and valleytronic properties of various materials. The layout of the present chapter initiates with the idea of first-principles calculation. Subsequently, the density functional theory (DFT) analysis for many-electron quantum systems is discussed.

## 2.2 First-principles calculation

First-principles methods are rooted in the primary interactions between atomic nuclei and their surrounding electrons. By utilizing the fundamental equations that govern these particles, researchers can calculate a wide variety of properties inherent to condensed matter. This predic-



tive capability allows for the characterization of material behavior across various experimental environments, offering a theoretical framework to solve complex problems in materials science. This chapter outlines the conceptual foundations and the specific electronic structure methodologies utilized throughout this research. Most matter exists in a condensed state, where energy levels are sufficiently low to allow for the formation of stable atomic or molecular structures, typically as solids or liquids. The intrinsic properties of these systems, whether naturally occurring or synthetic are dictated by the interplay between positively charged nuclei and negatively charged electrons. Because macroscopic phenomena and chemical bonding emerge directly from these microscopic interactions, an accurate model of these forces should, in theory, replicate all observed physical behaviors.

Interestingly, the underlying physics of these constituents is well-understood and governed by the principles of non-relativistic quantum mechanics. The challenge, therefore, is not a lack of physical understanding but the sheer numerical magnitude of the "many-body problem." The famous scientist, Paul Dirac, wrote *"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."*

Therefore, to deal with many-body problem, the development of accurate and efficient theoretical methods and computational techniques is the focus of ongoing research in this realm.

## 2.3 Introduction to theoretical framework

Computational modeling of many-electron systems faces many challenges. While the Schrödinger equation forms the basis for understanding these systems, its analytical solution is only possible for a very few simple cases. For systems with more than a few electrons, numerical solutions are become computationally impossible due to the limitations of computing resources. A common strategy in such cases is to approximate the complex problem with a simple and solvable problem, i.e., treating the difference as a perturbation.

Approximations are therefore inherent in the quantitative calculations of many-electron systems. The Born-Oppenheimer approximation [59] is a the first step. It involves decoupling the motion of the much heavier nuclei from the electrons. This simplification reduces the dimen-

sionality of the problem by expressing the total wavefunction as a product of electronic and nuclear wavefunctions. However, the electron-electron interaction still poses a significant challenge.

Early attempts at solving the many-electron problem focused on particle models. Hartree's method [60, 61] treated each electron independently, moving in an average potential created by all other electrons and the nuclei. This approach, while foundational, assumed a symmetric wavefunction, which is inconsistent with the fermionic nature of electrons and the Pauli exclusion principle.

Fock addressed this limitation by introducing antisymmetry into the wavefunction using Slater determinants [62]. This modification, while satisfying the Pauli's principle, introduced the concept of electron exchange and increased the complexity of the calculations. The resulting Hartree-Fock method, which finds the best single-determinant wavefunction, is reasonably accurate for geometries but struggles to capture electron correlation effects, which are essential for describing many chemical and physical properties.

This computational bottleneck has motivated the development of practical independent-particle approaches that effectively incorporate interaction and correlation effects. Density functional theory (DFT) [63] offers such an approach, providing an exact theory for many-body systems in an external potential. DFT postulates that all properties, including the total energy, can be expressed as functionals of the electron density, with the ground state density minimizing the energy.

Kohn and Sham [64] further developed DFT by demonstrating that the exact ground state density can be represented by a non-interacting auxiliary system. The Kohn-Sham method uses an auxiliary Hamiltonian with a kinetic energy term and an effective local potential that approximates exchange and correlation effects. This method has become a cornerstone of computational materials science.

While DFT offers a good balance between accuracy and computational cost, its results are strictly valid only at 0 K. To incorporate environmental effects like temperature and pressure, ab initio atomistic thermodynamics [65, 66, 67, 68] is employed. This approach calculates the free energy of formation to determine the equilibrium compositions and structures under specific external conditions.

## 2.4 Wavefunction

In quantum mechanics, the state of a system can be defined by the wavefunction,  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_I, \dots)$ , where  $\mathbf{r}_i$  is the position of  $i^{\text{th}}$  electron and  $\mathbf{R}_I$  is the position of  $I^{\text{th}}$  nucleus. If the wave function of a system is known at an instant, corresponding position, momentum, kinetic energy, etc. can also be determined at that instant. Necessary conditions for the wavefunction to be physically acceptable are:

1. Continuous everywhere.
2. Derivatives should exist and be continuous everywhere.
3. Square integrable.
4. Vanish at infinity.
5. Expectation value of any power of position and momentum should be finite.

Once we have the wavefunction ( $\Psi$ ) for a given state of the system, we can calculate the expectation value of any physical quantity ( $E$ ) having an operator. The eigenvalues of the observables has to be a real number.

$$E = \frac{\int \int \dots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \hat{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}{\int \int \dots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N} \quad (2.1)$$

It can be written in more convenient way using Dirac *bra* and *ket* notation:

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

If the wavefunction is normalized, it satisfies the condition

$$\langle \Psi | \Psi \rangle = 1. \quad (2.3)$$

Although the wavefunction  $\Psi$  itself has no direct physical interpretation, its modulus squared,  $|\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$ , represents the joint probability density of finding electron 1 at position  $\mathbf{r}_1$ , electron 2 at  $\mathbf{r}_2$ , and so forth. For a single-electron system, the quantity  $|\Psi(\mathbf{r})|^2 d\mathbf{r}$  gives the probability of locating the electron within an infinitesimal volume  $d\mathbf{r}$  around position  $\mathbf{r}$ . Normalization of the wavefunction ensures that the total probability of finding the electron(s) anywhere in space is unity, i.e., the integral of the probability density over all spatial coordinates equals one.

$$\int \Psi(\mathbf{r})^* \Psi(\mathbf{r}) d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi(\mathbf{r})^* \Psi(\mathbf{r}) r^2 \sin\theta dr d\theta d\phi = 1 \quad (2.4)$$

## 2.5 Time-independent many-body Schrödinger equation

The wavefunction of a quantum system is governed by Schrödinger equation (linear differential equation). For many body systems, the physical or chemical properties can be determined at microscopic level by solving this time independent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_I, \dots) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_I, \dots) \quad (2.5)$$

here,  $\hat{H}$  is the Hamiltonian operator which represents the total energy (kinetic and potential) of the system. For the determination of total energy ( $E$ ) of the system, one needs to construct its Hamiltonian ( $\hat{H}$ ) that can be expressed in the atomic units ( $\hbar = m_e = e = 1$ ) as:

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_I \frac{1}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.6)$$

where  $\mathbf{r}_i$  and  $\mathbf{R}_I$  are the positions of the  $i^{\text{th}}$  electron and the  $I^{\text{th}}$  nucleus, respectively.  $Z_I$  is the atomic number of the  $I$ -th atom, and  $\nabla_i^2$  is the Laplacian operator.  $|\mathbf{r}_i - \mathbf{R}_I|$  represents the distance between the  $I^{\text{th}}$  nucleus and the  $i^{\text{th}}$  electron,  $|\mathbf{r}_i - \mathbf{r}_j|$  is the distance between the  $i^{\text{th}}$  and  $j^{\text{th}}$  electrons, and  $|\mathbf{R}_I - \mathbf{R}_J|$  is the distance between the  $I^{\text{th}}$  and  $J^{\text{th}}$  nuclei.

In this equation, the first and fourth terms represent the kinetic energies of the electrons and nuclei, respectively. The second term describes the potential energy due to Coulomb attraction between the electrons and nuclei. The third and fifth terms represent the potential energies due to Coulomb repulsion between electrons and between nuclei, respectively.

In Cartesian coordinates, the interparticle distances are:

$$|\mathbf{r}_i - \mathbf{r}_j| = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

$$|\mathbf{r}_i - \mathbf{R}_I| = \sqrt{(x_i - X_I)^2 + (y_i - Y_I)^2 + (z_i - Z_I)^2}$$

We can write the Hamiltonian in simplified form as:

$$\hat{H} = \hat{T}_e + \hat{V}_{ext} + \hat{U}_{ee} + \hat{T}_{nucl} + \hat{U}_{nucl} \quad (2.7)$$

where,

$\hat{T}_e$  is the total kinetic energy of electrons.

$\hat{V}_{ext}$  is the external potential due to the Coulomb interaction between electrons and nuclei.

$\hat{U}_{ee}$  is electrostatic repulsion between the electrons.

$\hat{T}_{nucl}$  is the total kinetic energy of the nuclei.

$\hat{U}_{nuc}$  is the potential energy due to interaction among nuclei.

As the system size increases, the number of variables become large, and solving the Schrödinger equation becomes impractical. Much effort has been made to find practical approximations to reduce the complexity of the Schrödinger equation. The Born Oppenheimer approximation, which considers the dynamics of electrons and nuclei, has been a revolutionary simplification.

## 2.6 Born-Oppenheimer approximation

The Born-Oppenheimer approximation is a central idea that simplifies the description of many-body systems by separating electronic and nuclear motions in quantum mechanics. The physical basis of this approximation lies in the large mass difference between nuclei and electrons. Nuclear masses  $M_I$  are much larger than the electron mass  $m_e$ ; for example, a proton is approximately 1836 times heavier than an electron. Because of this disparity, nuclei move much more slowly than electrons when both possess comparable kinetic energies. From a dynamical perspective, this suggests that electrons exist in a state of constant adaptation; they respond almost instantaneously to any change in nuclear coordinates. Because the electronic cloud reaches its ground-state configuration at a timescale far shorter than that of nuclear displacement, the electrons can be viewed as moving within a field generated by effectively stationary nuclei. This "adiabatic" assumption allows the electronic wavefunction to depend only parametrically on the nuclear positions, thereby making it easier to solve Schrödinger equation.

Mathematically, this separation leads to the following wavefunction decomposition:

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

This approximation enables the separation of the total Hamiltonian into electronic ( $\hat{H}_{el}$ ) and nuclear ( $\hat{H}_{nuc}$ ) components, facilitating more efficient computational solutions. The nuclear Hamiltonian is expressed as:

$$\hat{H}_{nuc} = \hat{T}_{nuc} + \hat{U}_{nuc}\tag{2.9}$$

where  $\hat{T}_{nuc}$  represents the kinetic energy of the nuclei and  $\hat{U}_{nuc}$  describes the electrostatic ion-ion interactions, which can be computed using the Ewald summation method [69]. Given the large nuclear mass, the kinetic energy term is often negligible in first-order approximations.

The electronic Hamiltonian, governing electron dynamics, is given by:

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ext} + \hat{U}_{ee} \quad (2.10)$$

where  $\hat{T}_e$  is the kinetic energy of electrons,  $\hat{V}_{ext}$  is the external potential due to nuclei, and  $\hat{U}_{ee}$  accounts for electron-electron interactions. In atomic units,  $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ . The kinetic energy operator for the electrons  $\hat{T}_e$  is given as:

$$\hat{T}_e = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 \quad (2.11)$$

The potential  $\hat{V}_{ext}$  acting on the electrons due to the nuclei is given as:

$$\hat{V}_{ext} = \sum_{i=1}^N \sum_{I=1}^M V_I(|\mathbf{r}_i - \mathbf{R}_I|) \quad (2.12)$$

The electron-electron interaction  $\hat{U}_{ee}$  is given by:

$$\hat{U}_{ee} = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.13)$$

The Hamiltonian can be rewritten as:

$$\hat{H}_{el} = \sum_{i=1}^N \hat{h}_i + \hat{U}_{ee} \quad (2.14)$$

where  $\hat{h}_i$  depends only on the coordinates of the  $i^{\text{th}}$  electron. The Hamiltonian for the  $i^{\text{th}}$  electron, can be expressed as:

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 + \hat{v}_i \quad (2.15)$$

which depends only on the position  $\mathbf{r}_i$  of the  $i^{\text{th}}$  electron. However, the electron-electron interaction term  $\hat{U}_{ee}$  involves pairs of electrons and depends on their relative positions. Due to the complexity of  $\hat{U}_{ee}$ , it is not possible to apply the method of separation of variables to decouple the equation in the second-order differential Schrödinger equation. The solution to the Schrödinger equation for the electronic Hamiltonian, given by

$$\hat{H}_e \Psi_e(\mathbf{r}_e, \Theta_e) = E_e \Psi_e(\mathbf{r}_e, \Theta_e) \quad (2.16)$$

represents the behavior of electrons under the Born-Oppenheimer approximation [59]. This approximation successfully reduces the complexity of the original problem.

However, the Born-Oppenheimer approximation is not universally valid. It can fail when there are multiple potential energy surfaces that are close in energy or even cross each other, leading to non-adiabatic transitions. Despite these limitations, the Born-Oppenheimer approximation remains an effective approach in many cases.

Nonetheless, solving the above equation still presents significant challenges due to the many-body nature of electron-electron interactions, which introduce quantum correlations between electrons. Since the motion of electrons is interdependent, it is crucial to consider the instantaneous positions of all electrons. This necessitates the treatment of  $3N$  variables for an  $N$ -electron system, making it computationally expensive. To address this, several approximation methods have been developed, which are discussed in subsequent sections.

## 2.7 The Hartree approximation

In 1984, Hartree introduced an effective method to obtain one-electron wavefunction [60, 61]. To solve the Schrödinger equation efficiently, the wavefunction variables must be separable, meaning that each variable should depend only on the coordinates of an individual electron. To achieve this, an approximate Hamiltonian is constructed, where the electron-electron interactions are treated in an averaged manner. By solving the corresponding Schrödinger equation, one can obtain the exact one-electron eigenfunctions of this approximate Hamiltonian. This approach forms the basis of Hartree approximation, in which the many-electron wavefunction  $\Psi$  is represented as a product of single-electron wavefunctions ( $\phi_i(\mathbf{r}_i)$ ):

$$\Psi_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N} = \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \dots \phi_N(\mathbf{r}_N) \quad (2.17)$$

The densities corresponding to each electron can be found as:

$$\rho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2 \quad (2.18)$$

The total density of the electrons in the system is given as:

$$\rho_{total}(\mathbf{r}) = \sum_{i=1}^N \rho_i(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad (2.19)$$

However, to express the density that the  $k^{\text{th}}$  electron interacts with, its own contribution needs to be excluded from the total density.

$$\rho^k(\mathbf{r}) = \rho_{total}(\mathbf{r}) - \rho_k(\mathbf{r}) = \left( \sum_{i=1}^N \rho_i(\mathbf{r}) - |\phi_k(\mathbf{r})|^2 \right) = \sum_{i=1, i \neq k}^N |\phi_i(\mathbf{r})|^2 \quad (2.20)$$

Further, to evaluate the interaction of a given electron located at a point  $\mathbf{r}$ , with the electron density of rest of the electrons:

$$\hat{g}_k(\mathbf{r}) = \int \rho^k(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.21)$$

Therefore, using this assumption, we write:

$$\hat{U}_{ee} \approx \sum_{i=1}^N \hat{g}_i(\mathbf{r}) \quad (2.22)$$

Now, all the terms contained by  $\hat{H}_{el}$  are one-electron operators:

$$\hat{H}_{el} \approx \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 + \hat{v}_i + \hat{g}_i(\mathbf{r}) \right) \quad (2.23)$$

and the Schrödinger equation for many electron system can be resolved into  $N$  independent one- electron equations:

$$\left( -\frac{1}{2} \nabla_i^2 + \hat{v}_i + \hat{g}_i(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (2.24)$$

$\epsilon_i$  is the energy of the  $i^{\text{th}}$  electron. We begin the iterative process with an initial guess for these orbitals, often using hydrogen-atom orbitals,  $\phi_i$ . These initial orbitals are crucial, as they determine the Hartree potential,  $g_i$ . Solving all  $N$  single-particle Schrödinger equations produces a new set of  $\epsilon'_i$  and corresponding  $\phi'_i$ . We assume these new orbitals are an improvement over the initial guess. In the subsequent iterations, these updated orbitals serve as the starting point. This iterative process continues until the orbitals from two consecutive iterations show negligible change, indicating convergence of the self-consistent field orbitals (see Fig. 2.3). Once convergence is achieved, resulting self-consistent orbitals are employed to construct the many-electron wavefunction. From this, the total ground state energy,  $E$ , can be calculated. It is important to understand that this total energy is not simply the sum of individual orbital energies,  $\epsilon_i$ . Instead, in order to find the ground state wavefunction, we minimize the total energy of the system using variational principle. It says that if  $E_0$  is the ground state energy of the system, for any wavefunction  $\Psi$ :

$$\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \quad (2.25)$$

The reason for this distinction lies in the treatment of electron-electron interactions. Each iteration, whether calculating  $\phi_i$  and  $\epsilon_i$  or the updated  $\phi'_i$  and  $\epsilon'_i$ , inherently includes the Coulomb



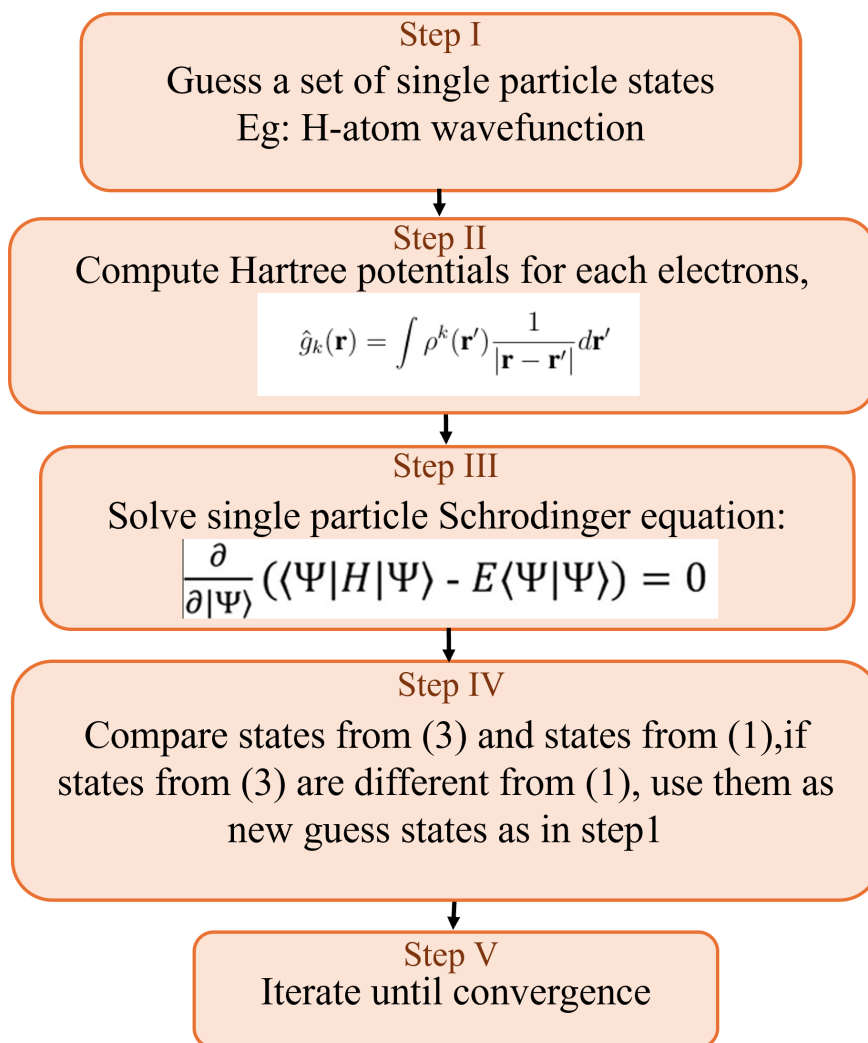


Figure 2.3: Flowchart of the Hartree method for many electron framework.

interactions between electrons. This leads to a double counting of these interactions. Therefore, the expression for the absolute total energy must account for and correct this double counting.

$$E = \sum_{i=1}^N \epsilon_i - \sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ij} \quad (2.26)$$

where,  $J_{ij}$  are known as Coulomb integrals and are defined as:

$$J_{ij} = \int \int \frac{\rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \int \int |\phi_i(\mathbf{r}_1)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\phi_j(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.27)$$

Hartree's method surely provides a useful approximation for many-electron wavefunctions. However, limitation of this approach is that it does not satisfy the antisymmetry requirement of electronic wavefunctions. This antisymmetry condition is essential, as electrons are fermions and must obey Pauli's exclusion principle. No two identical fermions can simultaneously occupy the same quantum state within a quantum system. Moreover, the Hartree approximation is a two-particle approach that neglects both the exchange and correlation effects.

## 2.8 The Hartree-Fock approximation

A few years later, Fock [70] included the exchange potential by considering Pauli's exclusion principle. Further, in the same year, Slater independently suggested the same solution [71]. They modified the Hartree method (one-electron wavefunction) and worked on describing the antisymmetric behavior of the wavefunction in the Hartree product. They associated the Hartree product with the single-determinant theory. Since electrons are fermions, the wavefunction of a many-electron system must be antisymmetric under the exchange of electron labels.

$$\hat{P}_{1,2}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) \quad (2.28)$$

where,  $\hat{P}_{1,2}$  is parity operator. The antisymmetric wavefunction is the sum of all the products obtained by interchanging electron labels. However, this approach becomes very tedious when generating a wavefunction. Slater suggested a more convenient method to construct the wavefunction using a single Slater determinant, where single-electron states serve as the elements

of the matrix. This determinant inherently exhibits the required antisymmetric nature.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_2) \\ \phi_1(\mathbf{r}_3) & \phi_2(\mathbf{r}_3) & \dots & \phi_N(\mathbf{r}_3) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix} \quad (2.29)$$

For the sake of simplicity, let us consider the case of a two electrons system:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)] \quad (2.30)$$

By interchanging the labels  $1 \rightarrow 2$ , we obtain:

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) \\ \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) \end{vmatrix} = \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) - \phi_2(\mathbf{r}_2)\phi_1(\mathbf{r}_1)] \quad (2.31)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1) \quad (2.32)$$

If two electrons are defined by the same spin-orbital ( $\phi_1 = \phi_2 = \phi$ ), then:

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi(\mathbf{r}_2) & \phi(\mathbf{r}_2) \\ \phi(\mathbf{r}_1) & \phi(\mathbf{r}_1) \end{vmatrix} = \frac{1}{\sqrt{2}} [\phi(\mathbf{r}_2)\phi(\mathbf{r}_1) - \phi(\mathbf{r}_2)\phi(\mathbf{r}_1)] = 0 \quad (2.33)$$

In the Hartree-Fock method, the Pauli's exclusion principle dictates that electrons with the same spin cannot occupy the same spatial location. Consequently, the wavefunction becomes zero, implying a zero probability of finding such electrons. A flowchart summarizing the HF method's solution steps is shown in Fig. 2.4. The indistinguishable nature of electrons is represented by a Slater determinant. While electrons move independently, they experience Coulomb repulsion from the average positions of other electrons. The antisymmetry introduces an "electron exchange" term. The HF method determines the best single-determinant wavefunction that minimizes the total energy, given by:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \quad (2.34)$$

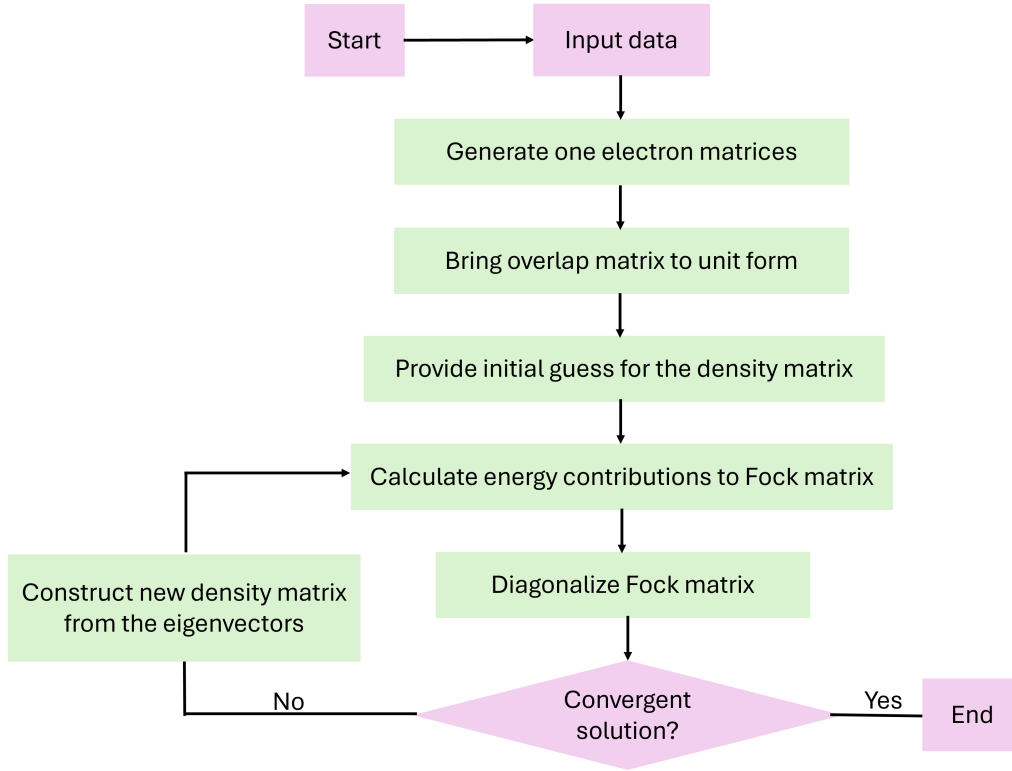


Figure 2.4: Schematic flowchart Hartree-Fock method for the solution of many electron system.

where  $H_i$  is defined as:

$$H_i = \int \phi_i^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + \hat{v}_i \right] \phi_i(\mathbf{r}) d\mathbf{r} \quad (2.35)$$

$J_{ij}$  and  $K_{ij}$  are the Coulomb and exchange integrals, respectively. The exchange integral is:

$$K_{ij} = \int \int \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(\mathbf{r}_2) \phi_j^*(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.36)$$

$K_{ij}$  resembles  $J_{ij}$  with exchanged wavefunctions  $\phi_i$  and  $\phi_j$ . They are equal only when  $i = j$ . When  $i = j$ , the second term in Eq. 2.34 vanishes, making the HF method self-interaction free. For  $K_{ij}$  to be non-zero, electrons  $i$  and  $j$  must have the same spin to satisfy orthogonality.

$$\left[ \hat{h}_1 + \sum_i (\hat{J}_i - \hat{K}_i) \right] \phi_k = \sum_{i=1} \epsilon_{ki} \phi_i \quad (2.37)$$

The Fock operator is:

$$\hat{F} = \hat{h}_1 + \sum_i (\hat{J}_i - \hat{K}_i) \quad (2.38)$$

$$\hat{F}\phi_k = \sum_{i=1} \epsilon_{ki}\phi_i \implies \epsilon_{ki} = \delta_{ki}\epsilon_k \quad (2.39)$$

$$\hat{F}\phi_k = \epsilon_k\phi_k \quad (2.40)$$

HF treats the exchange interaction between same-spin electrons exactly, often called the "exact exchange" approach. It's used for various materials science problems (e.g., adsorption, insulator electronic structure, solid defects). However, HF neglects electron-electron Coulomb correlation energy, defined as the difference between exact and HF ground state energies ( $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$ ). This correlation energy is crucial for explaining physical and chemical properties of atoms, molecules (e.g.,  $\text{H}_2$  dissociation), and solids. For instance, in water molecules, at least a quarter of hydrogen bond strength is accounted for by electron correlation. Correlation effects are vital when bonds form or break.

## 2.9 Functional

A function takes one or more numbers as inputs and produces another number as output. In contrast, a functional takes a function as its argument and yields a number as its output. Functionals are typically represented using square brackets, such as  $F[f] = a$ . Similar to functions, functionals can also have derivatives, which describe how the functional changes when the input function undergoes a small variation. The differential of a functional is defined as:

$$\delta F[f] = F[f + \delta f] - F[f] = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx. \quad (2.41)$$

Functionals provide a fundamental framework in variational calculus and physics, particularly in fields like quantum mechanics and functional analysis. A common example of a functional is the integral of a function over a given domain:

$$F[f] = \int_{-1}^{+1} f(x) dx. \quad (2.42)$$

The expectation value of an energy operator in quantum mechanics serves as an energy functional  $E[\psi]$ , which takes a wavefunction as input and returns an energy value. The functional derivative has similar properties to conventional derivatives of functions and is crucial in optimization problems involving functionals.

## 2.10 Density Functional Theory

In the field of condensed matter physics, Density Functional Theory (DFT) has emerged as an indispensable framework. The central innovation of DFT lies in its departure from traditional wavefunction-based approaches. While a standard many-body wavefunction depends on  $3N$  spatial variables (for a system of  $N$  electrons), DFT utilizes the electron density, a scalar function requiring only three spatial coordinates as its primary variable. This drastic reduction in dimensionality is what allows DFT to scale efficiently, enabling the simulation of complex systems comprising hundreds or thousands of atoms. Despite its simplicity, the electron density is mathematically sufficient to determine all ground-state properties of a quantum system. By leveraging this density-centric perspective, DFT provides a computationally feasible yet accurate means of solving the Schrödinger equation for interacting particles. The conceptual roots of using density as a fundamental descriptor can be traced back to the Thomas-Fermi model of 1927. However, the rigorous theoretical framework of modern DFT was solidified in 1964 through the seminal work of Hohenberg and Kohn. The profound impact of this development was recognized in 1998, when Walter Kohn was honored with the Nobel Prize in Chemistry. Today, DFT's ability to describe the ground-state characteristics of atoms, molecules, and solids remains the gold standard for materials modeling. The following sections will explore the formal theorems and mathematical derivations that underpin this theory.

### 2.10.1 The Thomas-Fermi Model

Developed independently in 1927, the Thomas-Fermi model represents an early attempt to express a system's total energy solely through its electronic density [72, 73]. This simplified approach assumes a locally uniform distribution of electrons, allowing the kinetic energy to be formulated as a functional of the local density. While it neglects important exchange and correlation effects, this model established the foundational principle that the ground-state density is sufficient to describe a many-body system.

$$T_{TF}[\rho(\mathbf{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d^3\mathbf{r}. \quad (2.43)$$

This expression is also used in the Local Density Approximation. The total energy of an

atom in the Thomas-Fermi model is given by:

$$E^{TF}[\rho(\mathbf{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(\mathbf{r}) d^3\mathbf{r} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r}|} d^3\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (2.44)$$

In this equation, the second term represents the nucleus-electron potential energy, while the third term corresponds to the Hartree energy (electron-electron repulsion). The total electron density and energy of the ground state can be obtained by minimizing this functional.

### 2.10.2 Hohenberg and Kohn Theorem

In 1964, Hohenberg and Kohn established DFT by demonstrating that the electronic Hamiltonian can be expressed as a functional of the electron density. They presented two fundamental theorems concerning the electron density  $\rho(\mathbf{r})$  of electrons in an external potential [63, 64] (see Fig. 2.5).

**Theorem I:** "For a system of interacting particles in an external potential,  $\hat{V}_{ext}(\mathbf{r})$  can be uniquely determined by its ground state electron density  $\rho(\mathbf{r})$  within an additive constant." This implies that the Hamiltonian is fully determined by the electron density, which can be extended to describe excited states and time-dependent potentials. Consequently, knowing the ground state density allows the determination of all system properties. The electron density for  $N$  electrons is given by:

$$\rho(\mathbf{r}) = N \sum_{s_1} \cdots \sum_{s_N} \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N |\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N)|^2 \quad (2.45)$$

where  $\mathbf{r}_i$  and  $s_i$  are the spatial and spin coordinates of the electrons, respectively, and

$$N = \int \rho(\mathbf{r}) d\mathbf{r} \quad (2.46)$$

To prove Theorem I, consider two different external potentials,  $\hat{V}_{ext}(\mathbf{r})$  and  $\hat{V}'_{ext}(\mathbf{r})$ , that supposedly yield the same electron density  $\rho(\mathbf{r})$  for non-degenerate states. These potentials correspond to different Hamiltonians,  $\hat{H}_{el}$  and  $\hat{H}'_{el}$ , and different ground state wavefunctions,  $\Psi$  and  $\Psi'$ , with ground state energies  $E_0$  and  $E'_0$ , respectively.

Using the variational theorem, we have:

$$E_0 = \langle \Psi | \hat{H}_{el} | \Psi \rangle < \langle \Psi' | \hat{H}_{el} | \Psi' \rangle \quad (2.47)$$

and

$$\langle \Psi' | \hat{H}_{\text{el}} | \Psi' \rangle = \langle \Psi' | \hat{H}'_{\text{el}} | \Psi' \rangle + \langle \Psi' | \hat{H}_{\text{el}} - \hat{H}'_{\text{el}} | \Psi' \rangle \quad (2.48)$$

This leads to:

$$E_0 < E'_0 + \int \rho(\mathbf{r}) [\hat{V}_{\text{ext}}(\mathbf{r}) - \hat{V}'_{\text{ext}}(\mathbf{r})] d\mathbf{r} \quad (2.49)$$

Similarly, applying the variational principle to  $\Psi'$  yields:

$$E'_0 < E_0 - \int \rho(\mathbf{r}) [\hat{V}_{\text{ext}}(\mathbf{r}) - \hat{V}'_{\text{ext}}(\mathbf{r})] d\mathbf{r} \quad (2.50)$$

Combining these inequalities results in a contradiction:

$$E_0 + E'_0 < E'_0 + E_0 \quad (2.51)$$

This contradiction proves that the external potential  $\hat{V}_{\text{ext}}(\mathbf{r})$  must be uniquely defined for the ground state.

**Theorem II:** "A universal functional for the energy  $E[\rho(\mathbf{r})]$  can be described in terms of the density  $\rho(\mathbf{r})$ , which is accepted for any external potential  $V_{\text{ext}}(\mathbf{r})$ . For any particular  $V_{\text{ext}}(\mathbf{r})$ , the exact ground state energy is the global minimum value of this functional and the density  $\rho(\mathbf{r})$  that minimizes this functional is the ground state density  $\rho_0(\mathbf{r})$ ."

We restrict the discussion to the class of admissible electron densities that can be generated by some external potential, commonly referred to as *V-representable* densities. Although this restriction is not essential for the validity of the theorem, as more general formulations exist [75, 76], it suffices for the present argument.

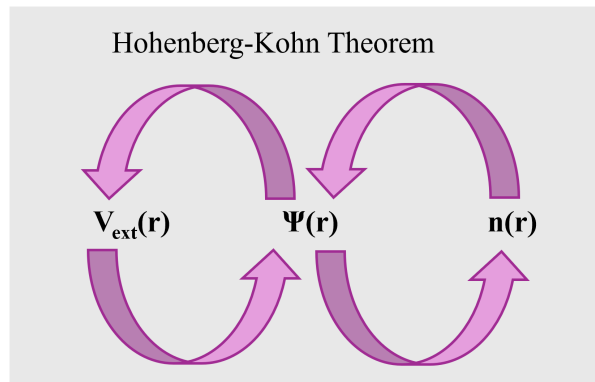


Figure 2.5: Hohenberg-Kohn approach in DFT.



Since all ground-state properties of a many-electron system are uniquely determined by the electron density  $n(\mathbf{r})$ , the total energy can be expressed as a functional of the density:

$$E_{\text{HK}}[n] = T[n] + E_{\text{int}}[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} = F_{\text{HK}}[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad (2.52)$$

where  $T[n]$  is the electronic kinetic energy functional and  $E_{\text{int}}[n]$  accounts for electron-electron interactions. The term  $F_{\text{HK}}[n]$  is universal in the sense that it depends only on the density and not on the external potential, whereas  $V_{\text{ext}}(\mathbf{r})$ , determined by the nuclear configuration, is system specific.

Let  $n_1(\mathbf{r})$  denote the exact ground-state density corresponding to the external potential  $V_{\text{ext}}^{(1)}(\mathbf{r})$ , with ground-state wavefunction  $\Psi_1$ . The associated ground-state energy is given by

$$E_1 = E_{\text{HK}}[n_1] = \langle \Psi_1 | \hat{H} | \Psi_1 \rangle. \quad (2.53)$$

Now consider an alternative trial wavefunction  $\Psi_2$ , which produces a different density  $n_2(\mathbf{r})$  but satisfies the same particle-number constraint. According to the variational principle,

$$\langle \Psi_1 | \hat{H} | \Psi_1 \rangle < \langle \Psi_2 | \hat{H} | \Psi_2 \rangle, \quad (2.54)$$

which implies

$$E_{\text{HK}}[n_1] < E_{\text{HK}}[n_2]. \quad (2.55)$$

This result demonstrates that the Hohenberg-Kohn energy functional attains its minimum value when evaluated at the true ground-state density. Consequently, the exact ground-state energy and density can, in principle, be obtained by minimizing  $E_{\text{HK}}[n]$  with respect to all admissible densities. It is important to note that this variational principle applies exclusively to the ground state and does not provide direct information about excited states.

While the Hohenberg-Kohn theorems rigorously establish the existence of a universal functional  $F_{\text{HK}}[n]$ , they do not prescribe its explicit form. In practice, the Kohn-Sham formalism provides a tractable approach for constructing and approximating this functional in realistic many-electron calculations.

### 2.10.2.1 Kohn-Sham equations

In 1965, Kohn and Sham [64] introduced a practical formulation of density functional theory by showing that the exact ground-state electron density of an interacting many-electron system can be reproduced by a fictitious system of non-interacting particles, as illustrated in Fig. 2.6. In this

approach, the many-body problem is mapped onto an auxiliary single-particle problem. The corresponding auxiliary Hamiltonian, known as the Kohn-Sham Hamiltonian ( $\hat{H}_{KS}$ ), contains the kinetic energy of non-interacting electrons and an effective local potential  $V_{\text{eff}}(\mathbf{r})$ , which accounts for the effects of electron–electron interactions.

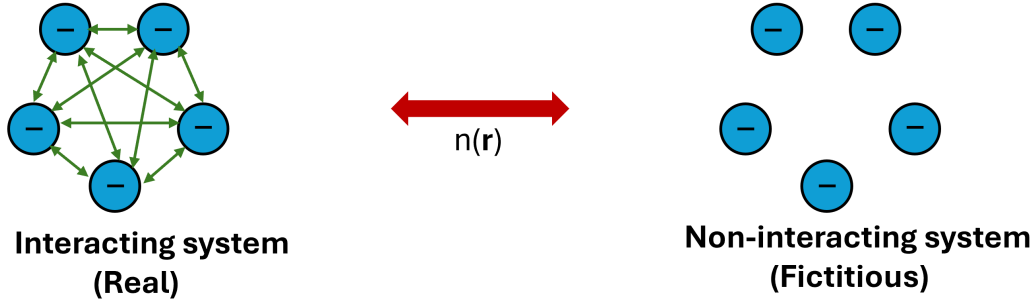


Figure 2.6: Schematic representation of interacting and non-interacting many-electron system having the same ground-state electron density.

The form of the equations for non-interacting particles, known as the Kohn-Sham equations, is:

$$\hat{H}_{KS}\phi_i = \left[ -\frac{1}{2}\nabla_i^2 + \hat{V}_{eff}(\mathbf{r}) \right] \phi_i^{KS}(\mathbf{r}) = \epsilon_i \phi_i^{KS}(\mathbf{r}) \quad (2.56)$$

where the effective potential is:

$$\begin{aligned} \hat{V}_{eff}(\mathbf{r}) &= \hat{V}_{ext}(\mathbf{r}) + \hat{V}_H(\mathbf{r}) + \hat{V}_{xc}(\mathbf{r}) \\ &= \sum_{\alpha} \frac{-Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\partial E_{xc}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \end{aligned} \quad (2.57)$$

In this framework,  $\hat{V}_H$  represents the classical electrostatic (Hartree) potential generated by the total electron density. The term  $\hat{V}_{xc}$  denotes the exchange-correlation potential, obtained as the functional derivative of the exchange-correlation energy  $E_{xc}$ . This contribution incorporates all many-body interactions that are not captured by the Hartree term alone. Equation 2.56 resembles the Hartree-Fock equations, but with a significantly simplified structure. In the Kohn-Sham approach, the effective operator depends only on the spatial coordinate  $\mathbf{r}$  and is identical for all electrons, rather than being explicitly dependent on individual particle indices. Solving Eq. 2.56 yields the Kohn-Sham orbitals  $\phi_i^{KS}(\mathbf{r})$ , which are then used to construct the

total electron density as follows:

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i^{KS}(\mathbf{r})|^2 \quad (2.58)$$

The effective potential  $\hat{V}_{\text{eff}}(\mathbf{r})$  is obtained self-consistently from the electron density. The procedure starts with an initial guess for the density, which is commonly taken as a sum of isolated atomic densities. This density is then iteratively updated until self-consistency is achieved. When spin degrees of freedom are included, the total electron density is written as the sum of spin-resolved contributions,  $\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r})$ .

The converged electron density is subsequently used to evaluate the total energy of the system.

$$E[\rho] = T_0[\rho] + \int [\hat{V}_{\text{ext}}(\mathbf{r}) + \hat{V}_H(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho] \quad (2.59)$$

The kinetic energy  $T_0[\rho]$  is taken from corresponding orbitals instead of density:

$$T_0[\rho] = \frac{1}{2} \sum_{i=1}^N \langle \phi_i^{KS} | \nabla_i^2 | \phi_i^{KS} \rangle \quad (2.60)$$

and the remaining energy as:

$$V_{\text{eff}}[\rho] = \int \hat{V}_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (2.61)$$

$E_{xc}[\rho]$  has all energy contributions not accounted for in the other terms:

1. Electron exchange
2. Electron correlation
3. The kinetic energy difference between the non-interacting and interacting systems.
4. Correction for self-interaction included in the classical Coulomb potential.

$E_{xc}$  is vital for understanding chemical bonds and determines the accuracy of methods using the Kohn-Sham equations.

### 2.10.3 Exchange and correlation energy

For practical use of the Kohn-Sham equations, it is crucial to know the form of the exchange-correlation energy functional. However, the exact analytical or mathematical form of the exchange-correlation energy is unknown and may remain so. Since the inception of DFT, various approximations have been proposed for the exchange-correlation (xc) functional to achieve a balance between accuracy and computational cost. There exists an extensive list of approximated exchange-correlation energy functionals with varying levels of complexity. These approximations can be categorized into three main parts: (a) local approximations, such as the local density approximation (LDA) [77], (b) semi-local approximations, including generalized gradient approximations (GGA) and meta-GGAs, and (c) non-local approximations, such as hybrid functionals and the random phase approximation (RPA). Furthermore, functionals can be classified as non-empirical, semi-empirical, and empirical.

Non-empirical functionals are formulated purely from first-principles calculations (and some physical rules). The motivation for first-principles calculations is to predict experimental results on complex materials, even under extreme conditions, without relying on experimental data. Semi-empirical and empirical functionals, where data is fitted to known atomic and molecular properties, are not considered first-principles.

The initial implementation of the Kohn-Sham method used local approximations for the exchange-correlation energy. For a homogeneous electron gas, the exchange-correlation energy is a local functional. Therefore, the LDA is the simplest approximation. In LDA, the density is assumed to vary gradually with position, and only the density contribution is considered, not its derivatives. The effect of spin polarization can be included by considering both spin densities i.e., spin-up  $\rho_{\uparrow}(\mathbf{r})$  and spin-down  $\rho_{\downarrow}(\mathbf{r})$ , known as the local spin density approximation (LSDA). The exchange-correlation energy is divided into two parts, the exchange energy and the correlation energy:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \quad (2.62)$$

#### Exchange energy:

The exchange energy arises from the antisymmetry requirement of the many-electron wavefunction, which is a fundamental consequence of the Pauli's exclusion principle. Since electrons with the same spin cannot occupy identical quantum states, they tend to avoid each other

in space. This effective separation lowers the Coulomb repulsion between like spin electrons, resulting in a reduction of the total electrostatic energy. This reduction is referred to as the exchange energy. From a theoretical perspective, the exchange energy represents the difference between the classical Hartree energy, which treats electrons as distinguishable, and the Hartree-Fock energy, which explicitly accounts for wavefunction antisymmetry. Within the local density approximation (LDA), the exchange energy is obtained by adopting the analytical result for a homogeneous electron gas, where it can be expressed in a closed numerical form [78]

$$E_x[\rho] = -\frac{9}{4} \left( \frac{3}{4\pi} \right)^{1/3} \int [\rho_{\uparrow}^{4/3}(\mathbf{r}) + \rho_{\downarrow}^{4/3}(\mathbf{r})] d\mathbf{r} \quad (2.63)$$

**Correlation energy:** The correlation energy originates from the mutual interaction between electrons beyond the mean-field description. Because electrons carry the same negative charge, their motions become correlated as they dynamically avoid one another. A major contribution to the correlation energy arises from the change in kinetic energy caused by these interactions. Specifically, the kinetic energy of an interacting electron system differs from that of a corresponding non-interacting reference system, leading to a contribution proportional to  $(T_e - T_0)$ . From a formal standpoint, the correlation energy is defined as the difference between the exact many-body ground-state energy and the energy obtained from the Hartree-Fock approximation, which includes exchange effects but neglects dynamic electron correlations.

$$E_c = E_{\text{exact}} - E_{\text{HF}} \quad (2.64)$$

The correlation energy is defined by:

$$E_c[\rho] = \int \rho(\mathbf{r}) \epsilon_c[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})] d\mathbf{r} \quad (2.65)$$

where  $\epsilon_c[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})]$  is the correlation energy per electron of a uniform electron gas with density  $\rho(\mathbf{r})$ . Its precise form is not known. Efforts are made to improve the correlation term based on quantum Monte Carlo simulations [79] and analytical expansions.

### Local Density Approximation (LDA)

The LDA model works well for systems close to a homogeneous electron gas, where the density varies slowly, especially for metals. The success of LDA is associated with systematic error cancellation. In homogeneous systems, LDA overestimates the exchange term and underestimates the correlation term, resulting in accurate predictions of  $E_{xc}^{\text{LDA}}$ . The error cancellation

in LDA is systematic, due to LDA satisfying sum rules for any density. However, LDA is inappropriate for systems with rapidly varying densities, such as atoms and molecules. Atomic structures, elastic, and vibrational properties can be determined for various systems. However, LDA struggles with weakly bonded systems (vdW and H-bonded), failing to predict correct chemical bond energetics, binding energies, reaction enthalpies, and activation energy barriers.

**Generalized Gradient Approximation (GGA)** The local density approximation becomes inadequate when the electron density varies significantly over space, as it is based on the assumption of a homogeneous electron gas. To address this limitation, the generalized gradient approximation (GGA) incorporates not only the local electron density but also its spatial variation through the density gradient [80, 81]. In this semi-local framework, the exchange-correlation energy depends explicitly on both  $\rho(\mathbf{r})$  and  $|\nabla\rho(\mathbf{r})|$ , and is written as

$$E_{xc}^{\text{GGA}}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|) d\mathbf{r} \quad (2.66)$$

Because GGA includes information about density inhomogeneity, it is classified as a semi-local approximation. Compared to LDA, GGA generally provides a more accurate description of equilibrium geometries, ground-state energies, and bonding characteristics. It yields improved predictions for bond lengths and lattice constants, particularly in covalently bonded and weakly interacting systems. However, its performance deteriorates for systems containing heavy elements, such as 5d transition metals, where relativistic effects and strong correlation become important [82].

### **Meta Generalized Gradient Approximation (meta GGA)**

Meta-GGA functionals extend the description of exchange-correlation effects by including additional ingredients beyond the electron density and its gradient. In particular, they depend on the Laplacian of the density,  $\nabla^2\rho(\mathbf{r})$  and the kinetic energy density,  $\tau(\mathbf{r})$  allowing a more refined treatment of inhomogeneous electronic systems.

Despite these improvements, semi-local exchange-orrelation functionals (including LDA, GGA, and meta-GGA) generally underestimate electronic band gaps. They also suffer from self-interaction errors originating from the Hartree term, which leads to systematic inaccuracies when describing localized states such as defects, surfaces, and strongly confined electrons. In contrast, the Hartree-Fock method is free from self-interaction errors because it treats exchange exactly. However, it completely neglects electron correlation effects. As a result, Hartree-Fock often provides an inaccurate description of chemical bonding and typically predicts band gaps

that are significantly larger than experimental values.

**Hybrid functional (HSE06)** To address the self-interaction errors inherent in GGA functionals, hybrid exchange-correlation schemes incorporate a fraction of exact Hartree-Fock (HF) exchange into the DFT framework. In general, the hybrid functional can be written as

$$E_{xc}^{\text{hyb}} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{DFT}} + E_c^{\text{DFT}} \quad (2.67)$$

where  $\alpha$  denotes the proportion of exact exchange mixed with the DFT exchange term.

To further improve computational efficiency and physical accuracy for extended systems, screened hybrid functionals introduce a range-separation parameter  $\omega$  that splits the Coulomb interaction into short-range (SR) and long-range (LR) components. Using the error function, the Coulomb potential is decomposed as

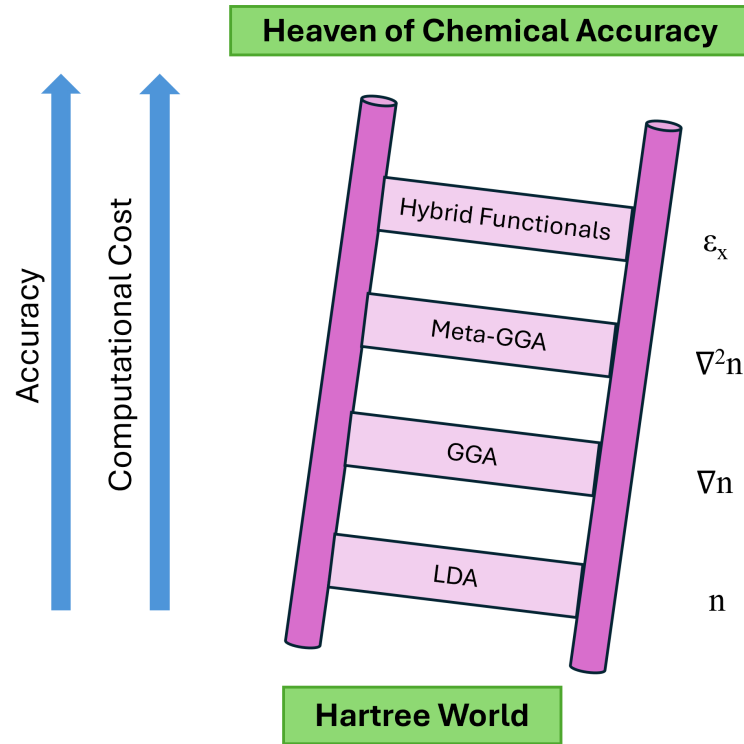


Figure 2.7: Schematic diagram of Jacob's ladder of density functional theory with different approximations for exchange-correlation energy.

$$\frac{1}{r} = \frac{1 - \text{erf}(\omega r)}{r} \Big|_{\text{SR}} + \frac{\text{erf}(\omega r)}{r} \Big|_{\text{LR}} \quad (2.68)$$

with the error function defined by

$$\text{erf}(\omega r) = \frac{2}{\sqrt{\pi}} \int_0^{\omega r} e^{-x^2} dx \quad (2.69)$$

Based on this idea, Heyd, Scuseria, and Ernzerhof proposed the HSE functional, where Hartree-Fock exchange is included only in the short-range part, while the Perdew-Burke-Ernzerhof (PBE) functional describes the long-range exchange and correlation [83]. The resulting exchange-correlation energy within the HSE06 scheme is expressed as

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}} \quad (2.70)$$

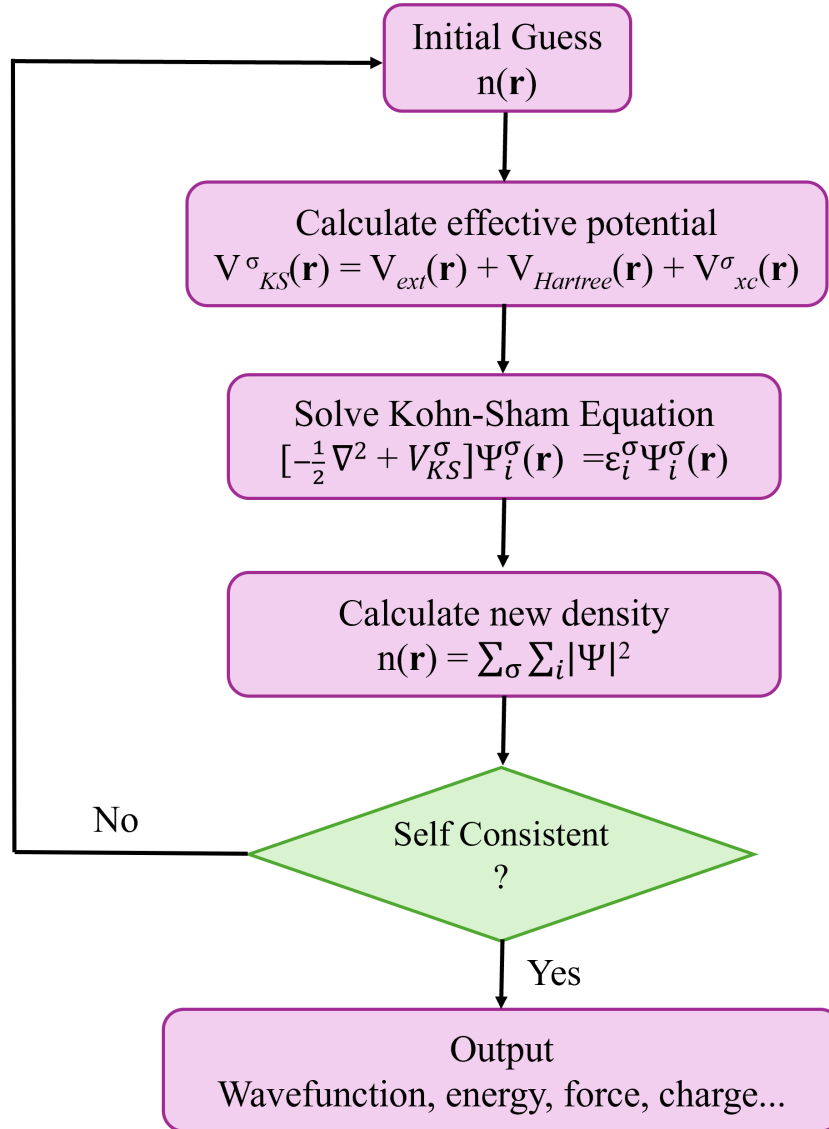


Figure 2.8: Schematic illustration of self-consistent loop for the solution of the Kohn-Sham equations.

The standard parameter values  $\alpha = 0.25$  and  $\omega = 0.11 \text{ bohr}^{-1}$  (equivalent to  $0.2 \text{ \AA}^{-1}$ ) are commonly employed and have been shown to perform reliably for metals and materials with small to moderate band gaps. Compared to semilocal functionals, HSE06 significantly reduces



self-interaction errors and yields improved predictions for electronic band gaps and reaction energy barriers. In some cases, the mixing parameter  $\alpha$  may be adjusted to achieve closer agreement with experimental results. The hierarchy of exchange-correlation approximations, often referred to as Jacob’s ladder of density functional theory, is illustrated schematically in Fig. 2.7, highlighting the trade-off between computational cost and accuracy. In this work, first-principles calculations are carried out using the VASP package [84, 85, 86] and QUANTUM ESPRESSO [87]. The self-consistent procedure employed to solve the Kohn-Sham equations is summarized in Fig. 2.8

## 2.11 DFT+U

In DFT, the electronic interaction energy is composed of the classical Coulomb repulsion (Hartree term) and an additional exchange-correlation term, which is responsible for capturing all quantum mechanical correlations and spin interactions [88]. The accuracy of a DFT calculation depends heavily on how well the exchange-correlation functional approximates the exact energy description of the system [89].

Modeling the exchange-correlation functional’s dependence on the electronic charge density remains a challenge, leading to limitations in describing many-body effects in strongly correlated systems. Consequently, systems governed by strong electron-electron interactions are poorly described within standard DFT approximations. A key manifestation of this limitation is the well-known bandgap problem, which leads to inaccurate predictions of intermolecular interactions, formation energies, and transition states [90].

The failure of DFT in describing correlated systems arises from the tendency of approximate exchange-correlation functionals to over-delocalize valence electrons and favor metallic ground states [91, 92]. This delocalization issue is attributed to the incomplete cancellation of the electronic self-interaction inherent in the Hartree term, resulting in residual self-interaction effects that cause excessive delocalization of wavefunctions [91]. Hybrid functionals attempt to mitigate this issue by incorporating a fraction of the exact HF exchange, which is self-interaction-free. However, this approach is computationally demanding and impractical for large systems. Despite this improvement, HF-based methods, which rely on a single-determinant description of the electronic structure, still fail to capture the physics of strongly correlated materials like Mott insulators. Accurately describing such systems requires

a full account of the multideterminant nature of the  $N$ -electron wavefunction and the many-body interactions within the system [92]. Therefore, DFT using standard exchange-correlation functionals, such as the Local Density Approximation LDA or GGA, provides an inadequate description of strongly correlated materials.

### 2.11.1 Mott Insulators and the Hubbard Model

Conventional band theories often predict that strongly correlated materials should exhibit metallic behavior. However, experimental measurements reveal insulating properties, contradicting these predictions. This discrepancy, highlighted by Nevill Mott, arises due to the neglect of interelectron Coulomb interactions in standard band theories. Mott insulators, unlike conventional band insulators, exhibit an energy gap between bands of similar character (e.g., 3d suborbitals), driven by crystal field splitting or Hund's rule [93]. The insulating nature of Mott insulators originates from strong electron-electron repulsion, which forces localization in atomic-like orbitals, a phenomenon known as Mott localization.

The localization of electrons in Mott insulators is governed by the competition between the on-site Coulomb repulsion  $U$  and the electron hopping amplitude  $t$ , which quantifies the probability of electrons transitioning between neighboring sites. The bandgap energy  $E_{\text{gap}}$  is determined by these parameters as:

$$E_{\text{gap}} = U - 2zt, \quad (2.71)$$

where  $z$  represents the number of nearest-neighbor atoms, indicating the connectivity of the electronic states [92].

To better describe correlated materials, alternative models have been introduced, including the Hubbard model, which explicitly accounts for on-site electronic repulsion. The Hubbard Hamiltonian, in its simplest form, is given by [92]:

$$H_{\text{Hub}} = t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}, \quad (2.72)$$

where  $c_{i,\sigma}^\dagger$  and  $c_{j,\sigma}$  are the electronic creation and annihilation operators at sites  $i$  and  $j$ , respectively, and  $n_{i,\sigma}$  is the number operator for electrons with spin  $\sigma$  at site  $i$ . The hopping amplitude  $t$  is proportional to the bandwidth of valence electrons, while the on-site Coulomb interaction  $U$  measures the energy penalty for double occupancy of an atomic orbital. The

system behaves as an insulator when  $U \gg t$ , as electrons lack sufficient energy to overcome the Coulomb repulsion and remain localized. Conversely, when  $t \gg U$ , the electrons are more delocalized, and the system exhibits metallic behavior.

DFT accurately predicts electronic properties in regimes where  $t \gg U$ , but as  $U$  increases, its performance deteriorates. The HF method, although self-interaction-free, fails to describe the correlated electronic ground state because it relies on a single-determinant approximation. Hence, more sophisticated approaches are necessary to accurately capture the electronic structure of Mott insulators and other strongly correlated systems.

The extent of electron delocalization varies significantly across different orbital types due to their spatial extent and overlap. The general trend follows:

- ***s*-orbitals:** These are the most delocalized due to their spherical symmetry and lack of nodal planes, allowing strong overlap and extensive hybridization in metallic and covalent bonding.
- ***p*-orbitals:** More localized than *s*-orbitals, but still contribute significantly to bonding and delocalization in materials, particularly in conjugated systems and semiconductors.
- ***d*-orbitals:** Tend to be more localized than *s* and *p* orbitals, particularly in transition metals. Their delocalization strongly depends on crystal field effects and hybridization with other orbitals.
- ***f*-orbitals:** The most localized due to their complex shapes and poor spatial overlap with neighboring orbitals, leading to strongly correlated behavior in rare-earth and actinide compounds.

The improper treatment of *d* and *f* electrons in standard DFT is one of the primary reasons for the failure of conventional exchange-correlation functionals in describing strongly correlated materials. The DFT+U method corrects this by introducing an explicit on-site Coulomb interaction term that reduces the artificial delocalization of these electrons, improving the description of their localization and resulting electronic properties. Another advantage of this method is that it works within the realm of DFT, therefore, no extra efforts are needed to implement it in the existing DFT codes. Its computational cost is only slightly higher than the DFT methods.

## 2.12 Basis set

The basis set plays a crucial role in solving the electronic structure problem, effectively providing a means to represent the unknown wavefunction. It involves expressing the wavefunction as a combination of known basis functions. Selecting appropriate basis functions needs careful consideration of several factors listed follows:

- The basis functions should be chosen such that they accurately express the wavefunction or electron density while minimizing the computational cost. The precision and efficiency of a method largely depend on the selection of these basis functions. A well-chosen basis is sufficiently extensive such that further increasing its size (e.g., by adding more plane waves) does not significantly change the results.
- The choice of basis functions must accurately reflect the essential physical characteristics of the system under study. In addition, when dealing with periodic systems such as crystalline solids, the basis functions are required to explicitly obey Bloch's theorem.

A notable drawback of the basic expansion scheme is that the basis functions themselves are fixed, which can make it difficult to achieve convergence of the wavefunctions. To address this limitation, approaches employing energy-dependent or adaptive basis functions have been developed, allowing the form of the wavefunction to adjust during the calculation. Since the present work is concerned mainly with crystalline and periodically repeating systems, electronic structure methods based on plane waves are particularly appropriate. These methods provide a natural description of periodicity and offer controlled convergence through a small number of parameters. In order to balance computational efficiency with accuracy, this thesis briefly introduces the plane-wave basis formalism, followed by a discussion of pseudopotential techniques and the projector augmented-wave method, which together form the foundation of modern first-principles calculations for extended solids.

### 2.12.1 The Plane wave basis set

Solving the single-particle Kohn-Sham equations in extended systems requires efficient numerical techniques. A widely used approach is to express the electronic eigenstates as a linear combination of basis functions, which converts the Schrödinger equation into an algebraic eigenvalue problem for the expansion coefficients. For periodic and extended systems, plane

waves form a natural choice of basis due to their orthonormality and independence from atomic positions. This property simplifies the eigenvalue problem and removes Pulay force contributions, allowing atomic forces to be evaluated directly using the Hellmann-Feynman theorem.

In practice, the plane wave basis is limited by a maximum kinetic energy or wave-vector cutoff, which controls the accuracy of the calculation. However, the strong spatial variation of valence wavefunctions near atomic cores would require an impractically large number of plane waves. To address this issue, plane wave methods are commonly used together with pseudopotentials, which replace the core electrons with an effective potential. The use of Fast Fourier Transforms further improves computational efficiency by enabling rapid evaluation of integrals and operators.

This section introduces the basic concepts used to describe periodic systems and the expansion of wavefunctions in a plane wave basis. The pseudopotential approach is discussed in the following sections.

### **Bloch's Theorem**

According to the Bloch's theorem, the eigenstates of the single-particle Schrödinger equation within a periodic crystal, when represented using plane waves, take the following form:

$$\psi(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k} \cdot \mathbf{T}} \psi(\mathbf{r}) \quad (2.73)$$

where  $\mathbf{T}$  denotes an arbitrary translation vector in the Bravais lattice, and  $\mathbf{k}$  is the wave vector. The allowed values of  $\mathbf{k}$  are confined to the reciprocal unit cell, commonly the first Brillouin zone. For each  $\mathbf{k}$ , there exist distinct, independent eigenstates, each labeled by a band index  $n$ .

An alternative expression of Bloch's theorem states that all eigenfunctions  $\psi_{n\mathbf{k}}$  of the single-particle Schrödinger equation with a periodic potential can be written as the product of a plane wave and a function  $u_{n\mathbf{k}}$  that has the same periodicity as the Bravais lattice:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (2.74)$$

where  $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{n\mathbf{k}}(\mathbf{r})$ . For any vector  $\mathbf{T}$  in the Bravais lattice, Bloch's theorem allows us to confine eigenfunction calculations to a single unit cell. Equation 2.74 can then be used to determine the eigenfunctions in other unit cells. It is also common practice to normalize the

eigenfunctions within a single unit cell:

$$\int_{\Omega_c} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{r} = 1 \quad (2.75)$$

Due to the periodicity of the functions  $u_{n\mathbf{k}}(\mathbf{r})$ , they can be expanded in a plane-wave series. Equation 2.74 then becomes:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \quad (2.76)$$

where  $c_{n\mathbf{k}}(\mathbf{G})$  are the Fourier coefficients.

The Kohn-Sham equations, expressed using Bloch states, are:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right) \psi_{j\mathbf{k}}(\mathbf{r}) = \epsilon_{j\mathbf{k}} \psi_{j\mathbf{k}}(\mathbf{r}) \quad (2.77)$$

where

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})]. \quad (2.78)$$

The electron density,  $n(\mathbf{r})$ , is calculated as:

$$n(\mathbf{r}) = \frac{2}{\Omega_c} \frac{1}{(2\pi)^3} \sum_j \int_{BZ} |\psi_{j\mathbf{k}}(\mathbf{r})|^2 \Theta(E_F - \epsilon_{j\mathbf{k}}) d\mathbf{k} \quad (2.79)$$

where  $n$  is the electron density, and  $j$  is the band index.  $\Theta$  is the Heaviside step function, which equals one for positive arguments and zero for negative arguments.  $E_F$  is the Fermi energy, defining the energy limit for the occupied single particle states.

### Fourier representation of the Kohn-Sham equation

When using a plane-wave basis, the Kohn-Sham equation simplifies considerably. Substituting Equation 2.76 into Equation 2.77 and using some basic algebra, leads to following matrix eigenvalue equation[77]:

$$\sum_{\mathbf{G}} \left( \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}'\mathbf{G}} + V_{eff}(\mathbf{G}' - \mathbf{G}) \right) c_{j\mathbf{k}}^{\mathbf{G}} = \epsilon_{j\mathbf{k}} c_{j\mathbf{k}}^{\mathbf{G}'} \quad (2.80)$$

In practice, the plane-wave expansion of the wavefunction is truncated by including only plane waves with kinetic energies below a cutoff,  $E_{cut}$ :

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{cut} \quad (2.81)$$

Convergence of a given property requires systematically increasing  $E_{cut}$ .

The Fourier representation of the electron density is:

$$n(\mathbf{G}) = \frac{2}{N_{kpt}} \sum_{j\mathbf{k}} f_{j\mathbf{k}} \sum_{\mathbf{G}'} (c_{j\mathbf{k}}^{\mathbf{G}'-\mathbf{G}})^* c_{j\mathbf{k}}^{\mathbf{G}'} \quad (2.82)$$

Since the electron density,  $n$  (proportional to  $|\psi|^2$ ), requires Fourier components with twice the spatial extent of those needed for the wavefunction,  $\psi$ , calculating all Fourier components using Equation 2.82 involves a double summation, scaling as  $N_G^2$ , here  $N_G$  is the number of  $\mathbf{G}$  vectors for the density. This gets computationally expensive for bigger systems.

If the Bloch states are known on a real-space grid of  $N_R$  points, the electron density can be calculated in  $N_R$  operations. However, this is also expensive. The Fast Fourier Transform provides an efficient way to switch between real and reciprocal space, requiring only  $N \ln N$  operations, where  $N = N_R = N_G$  [77]. Therefore, the use of plane waves, combined with the Fast Fourier Transform, significantly speeds up the evaluation of these expressions.

### 2.12.2 Plane wave pseudopotential method

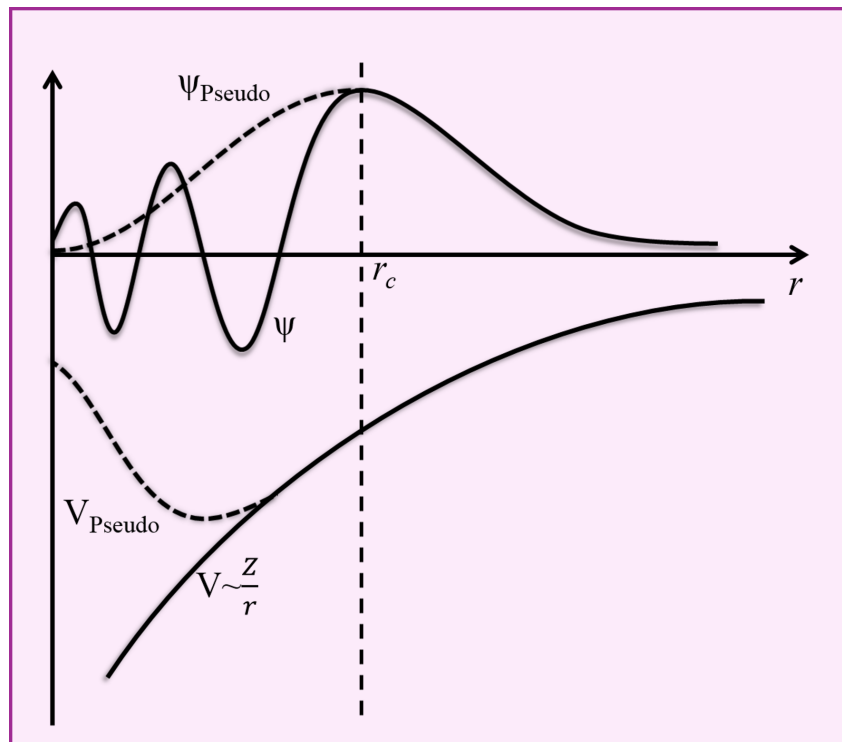


Figure 2.9: Representation of the pseudopotential approximation. The solid and dashed lines represent the all-electron and pseudo-wavefunctions, respectively [7].

Although substantial progress has been made in solving the Kohn-Sham equations, their practical implementation remains computationally demanding. The primary difficulty arises from the explicit treatment of the wavefunctions associated with all  $N$  electrons in the system. Moreover, near the atomic nuclei, valence electron wavefunctions exhibit strong oscillatory behavior due to the presence of tightly bound core states. These rapid variations correspond to large kinetic energies, which in turn require a very large number of plane waves and a high kinetic energy cutoff ( $E_{\text{cut}}$ ) for an accurate representation. As a result, the computational cost increases significantly. To reduce this computational cost, the pseudopotential approximation is commonly adopted. This approach is based on the observation that the essential physical properties of solids are mainly governed by valence electrons, whereas core electrons play a limited role. Instead of treating the strong Coulomb potential of the atomic core explicitly, it is replaced by an effective pseudopotential, denoted as  $V_{\text{Pseudo}}$ . Within this framework, electrons are classified into core and valence groups, separated by a cutoff radius  $r_c$ , as schematically shown in Fig. 2.9. The magnitude of  $r_c$  determines the nature of the pseudopotential, smaller values correspond to harder pseudopotentials, while larger values lead to softer or ultrasoft pseudopotentials.

In the pseudopotential formalism, the true all-electron wavefunctions are substituted by smoother pseudo wavefunctions,  $\Psi_{\text{Pseudo}}$ , for the valence electrons. The pseudopotential  $V_{\text{Pseudo}}$  acts on these pseudo wavefunctions instead of the original all electron states [81, 77, 94]. Importantly, beyond the cutoff radius  $r_c$ , the pseudo wavefunctions are constructed to match the all electron wavefunctions exactly.

A further benefit of pseudopotentials is that relativistic effects, including spin-orbit coupling, can be incorporated directly into the effective potential, while the valence electrons are treated within a non-relativistic framework. Due to these advantages, several forms of pseudopotentials have been developed and are widely employed in density functional theory calculations to achieve a balance between accuracy and computational efficiency.

### 2.12.3 Norm-conserving pseudopotential

In the norm-conserving pseudopotential approach, the effective pseudopotential and its associated pseudo-wavefunctions are constructed to exactly reproduce the true all-electron potential and wavefunctions outside a chosen core radius, denoted by  $r_c$ . Within the core region ( $r < r_c$ ), the pseudo-wavefunctions differ from the true wavefunctions. However, this difference is sub-



ject to a constraint that the norm of the pseudo-wavefunction inside the core must be equal to that of the true wavefunction.

$$\int_0^{r_c} r^2 \Psi^{PS*}(r) \Psi^{PS}(r) dr = \int_0^{r_c} r^2 \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) d\mathbf{r} \quad (2.83)$$

where  $\Psi^{PS}$  denotes the pseudo-wavefunction and  $\Psi$  represents the corresponding all-electron wavefunction. This norm-conservation condition ensures that the integrated charge density within the core region remains unchanged, thereby preserving the correct electron count.

Since the radial wavefunctions and eigenvalues depend on the angular momentum quantum number  $l$ , the resulting pseudopotential must also be angular-momentum dependent. Such pseudopotentials are therefore referred to as "semi-local". An important consequence of enforcing norm conservation is improved transferability i.e., the pseudopotential can reliably reproduce the scattering properties of an ion across different chemical and structural environments. For this reason, norm-conserving pseudopotentials have been widely used in first-principles electronic structure calculations [95].

### 2.12.4 Ultrasoft pseudopotential

Norm-conserving pseudopotentials are often inefficient for systems that contain highly localized valence states, such as  $2p$  and  $3d$  orbitals. The main difficulty arises from representing these localized pseudo-wavefunctions using a plane-wave basis, which requires a very large number of plane waves and therefore a high computational cost. To address this limitation, ultrasoft pseudopotentials were introduced.

In the ultrasoft pseudopotential method, the norm-conservation condition is relaxed, allowing the pseudo-wavefunctions to be smoother within the core region. As a result, fewer plane waves are needed to describe the electronic states accurately, leading to a significant reduction in the required plane-wave energy cutoff. These pseudopotentials are fully nonlocal inside the core region and become local outside the core radius [96]. Their dependence on the self-consistent charge density improves their transferability across different chemical environments.

Within this framework, the pseudo-wavefunction is separated into two parts. The first part is the ultrasoft valence wavefunction, which does not conserve the norm inside the core region. The second part is the augmentation charge, which compensates for the missing charge within the core so that the correct total electron density is recovered. While the ultrasoft valence wavefunction allows for a much lower plane-wave cutoff, the inclusion of augmentation

charges introduces additional terms into the Kohn-Sham equations. These extra terms increase the computational effort required in each self-consistent iteration. However, the overall computational cost is often reduced because the lower plane-wave cutoff outweighs the added complexity. For this reason, ultrasoft pseudopotentials are widely used in calculations involving elements with localized valence orbitals.

### 2.12.5 Projector augmented-wave method (PAW)

The Projector Augmented Wave (PAW) method, introduced by Peter Blöchl in 1994 [86], was developed to combine the advantages of pseudopotential techniques with the accuracy of all-electron approaches such as the linear augmented plane wave method. A central difficulty in electronic structure calculations is the correct description of valence wavefunctions close to the atomic nuclei. In this region, wavefunctions exhibit rapid oscillations in order to remain orthogonal to the tightly bound core states and to satisfy the Pauli exclusion principle. Accurately capturing these oscillations using plane waves alone requires a very large number of Fourier components, which greatly increases computational cost.

The PAW formalism overcomes this problem by introducing a transformation that replaces the strongly oscillating all-electron wavefunctions with smoother auxiliary wavefunctions. This allows the use of a plane-wave basis with improved efficiency, while still retaining access to the full all-electron information when needed. In practice, space is divided into atom-centered regions, known as augmentation spheres, and the interstitial region between them. Inside each augmentation sphere, the wavefunction is expanded in terms of atomic-like partial waves, whereas in the interstitial region it is represented using smooth plane waves.

PAW datasets generally employ relatively small core radii ( $r_c$ ). Although this choice increases the required plane-wave cutoff energy ( $E_{\text{cut}}$ ) and the size of the basis set, it enables an accurate reconstruction of the nodal structure of the wavefunction in the core region. As a result, the PAW method provides a highly reliable description of the electronic structure, closely reproducing all-electron results. Formally, one may define a Hilbert space consisting of true all-electron wavefunctions that are orthogonal to the core states. Since a direct numerical treatment of these functions is demanding, a corresponding pseudo-Hilbert space is introduced, containing smoother pseudo-wavefunctions. The two spaces are connected through a linear transformation operator  $T$ , which relates the all-electron wavefunction  $|\Psi\rangle$  to the pseudo-wavefunction

$|\tilde{\Psi}\rangle$ .

$$|\Psi\rangle = T|\tilde{\Psi}\rangle \quad (2.84)$$

We can write the operator  $T$  in the following form:

$$T = 1 + T_0 \quad (2.85)$$

In the PAW formalism, the operator  $T_0$  acts only inside the augmentation region surrounding each atom. Let  $|\phi_i\rangle$  and  $|\tilde{\phi}_i\rangle$  denote the all-electron and pseudo partial waves, respectively. Since both sets form complete bases within the augmentation sphere, a linear transformation between them can be introduced as:

$$|\phi_i\rangle = (1 + T_0)|\tilde{\phi}_i\rangle \quad (2.86)$$

Because  $T_0$  is nonzero only inside the augmentation region, the all-electron and pseudo partial waves coincide outside this region. Owing to the completeness of the pseudo partial waves within the augmentation sphere, any pseudo wavefunction can be expanded as:

$$|\tilde{\Psi}\rangle = \sum_i c_i |\tilde{\phi}_i\rangle \quad (2.87)$$

where  $c_i$ 's are the expansion coefficients. This pseudo wavefunction is then mapped by  $T$  into:

$$T|\tilde{\Psi}\rangle = |\Psi\rangle = \sum_i c_i |\phi_i\rangle \quad (2.88)$$

By subtracting equation (2.87) from equation (2.88), we can obtain the all-electron wavefunction:

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i c_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \quad (2.89)$$

Since  $T$  is a linear operator, the coefficients  $c_i$  should be linear functionals of  $|\tilde{\Psi}\rangle$ . Projector functions probe the character of the wavefunction. The general form of a linear function can be expressed as the scalar product with some constant function, represented by  $(\langle\tilde{p}_i|)$ , known as the projector function. Further:

$$c_i = \langle\tilde{p}_i|\tilde{\Psi}\rangle \quad (2.90)$$

The pseudo partial waves form a complete basis:

$$c_i = \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij} \quad (2.91)$$

Now, the projection operator  $T$ :

$$T = 1 + \sum_i [|\phi_i\rangle - |\tilde{\phi}_i\rangle] \langle \tilde{p}_i| \quad (2.92)$$

The expectation value of any local operator  $O$  can be defined in terms of pseudo functions  $\langle \tilde{\Phi}_i | \tilde{O} | \tilde{\Phi}_i \rangle$ , where  $\tilde{O}$  is the pseudo operator:

$$\tilde{O} = T^\dagger O T = O + \sum_{ij} |\tilde{p}_i\rangle [\langle \phi_i | O | \phi_j \rangle - \langle \tilde{\phi}_i | O | \tilde{\phi}_j \rangle] \langle \tilde{p}_j| \quad (2.93)$$

This formulation makes the numerical treatment of the many-electron problem computationally efficient. The smooth pseudo wavefunctions can be represented using a relatively small plane-wave basis, while the rapidly varying all-electron partial waves are handled on atom-centered radial grids, where they are naturally expressed as products of radial functions and spherical harmonics. In this thesis, all electronic structure calculations are performed within the PAW framework using the Vienna *Ab initio* Simulation Package (VASP) [97, 98, 99].

## 2.13 Tight-Binding Method and the Linear Combination of Atomic Orbitals (LCAO)

The tight-binding (TB) method provides a computationally efficient approach to calculating the electronic structure of materials, particularly for large systems where first-principles methods like DFT become computationally expensive. It offers a good balance between accuracy and computational cost, making it a valuable tool for investigating systems with many atoms or for gaining qualitative insights into electronic structure. This section details the theoretical foundation of the tight-binding method and its connection to the Linear Combination of Atomic Orbitals (LCAO) approach.

The core idea of the tight-binding method is based on the assumption that the valence electrons in a solid are primarily localized around the atomic cores. These electrons are "tightly bound" to their respective atoms, hence the name of the method. However, these electrons can

still "hop" or "transfer" between neighboring atoms, leading to the formation of electronic bands. This hopping is mediated by the overlap of atomic orbitals on adjacent atoms.

The tight-binding method constructs the electronic wavefunctions,  $\Psi(\mathbf{r})$ , as a LCAO. This LCAO approach expresses the multi-electron wavefunction as:

$$\Psi(\mathbf{r}) = \sum_{i,\alpha} c_{i\alpha} \phi_{\alpha}(\mathbf{r} - \mathbf{R}_i) \quad (2.94)$$

where:

- $i$  runs over all atoms in the system
- $\alpha$  runs over all atomic orbitals on each atom (e.g.,  $s$ ,  $p$ ,  $d$  orbitals)
- $c_{i\alpha}$  are the expansion coefficients, which are to be determined
- $\phi_{\alpha}(\mathbf{r} - \mathbf{R}_i)$  is the atomic orbital  $\alpha$  centered on atom  $i$  at position  $\mathbf{R}_i$

The coefficients  $c_{i\alpha}$  represent the contribution of each atomic orbital to the overall wavefunction. To determine these coefficients and the corresponding energy eigenvalues, we solve the Schrödinger equation:

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2.95)$$

Substituting the LCAO expansion into the Schrödinger equation and using the variational principle leads to the generalized eigenvalue problem:

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \quad (2.96)$$

where:

- $\mathbf{H}$  is the Hamiltonian matrix, with elements  $H_{ij}^{\alpha\beta} = \langle \phi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | \hat{H} | \phi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle$  representing the interaction between atomic orbitals  $\alpha$  on atom  $i$  and  $\beta$  on atom  $j$ .
- $\mathbf{S}$  is the overlap matrix, with elements  $S_{ij}^{\alpha\beta} = \langle \phi_{\alpha}(\mathbf{r} - \mathbf{R}_i) | \phi_{\beta}(\mathbf{r} - \mathbf{R}_j) \rangle$  representing the overlap between atomic orbitals.
- $\mathbf{c}$  is the vector of expansion coefficients  $c_{i\alpha}$ .
- $E$  are the energy eigenvalues.

The Hamiltonian matrix elements,  $H_{ij}^{\alpha\beta}$ , are crucial to the tight-binding method. They are often approximated using a small number of parameters, called *hopping integrals* or *transfer integrals*, which represent the strength of the interaction between atomic orbitals on neighboring atoms. These hopping integrals can be derived from first-principles calculations (*ab initio* tight-binding), fitted to experimental data (empirical tight-binding), or obtained using the Slater-Koster parameterization.

The overlap matrix,  $S$ , accounts for the overlap between atomic orbitals. If the atomic orbitals are orthogonal (which is sometimes assumed as an approximation), the overlap matrix becomes the identity matrix, simplifying the eigenvalue problem.

Solving the generalized eigenvalue problem yields the energy eigenvalues,  $E$ , which represent the electronic band structure of the system, and the eigenvectors,  $c$ , which provide the coefficients of the LCAO expansion and thus the form of the electronic wavefunctions.

The tight-binding method, with its simplified Hamiltonian and efficient computational implementation, allows for the study of large and complex systems, providing valuable insights into their electronic properties. The accuracy of the method depends heavily on the choice of the atomic orbitals and the parameterization of the hopping integrals. While less accurate than first-principles methods, it captures the essential physics of electronic bonding and band formation, making it a powerful tool in condensed matter physics and materials science.

## 2.14 Wannier Functions and Maximally Localized Wannier Functions

Within the independent-particle approximation, the electronic ground state of a periodic system is typically expressed in terms of a set of extended Bloch states,  $\psi_{n\mathbf{k}}(\mathbf{r})$ . These states are characterized by the quantum numbers  $n$  and  $\mathbf{k}$ , which denote the band index and crystal momentum, respectively. While Bloch states are widely used in electronic structure calculations, alternative representations exist that provide different physical insights.

One such representation is the Wannier representation, which describes the electronic states in terms of localized functions labeled by  $\mathbf{R}$ , the lattice vector of the unit cell in which the function is localized, and a band-like index  $n$ . The transformation from Bloch states to Wannier functions is given by:

$$|W_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{n\mathbf{k}}\rangle, \quad (2.97)$$

where  $V$  is the unit cell volume and the integral is performed over the entire Brillouin zone.

Wannier functions provide a real-space picture of the electronic structure of a system. They offer valuable insight into the nature of chemical bonding and serve as a powerful tool in the study of dielectric properties through the modern theory of polarization. Unlike Bloch states, which are delocalized over the crystal, Wannier functions can be highly localized, making them useful in constructing tight-binding models and studying electron transport properties.

### 2.14.1 Maximally Localized Wannier Functions

The construction of Wannier functions is not unique due to the phase indeterminacy  $e^{i\phi_n(\mathbf{k})}$  of Bloch states at each wavevector  $\mathbf{k}$ . This indeterminacy is more general for a group of isolated bands, such as the valence states of an insulator, since they can undergo arbitrary unitary transformations  $U_{mn}(\mathbf{k})$  among themselves:

$$|\psi_{m\mathbf{k}}\rangle' = \sum_n U_{mn}(\mathbf{k}) |\psi_{n\mathbf{k}}\rangle. \quad (2.98)$$

To obtain well-defined and localized Wannier functions, Marzari and Vanderbilt developed an iterative procedure to refine these degrees of freedom [100]. This method minimizes the second moment of the Wannier functions around their centers, leading to *maximally localized Wannier functions* (MLWFs). The spread functional to be minimized is given by:

$$\Omega = \sum_n \left[ \langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2 \right], \quad (2.99)$$

where  $\langle \mathbf{r} \rangle_n$  represents the Wannier center of the  $n$ th function.

The Marzari-Vanderbilt method was initially designed for isolated subgroups of bands—those separated from all other bands by finite energy gaps throughout the Brillouin zone. A common example is the set of valence bands in an insulator. However, in many cases, such as for metallic systems, the bands of interest are not isolated.

For partially filled bands near the Fermi level, the relevant bands may mix with others that extend further in energy. These are referred to as entangled bands. To address this issue, an extension of the MV method, known as the disentanglement procedure, is used. This approach identifies an optimal subspace within the entangled bands and applies the Wannier localization procedure within this selected manifold.

In this thesis, the Wannier90 [101] code was employed to construct MLWFs for both isolated and entangled band structures, allowing for accurate interpolation of electronic bands and transport properties.

Wannier functions  $w_{n\mathbf{R}}(\mathbf{r})$  labeled by Bravais lattice vectors  $\mathbf{R}$  may be constructed as:

$$|w_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} \sum_{m=1}^N U_{mn}(\mathbf{k}) |\psi_{m\mathbf{k}}\rangle e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}, \quad (2.100)$$

where  $U_{mn}(\mathbf{k})$  is a unitary matrix that mixes the bands at wavevector  $\mathbf{k}$ . The Brillouin zone integral can be interpreted as a unitary transformation. Different choices of  $U(\mathbf{k})$  generate different Wannier functions, leading to different spatial spreads while always describing the same manifold.

The Marzari-Vanderbilt procedure seeks to minimize the quadratic spreads of the Wannier functions about their centers:

$$\Omega = \sum_n \langle (\mathbf{r} - \mathbf{r}_n)^2 \rangle_n = \sum_n \left[ \langle r^2 \rangle_n - |\mathbf{r}_n|^2 \right], \quad (2.101)$$

where the expectation value is defined as

$$\langle \hat{O} \rangle_n \equiv O_n = \langle w_{n0} | \hat{O} | w_{n0} \rangle. \quad (2.102)$$

This spread functional can be decomposed into two non-negative contributions:

$$\Omega = \Omega_I + \tilde{\Omega}, \quad (2.103)$$

where

$$\Omega_I = \sum_n \left[ \langle w_{n0} | r^2 | w_{n0} \rangle - \sum_{m\mathbf{R}} |\langle w_{m\mathbf{R}} | \mathbf{r} | w_{n0} \rangle|^2 \right], \quad (2.104)$$

$$\tilde{\Omega} = \sum_n \sum_{m\mathbf{R} \neq n0} |\langle w_{m\mathbf{R}} | \mathbf{r} | w_{n0} \rangle|^2. \quad (2.105)$$

It can be shown that  $\Omega_I$  is gauge invariant, i.e., insensitive to changes in the matrices  $U(\mathbf{k})_{mn}$  [102]. Therefore, minimizing the spread functional for an isolated set of bands is equivalent to minimizing  $\tilde{\Omega}$ .

### 2.14.1.1 Reciprocal-Space Formulation

As shown by Blount [103], matrix elements of the position operator between Wannier functions may be expressed in reciprocal space as:

$$\langle w_{n\mathbf{R}} | \mathbf{r} | w_{m0} \rangle = i \frac{V}{(2\pi)^3} \int e^{i\mathbf{k}\cdot\mathbf{R}} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{m\mathbf{k}} \rangle d\mathbf{k}, \quad (2.106)$$

$$\langle w_{n\mathbf{R}} | r^2 | w_{m0} \rangle = - \frac{V}{(2\pi)^3} \int e^{i\mathbf{k}\cdot\mathbf{R}} \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}}^2 | u_{m\mathbf{k}} \rangle d\mathbf{k}, \quad (2.107)$$



where  $u_{n\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r})$  is the periodic part of the Bloch function.

To numerically evaluate these integrals, the Brillouin zone is discretized on a uniform Monkhorst-Pack mesh [104]. The gradient and Laplacian operators can be approximated by finite-difference formulas on the  $\mathbf{k}$ -space mesh. If  $f(\mathbf{k})$  is a smooth function, then

$$\nabla_{\mathbf{k}}f(\mathbf{k}) = \sum_{\mathbf{b}} \omega_{\mathbf{b}} \mathbf{b} [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})], \quad (2.108)$$

$$\langle f(\mathbf{k}) | \nabla_{\mathbf{k}}^2 | f(\mathbf{k}) \rangle = \sum_{\mathbf{b}} \omega_{\mathbf{b}} [f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k})]^2, \quad (2.109)$$

where  $\mathbf{b}$  are the displacement vectors connecting  $\mathbf{k}$  to its nearest neighbors and  $\omega_{\mathbf{b}}$  are weight factors.

The overlap matrix elements

$$M_{mn}(\mathbf{k}, \mathbf{b}) = \langle u_{m\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle \quad (2.110)$$

allow us to express the two components of the spread functional:

$$\Omega_I = \frac{1}{N_{\mathbf{k}p}} \sum_{\mathbf{k}, \mathbf{b}} \omega_{\mathbf{b}} \sum_{m=1}^N \left[ 1 - \sum_{n=1}^N |M_{mn}(\mathbf{k}, \mathbf{b})|^2 \right], \quad (2.111)$$

$$\tilde{\Omega} = \frac{1}{N_{\mathbf{k}p}} \sum_{\mathbf{k}, \mathbf{b}} \omega_{\mathbf{b}} \left[ \sum_n (-\text{Im} \ln M_{nn}(\mathbf{k}, \mathbf{b}) - \mathbf{b} \cdot \bar{\mathbf{r}}_n)^2 + \sum_{m \neq n} |M_{mn}(\mathbf{k}, \mathbf{b})|^2 \right]. \quad (2.112)$$

Here,  $N_{\mathbf{k}p}$  is the number of  $\mathbf{k}$ -points, and the Wannier center is given by:

$$\bar{\mathbf{r}}_n = -\frac{1}{N_{\mathbf{k}p}} \sum_{\mathbf{k}, \mathbf{b}} \omega_{\mathbf{b}} \mathbf{b} \text{Im} \ln M_{nn}(\mathbf{k}, \mathbf{b}). \quad (2.113)$$

Using these expressions, the gradient of the spread functional with respect to infinitesimal unitary rotations of  $\psi_{n\mathbf{k}}(\mathbf{r})$  can be computed. This enables an optimization of  $U_{mn}(\mathbf{k})$  via steepest descent or conjugate-gradient minimization.

Furthermore,  $\tilde{\Omega}$  can be decomposed into diagonal and off-diagonal parts:

$$\tilde{\Omega} = \Omega_D + \Omega_{OD}, \quad (2.114)$$

where

$$\Omega_D = \sum_n \sum_{\mathbf{R} \neq 0} |\langle w_{n\mathbf{R}} | \mathbf{r} | w_{n0} \rangle|^2, \quad (2.115)$$

$$\Omega_{OD} = \sum_{m \neq n} \sum_{\mathbf{R}} |\langle w_{m\mathbf{R}} | \mathbf{r} | w_{n0} \rangle|^2. \quad (2.116)$$

These formulations form the basis of the iterative Wannierization process implemented in Wannier90.

# Reversible switching of anomalous valley hall effect to quasi-half-valley metal state in 2D magnetic MXenes: A case study of Cr<sub>2</sub>CSF

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## 3.1 Introduction

Valley, the energy extreme of valence or conduction bands, in a two-dimensional (2D) lattice can be used as a degree of freedom for the carriers in condensed matter materials [105, 106]. Given the considerable separation in the momentum space, scattering between these valleys can be effectively suppressed, allowing electrons or holes to be manipulated for a long period. Therefore, the valley index is robust against the long-range impurity scattering [107, 34, 108]. Among 2D materials, the transition metal dichalcogenides have acquired significant attention due to their exceptional and tunable properties [109, 110, 111, 112, 113, 114, 115]. To make use of the valley index of these nonmagnetic materials as an information carrier, it is essential to remove the energy degeneracy between inequivalent valleys by breaking the time-reversal symmetry, a process known as valley polarization [116]. Valley polarization involves selectively populating carriers in specific valleys, offering a unique means of encoding and manipulating information. This leads to applications in valleytronic devices, where the valley index can be used to represent and process information, leading to advancements in low-power electronics, quantum computing, and optoelectronic devices [117, 118, 119, 120]. To effectively exploit these applications, materials exhibiting spontaneous valley polarization are highly sought after. Subsequently, attempts have been made to extrinsically induce valley polarization by employing various approaches, such as optical pumping [111, 112], application of magnetic fields [113], utilization of magnetic substrates [114], and introduction of magnetic doping [115]. Nevertheless, these methods are quite fragile and often come at the cost of altering the intrinsic

energy band structures and crystal configurations [113, 121].

Therefore, to conquer these challenges, it is urgent to seek materials showing anomalous valley Hall (AVH) effect rooted in spontaneous valley polarization. Indeed, there has been an exciting development in this field in the form of ferrovalley (FV) semiconductors, which break both time-reversal and space-inversion symmetries. These FV materials exhibit this unique characteristic, offering an unprecedented solution to the aforementioned challenges and hold significant potential for advancements in valleytronics applications. However, such materials are currently scarce and only a handful of potential systems have been suggested which include 2H-VSe<sub>2</sub> [122], 2H-FeCl<sub>2</sub> [123], Nb<sub>3</sub>I<sub>8</sub> [124], VSi<sub>2</sub>N<sub>4</sub> [125], and GdI<sub>2</sub> [126]. Nevertheless, most of these existing systems suffer from in-plane magnetization [122, 124, 126], which substantially hinders the emergence of natural valley polarization. Therefore, there exists a pressing need to explore new candidates that exhibit spontaneous valley polarization, particularly those inherently characterized by robust out-of-plane magnetization.

MXenes, which are 2D transition metal carbon and nitrogen compounds, have gained much attention following their successful experimental preparation [127, 128, 129]. The general formula of MXene can be written as  $M_{n+1}X_nT$  ( $n = 1 - 3$ ), where M denotes a transition metal; X denotes C or N; T denotes surface terminations like Cl, F, O, OH [130]. They have been investigated in applications like nanocomposites and hybrid materials [131, 132]. More recently, they have been proposed in valleytronics and only a few systems have been studied for their valley-dependent properties [133, 134]. Ferromagnetic (FM) MXenes like Cr<sub>2</sub>C display an adjustable magnetism upon symmetric or asymmetric surface functionalization along with high Curie or Néel temperatures [135].

In this study, we have presented the discovery of various intrinsic valley-related Hall effects in 2D Cr<sub>2</sub>CSF MXene based on first-principles calculations. Our findings have revealed that this material acts as a FM semiconductor, with band edges situated at the +K and -K points. Notably, the material exhibits significant out-of-plane magnetization with a large magnetic anisotropy energy (MAE). This, combined with time-reversal symmetry breaking, results in spontaneous valley polarization, as corroborated by SOC model Hamiltonian studies. We find that this spontaneous valley polarization facilitates the anomalous valley Hall (AVH) effect, enabling effective charge carrier separation under in-plane electric fields and electron doping. Moreover, uniaxial strain yields quasi-half valley metal (QHVM) phase in Cr<sub>2</sub>CSF monolayer.

## 3.2 Methodology

The calculations are performed at density functional theory (DFT) [63, 64] level with the projector augmented wave (PAW) [85, 86] method implemented in Vienna *ab initio* Simulation Package (VASP) [136] code. The exchange-correlation interactions are treated by generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional [80]. The cutoff energy of 520 eV is used for the plane wave basis set such that the total energy calculations are converged within  $10^{-5}$  eV. The vacuum in  $z$ -direction is set to 30 Å to avoid artificial interactions caused by the periodic boundary conditions. The  $11 \times 11 \times 1$   $k$ -grid is used to sample the 2D Brillouin zone. All the structural parameters are fully optimized until the Hellmann-Feynman forces are smaller than 1 meV/Å. Considering the strong correction effect for the localized 3d electrons of Cr atoms, the GGA+U method is employed [137]. This is implemented using Dudarev et al.'s rotationally invariant approach where only the effective U ( $U_{eff}$ ) based on the difference between the on-site Coulomb interaction parameter and exchange parameters is meaningful [138]. Following the previous works [139, 140], the U value for Cr 3d orbitals is chosen as 3.5 eV. Hybrid functional Heyd-Scuseria Ernzerhof (HSE06) is also used to confirm the results of GGA+U calculations [141]. The dynamical stabilities are calculated using density functional perturbation theory using PHONOPY code [142] with a  $6 \times 6 \times 1$  supercell. To calculate the Curie temperature, Monte Carlo (MC) simulations are performed on a  $16 \times 16$  2D honeycomb lattice with  $10^4$  steps for each temperature, using the open-access software MCSOLVER based on the Wolff algorithm of the classical Heisenberg model [143]. Berry curvatures are obtained from the maximally localized Wannier functions as implemented in WANNIER90 [101].

## 3.3 Results and Discussions

### 3.3.1 Structure and magnetism

Cr<sub>2</sub>CSX (X = F, O, H, Cl, Br, and I) can be surface engineered by functionalizing Cr<sub>2</sub>C MXene in different ways. This results in four distinct types of structures as detailed in Fig. 5.6 [135]. Type II is the most energetically stable configuration among all Janus Cr<sub>2</sub>CSX MXenes [see 3.1]. We have taken Cr<sub>2</sub>CSF as a prototype for studying the valley properties because of its higher value of spontaneous valley polarization and other promising characteristics which will

be discussed in the subsequent sections. The energetic stability of Type II structure of  $\text{Cr}_2\text{CSF}$  has also been confirmed by HSE06 functional calculations [see 3.2]. Each unit cell of  $\text{Cr}_2\text{CSF}$  contains one C, one S, one F, and two Cr atoms, which are stacked in the sequence of F-Cr-C-Cr-S as shown in Fig. 5.1(a). It exhibits a hexagonal lattice structure characterized by the  $P3m1$  space group [Fig. 5.1(b)]. To probe the bonding nature of  $\text{Cr}_2\text{CSF}$  MXene, we have calculated the electron localization function within the plane encompassing F-Cr-C-Cr-S. Fig. 5.1(c) suggests an ionic bonding character for all the bonds as the electrons are predominantly localized around the atoms.

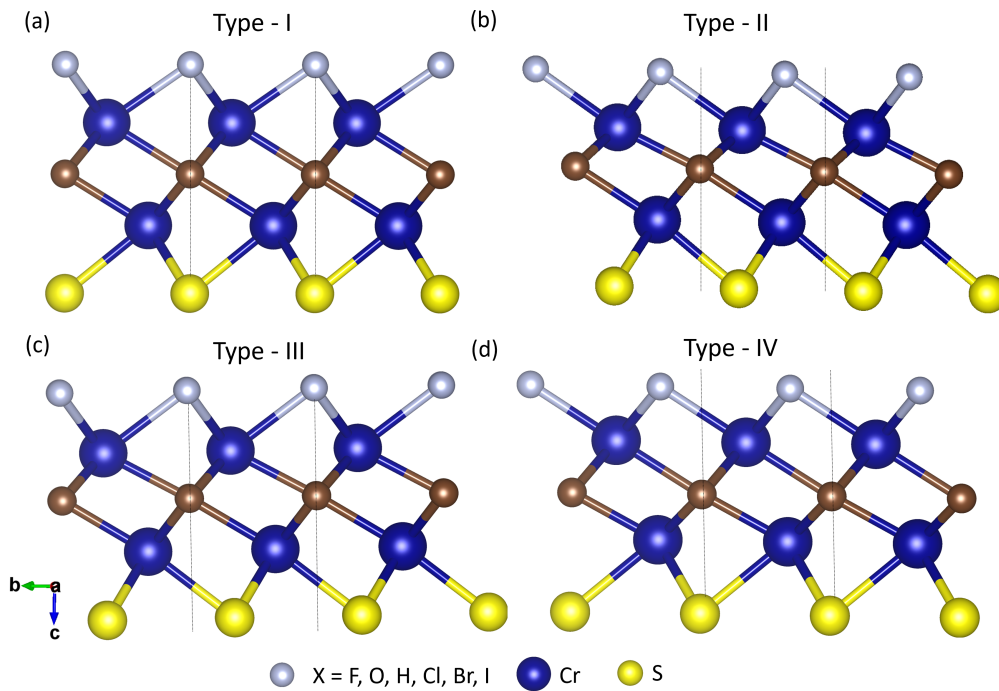


Figure 3.1: Crystal structure of (a) Type I, (b) Type II, (c) Type III, and (d) Type IV  $\text{Cr}_2\text{CSX}$  (X = F, O, H, Cl, Br, I) MXene.

Table 3.1: Four types of functionalization adsorption sites on Cr<sub>2</sub>CSX MXenes. The most stable type has been set up to zero for each MXene (in units of eV).

| MXenes               | Type I | Type II | Type III | Type IV |
|----------------------|--------|---------|----------|---------|
| Cr <sub>2</sub> CSH  | 0.83   | 0       | 0.63     | 0.19    |
| Cr <sub>2</sub> CSF  | 0.72   | 0       | 0.58     | 0.22    |
| Cr <sub>2</sub> CSCl | 0.53   | 0       | 0.14     | 0.05    |
| Cr <sub>2</sub> CSBr | 0.37   | 0       | 0.02     | 0.06    |
| Cr <sub>2</sub> CSI  | 0.46   | 0       | 0.25     | 0.26    |
| Cr <sub>2</sub> CSO  | 1.13   | 0       | 0.87     | 0.05    |

Table 3.2: Energies of different types of configurations of Cr<sub>2</sub>CSF MXene using HSE06 functional. The most stable type has been set up to zero (in units of eV).

| MXene    | Cr <sub>2</sub> CSF |
|----------|---------------------|
| Type I   | 1.31                |
| Type II  | 0                   |
| Type III | 1.61                |
| Type IV  | 0.67                |

Afterward, the absence of negative frequencies in the phonon dispersion plot of Cr<sub>2</sub>CSF confirms the dynamical stability [Fig. 5.2(a)]. The spin-polarized charge density for Cr<sub>2</sub>CSF is illustrated in Fig. 5.2(b), depicting the spontaneous spin polarization. Further, to ascertain the preferred magnetic ground state configuration of Cr<sub>2</sub>CSF MXene, we have analyzed the FM and three antiferromagnetic (AFM) states [Fig. 5.7]. Cr<sub>2</sub>CSF prefers the FM coupling over AFM couplings which is 643, 533, and 833 meV lower in energy compared to the AFM1, AFM2 and AFM3 couplings, respectively. The valence electronic configuration of the Cr atom is 3d<sup>5</sup>4s<sup>1</sup>. According to local symmetry of the crystal field surrounding the Cr magnetic ions, the five fold degenerate 3d orbitals split into three categories i.e.,  $A'(d_{z^2})$ ,  $E'(d_{yz} + d_{xz})$  and  $E''(d_{x^2-y^2} + d_{xy})$ , as shown in Fig. 5.2(c) [144]. Upon functionalization, both the Cr atoms are coordinated to different atoms. Cr<sub>F</sub> atoms (Cr atom bound to F atom) have the electronic configuration of 3d<sup>3</sup>4s<sup>0</sup> while the electronic configuration of Cr<sub>S</sub> atoms (Cr atom bound to S atom) is 3d<sup>2</sup>4s<sup>0</sup>. As anticipated, the calculated magnetic moment per unit cell for Cr<sub>2</sub>CSF is 5  $\mu_B$ , where  $\mu_B$  is Bohr magneton. Here, Cr<sub>F</sub> and Cr<sub>S</sub> atoms have the magnetic moment

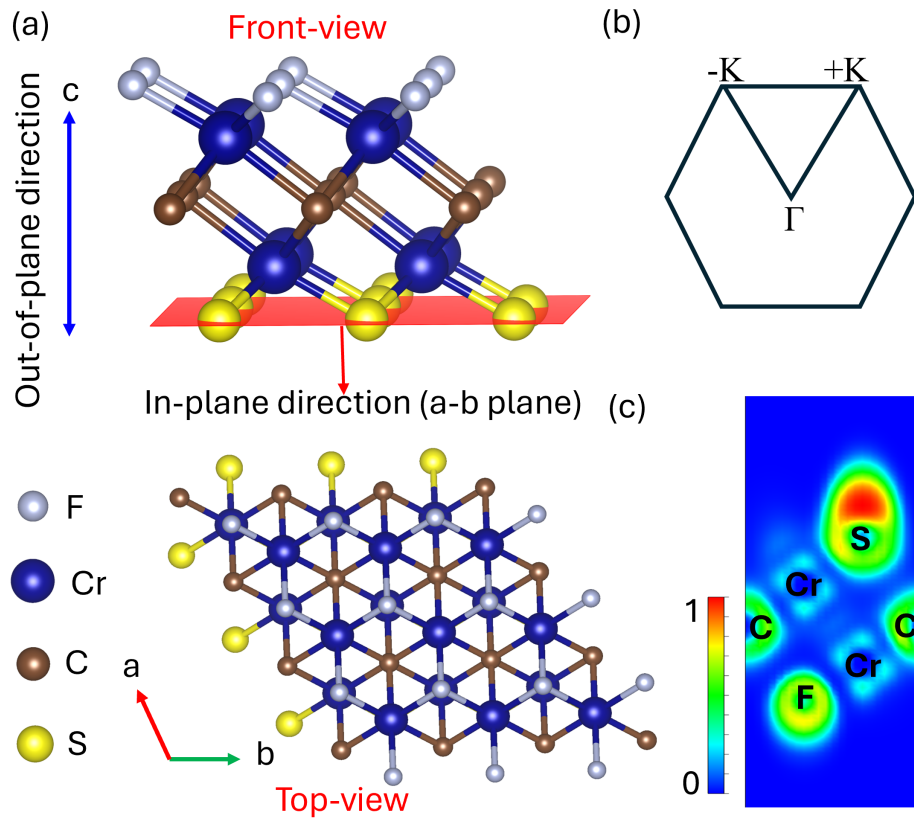


Figure 3.2: (a) Side and top views of Cr<sub>2</sub>CSF (Here c-direction represents out-of-plane direction, and a-b plane represents in-plane direction). (b) Hexagonal 2D Brillouin zone. (c) Electron localization function map of Cr<sub>2</sub>CSF, which is renormalized to values between 0 for charge depletion and 1 for charge accumulation.

$2.9 \mu_B$  and  $2.7 \mu_B$ , respectively. This preferred FM coupling in Cr<sub>2</sub>CSF is attributed to the double-exchange mechanism [135]. This mechanism explains how magnetic interactions arise between ions in different oxidation states, through the transfer of electrons between these ions. In Cr<sub>2</sub>CSF, the presence of chromium ions in multiple oxidation states facilitates the double-exchange process. Electrons hop between Cr ions with different valences, which enhances the alignment of their magnetic moments. This electron transfer leads to a FM coupling, resulting in a net macroscopic magnetic moment.

Furthermore, the MAE of Cr<sub>2</sub>CSF MXene has been calculated to determine its magnetization easy axis. MAE is defined as the energy difference between the in-plane and the out-of-plane magnetization:  $\text{MAE} = E_{x/y} - E_z$ . The negative/positive MAE means an easy axis along the in-plane/out-of-plane direction. Due to  $C_{3v}$  point group symmetry, energy is degenerate for magnetization along arbitrary in-plane direction. Therefore, we have chosen in-plane

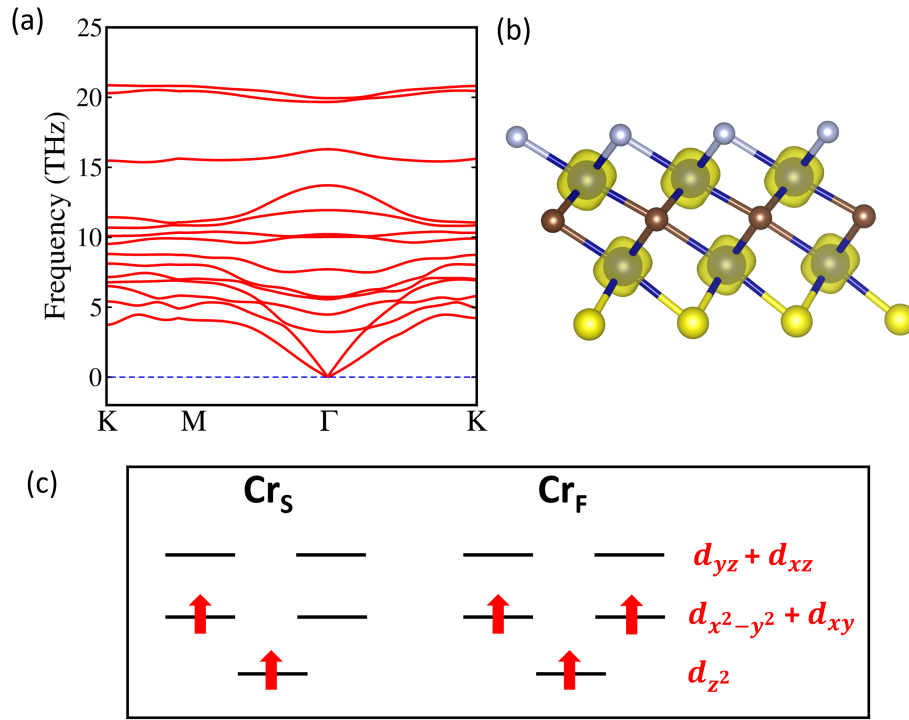


Figure 3.3: (a) Phonon dispersion map of Cr<sub>2</sub>CSF. (b) Spin-polarized charge densities on Cr<sub>2</sub>CSF MXene, where spin-up density is shown in yellow. (c) The predicted occupations of *d* orbitals of Cr<sub>S</sub> and Cr<sub>F</sub> atoms.

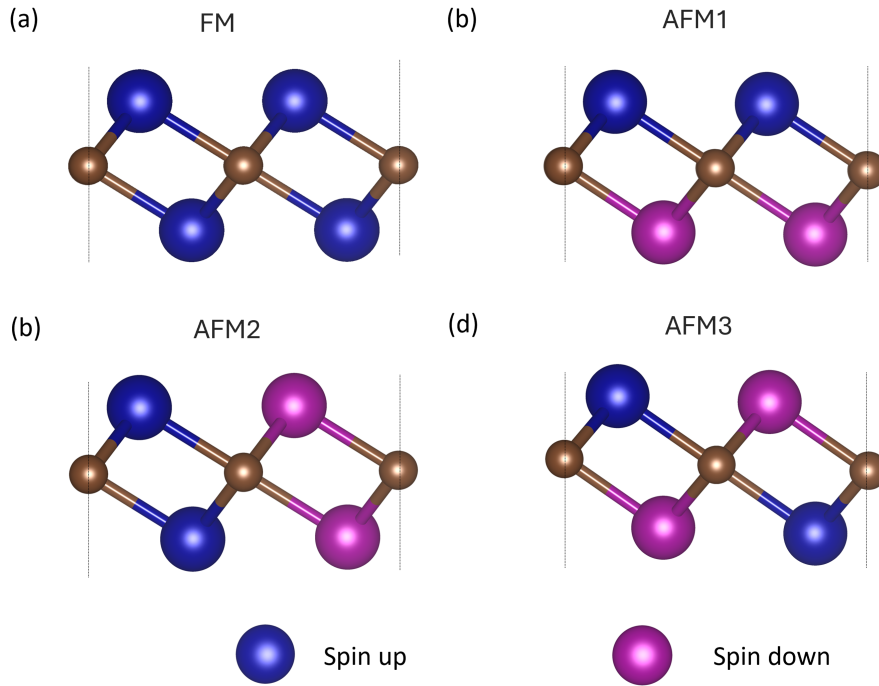


Figure 3.4: Crystal structure of (a) one FM and (b), (c), (d) three AFM states of Cr<sub>2</sub>C MXene.



Table 3.3: Energies of different types of magnetic configurations of Cr<sub>2</sub>CSF MXene (1×2×1 supercell) using HSE06 functional. The most stable type has been set up to zero (in units of eV).

| MXene | Cr <sub>2</sub> CSF |
|-------|---------------------|
| FM    | 0                   |
| AFM1  | 0.9                 |
| AFM2  | 1.55                |
| AFM3  | 0.95                |

direction to be along  $x$  direction [145, 146]. The MAE for monolayer Cr<sub>2</sub>CSF is calculated to be 1.16 meV per unit cell, suggesting that its easy axis is along the out-of-plane direction. This substantially high MAE value suggests that the out-of-plane magnetization is robust. This stability is advantageous for establishing the long-range magnetic order, and is tantalizing for realizing the spontaneous valley polarization. The observed value of MAE in our material exceeds that of Ni, Fe, and Co, which typically have MAE values of the order 1  $\mu$ eV per unit cell [147] and is higher than that for VSi<sub>2</sub>P<sub>4</sub> [148], Cr<sub>2</sub>Se<sub>3</sub> [140], and Cr<sub>2</sub>S<sub>3</sub> [149]. Evidently, in materials suffering from in-plane magnetization, achieving out-of-plane magnetization through external methods is challenging [150, 114, 151]. However, in Cr<sub>2</sub>CSF no such external means are required, making it more superior for practical applications. Moreover, Curie temperature of Cr<sub>2</sub>CSF is estimated based on the Ising model using DFT-derived spin exchange parameters. The spin Hamiltonian can be described as follows [135]:

$$H = J_1 \sum_{\langle i,j \rangle} S_i S_j + J_2 \sum_{\langle i,k \rangle} S_i S_k + J_3 \sum_{\langle i,l \rangle} S_i S_l, \quad (3.1)$$

where  $J_1, J_2, J_3$  are the exchange coupling constants for nearest ( $\langle i, j \rangle$ ), next-nearest ( $\langle i, k \rangle$ ), and next-next-nearest ( $\langle i, l \rangle$ ) neighbors, respectively, and  $S_i$  represents the spin variable at site  $i$ . By mapping the DFT energies to the Hamiltonian,  $J_1, J_2$ , and  $J_3$  can be calculated from the following equations:

$$\begin{aligned} E_{\text{FM}} &= E_0 - (3J_1 + 6J_2 + 3J_3) S^2, \\ E_{\text{AFM1}} &= E_0 - (-3J_1 + 6J_2 - 3J_3) S^2, \\ E_{\text{AFM2}} &= E_0 - (J_1 - 2J_2 - 3J_3) S^2, \\ E_{\text{AFM3}} &= E_0 - (-J_1 - 2J_2 + 3J_3) S^2. \end{aligned} \quad (3.2)$$

The Curie Temperature for Cr<sub>2</sub>CSF MXene is estimated using the Ising model with DFT-derived spin exchange parameters. Figure 5.8 illustrates the dependence of specific heat ca-

Table 3.4: Coupling constants  $J_1$ ,  $J_2$  and  $J_3$  (in units of meV) along with the Curie temperature (in K).

| MXene | Cr <sub>2</sub> CSF |
|-------|---------------------|
| $J_1$ | 29.16               |
| $J_2$ | 75                  |
| $J_3$ | 43.05               |
| T     | 896                 |

capacity on temperature. The simulated  $T_c$  is as high as 896 K, which is well above the room temperature.

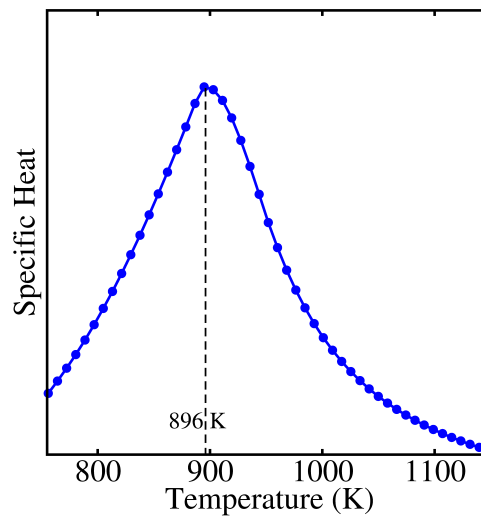


Figure 3.5: Dependence of specific heat capacity on the temperature.

### 3.3.2 Electronic properties

We have further turned to the electronic structure calculations of Cr<sub>2</sub>CSF MXene. Figure 5.3(a) presents the band structure of Cr<sub>2</sub>CSF. Because of the intrinsic spin-polarization, the spin-up and spin-down channels split significantly. The bands near Fermi level are contributed by spin-down states in the valence band and spin-up states in the conduction band. As the extrema of conduction and valence bands arise from opposite spin channels, it is therefore called a bipolar FM semiconductor [152]. Cr<sub>2</sub>CSF has an indirect band gap of 0.34 eV. The conduction band minimum (CBm) is situated at +K and −K points, giving rise to a pair of energetically equivalent valleys within the conduction band. In case of the valence band, although the valence band maximum (VBM) is located at the  $\Gamma$  point, local extrema at the +K and −K points are also formed, providing the valence band with a pair of degenerate valleys. Both of these valley

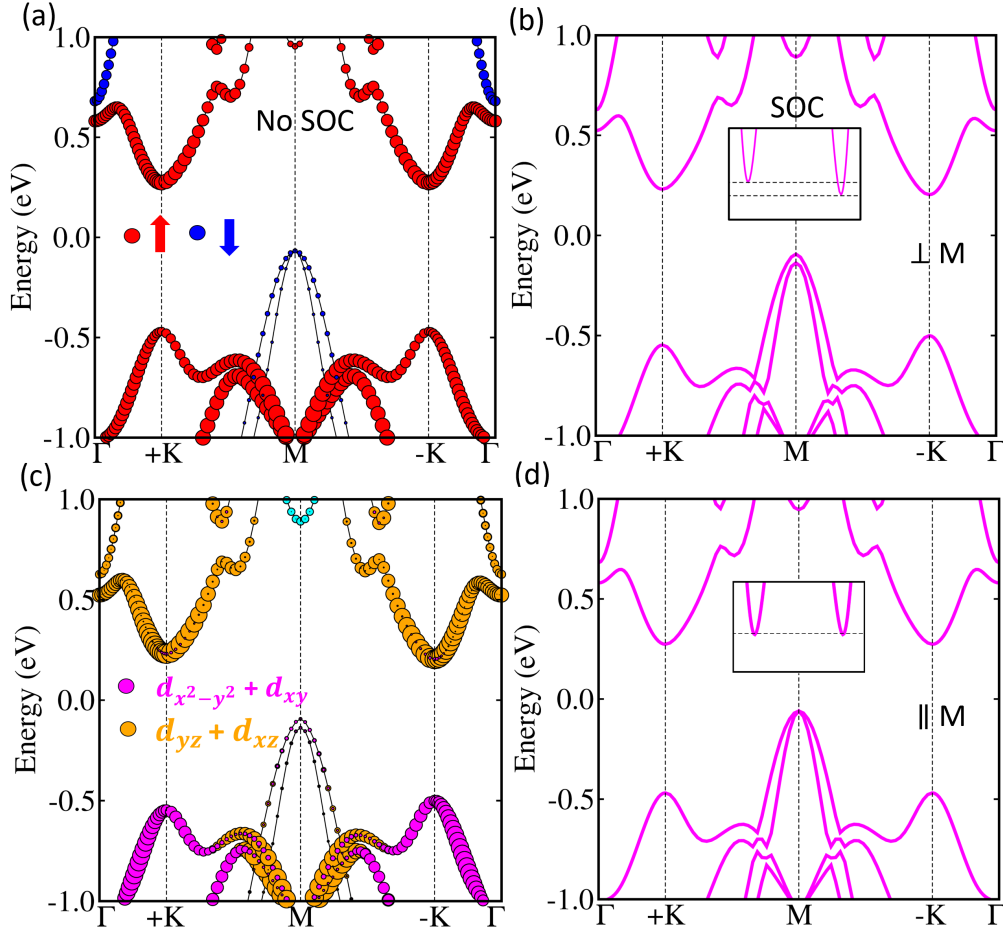


Figure 3.6: Band structure of  $\text{Cr}_2\text{CSF}$  (a) without SOC, (b) with SOC for out-of-plane magnetization (inset is showing the valley splitting in conduction band). (c) Orbital projected band structure for Cr atom. (d) Band structure for in-plane magnetization with SOC.

pairs originate from the spin-up channels. When SOC is included, the valley at  $+K$  shifts upwards and  $-K$  shifts downwards, producing a spontaneous valley polarization of 27.1 meV in the conduction band (see Fig. 5.3(b)). However, in the valence band, the valley at  $+K$  shifts downwards and  $-K$  shifts upwards, leading to a spontaneous valley polarization of 46.8 meV and giving a total valley polarization of 73.9 meV. Nevertheless, the valleys in valence band lie far away from the Fermi level, rendering them not suitable for practical applications. Therefore, we have solely focused on the pair of valleys in the conduction band. Alongside, we have plotted the band structures for  $\text{Cr}_2\text{CSX}$  ( $X = \text{O}, \text{H}, \text{Cl}, \text{Br}, \text{and I}$ ) [see Fig. 3.7].  $\text{Cr}_2\text{CSCl}$  and  $\text{Cr}_2\text{CSI}$  show a small valley polarization of 19.8 meV and 0.8 meV, respectively, in the conduction band, whereas no significant valley polarization has been observed for  $\text{Cr}_2\text{CSO}$ ,  $\text{Cr}_2\text{CSI}$  and  $\text{Cr}_2\text{CSH}$ .

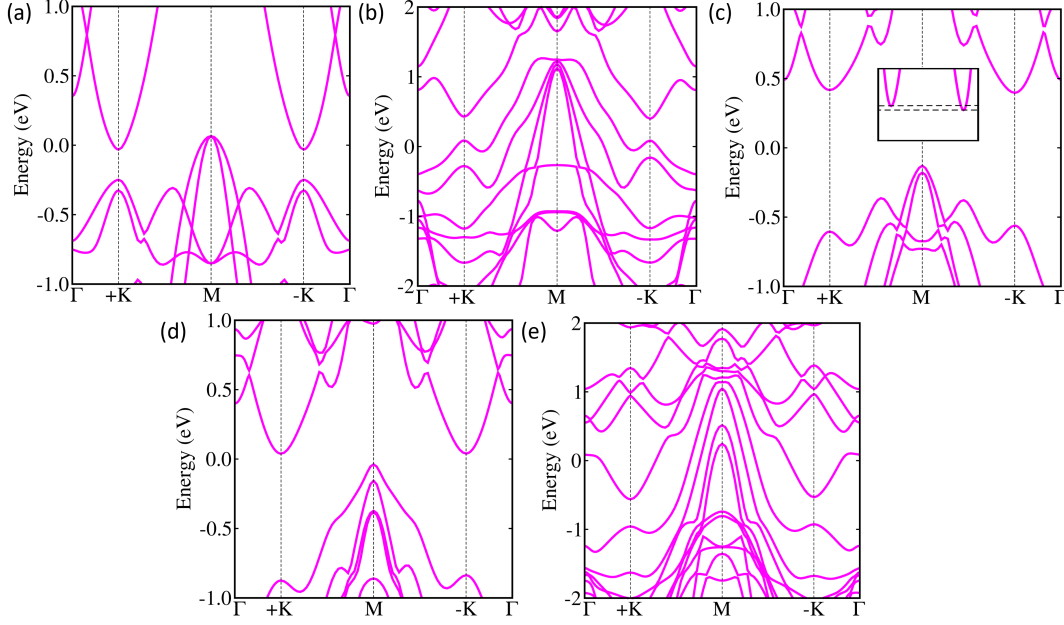


Figure 3.7: Band structure of (a) Cr<sub>2</sub>CSH, (b) Cr<sub>2</sub>CSO, (c) Cr<sub>2</sub>CSCl, (d) Cr<sub>2</sub>CSBr, (e) Cr<sub>2</sub>CSI MXene in presence of SOC.

### 3.3.3 SOC Hamiltonian model

The spontaneous valley polarization in the monolayer Cr<sub>2</sub>CSF arises from the interplay of time-reversal symmetry breaking, inversion symmetry breaking, and strong SOC interaction. In addition to above, the out-of-plane magnetic anisotropy is essential for spontaneous polarization of valleys [140]. To gain a deeper understanding of the influence of magnetization orientation on valley polarization, we have employed a simple model to describe the SOC term as follows [153, 154]:

$$\hat{H}_{\text{SOC}}^0 + \hat{H}_{\text{SOC}}^1 = \lambda \hat{L} \cdot \hat{S} \quad (3.3)$$

Here,  $\hat{H}_{\text{SOC}}^0$  represents the interaction between identical spin states, while  $\hat{H}_{\text{SOC}}^1$  represents the interaction between opposite spin states.  $\hat{L}$  and  $\hat{S}$  represent the operators for orbital angular momentum and spin angular momentum, respectively. Further, due to the FM spin splitting, the valleys are predominantly contributed by either the spin-up or spin-down states. In Cr<sub>2</sub>CSF, both the valleys of conduction band are contributed by spin-up states only and interactions between opposite spin states have a negligible effect on the valleys. Therefore, we have focused on same spin states and  $\hat{H}_{\text{SOC}}^1$  has been neglected.  $\hat{H}_{\text{SOC}}^0$  can be expressed as [154, 155]:

$$\hat{H}_{\text{SOC}}^0 = \lambda \hat{S}_{z'} \left( \hat{L}_z \cos \theta + \frac{1}{2} \hat{L}_+ e^{-i\phi} \sin \theta + \frac{1}{2} \hat{L}_- e^{i\phi} \sin \theta \right) \quad (3.4)$$

Here, the magnetization is out-of-plane, i.e.,  $\theta = 0$  (see Fig. 3.8). Therefore, the above equation is simplified to:

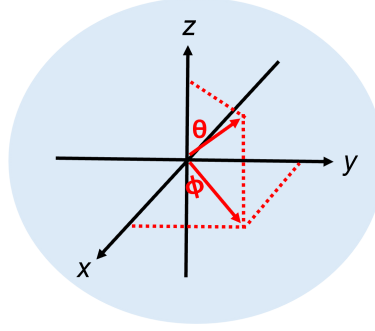


Figure 3.8: Visual representation of polar angles  $\theta$  and  $\phi$ .

$$\hat{H}_{\text{SOC}}^0 = \lambda \hat{S}_z \hat{L}_z \quad (3.5)$$

To proceed further, we have seen in Fig. 5.3 (c) that the valleys in conduction band are predominantly composed of  $d_{xz}$  and  $d_{yz}$  orbitals of the Cr atoms. Therefore, the basis wave vectors have been chosen in the following form:

$$|\phi_c^\tau\rangle = \frac{1}{\sqrt{2}} (|d_{xz}\rangle + i\tau|d_{yz}\rangle) \otimes |\uparrow\rangle \quad (3.6)$$

where c represents the conduction band and  $\tau = \pm 1$  corresponds to  $+K/-K$  valley. The energy level at  $+K/-K$  can be denoted by following formula:

$$\begin{aligned} E_c^{+K/-K} &= \langle \phi_c^\tau | \hat{H}_{\text{SOC}}^0 | \phi_c^\tau \rangle \\ &= \frac{i\tau}{2} (\langle d_{xz}, \uparrow | \hat{H}_{\text{SOC}}^0 | d_{yz}, \uparrow \rangle \\ &\quad - \langle d_{yz}, \uparrow | \hat{H}_{\text{SOC}}^0 | d_{xz}, \uparrow \rangle) \\ &= \frac{i\tau}{2} \lambda \beta (\langle d_{xz} | \hat{L}_z | d_{yz} \rangle - \langle d_{yz} | \hat{L}_z | d_{xz} \rangle) \end{aligned} \quad (3.7)$$

where  $\beta = \langle \uparrow | \hat{S}_z | \uparrow \rangle$ ,  $\hat{L}_z | d_{xz} \rangle = i | d_{yz} \rangle$ , and  $\hat{L}_z | d_{yz} \rangle = -i | d_{xz} \rangle$ . Therefore, the valley polarization in the conduction band of  $\text{Cr}_2\text{CSF}$  is obtained through

$$\begin{aligned} \Delta E_c &= E_c^{+K} - E_c^{-K} \\ &= i\lambda\beta \langle d_{xz} | \hat{L}_z | d_{yz} \rangle - i\lambda\beta \langle d_{yz} | \hat{L}_z | d_{xz} \rangle \\ &= 2\lambda\beta \end{aligned} \quad (3.8)$$

On the other hand, if magnetic orientation is in-plane, i.e.,  $\theta = \frac{\pi}{2}$ , we get:

$$\hat{H}_{\text{SOC}}^0 = \lambda \hat{S}_{z'} \left( \frac{1}{2} \hat{L}_+ e^{-i\phi} + \frac{1}{2} \hat{L}_- e^{i\phi} \right) \quad (3.9)$$

In this case,  $\Delta E_c = 0$ , i.e., no spontaneous valley polarization. To show this, we have plotted the band structure of Cr<sub>2</sub>CSF by taking the magnetization direction as in-plane and no valley polarization has been observed in this case [see Fig. 5.3(d)]. Therefore, we can conclude that SOC and out-of-plane magnetic orientation are necessary for achieving spontaneous valley polarization. Additionally, the valleys of valence band are also discussed in section of VII SM.

Berry curvature has been an invaluable tool for examining the Hall effect. Particularly in hexagonal systems where space inversion symmetry is broken, it has been observed that charge carriers within the  $+K$  and  $-K$  valleys tend to acquire a non-zero Berry curvature. Consequently, when time-reversal symmetry is also broken, an interesting characteristic emerges: a contrasting feature between valleys becomes apparent. Therefore, to understand the valley-related properties of Cr<sub>2</sub>CSF we have calculated the Berry curvature using Kubo formula [156]:

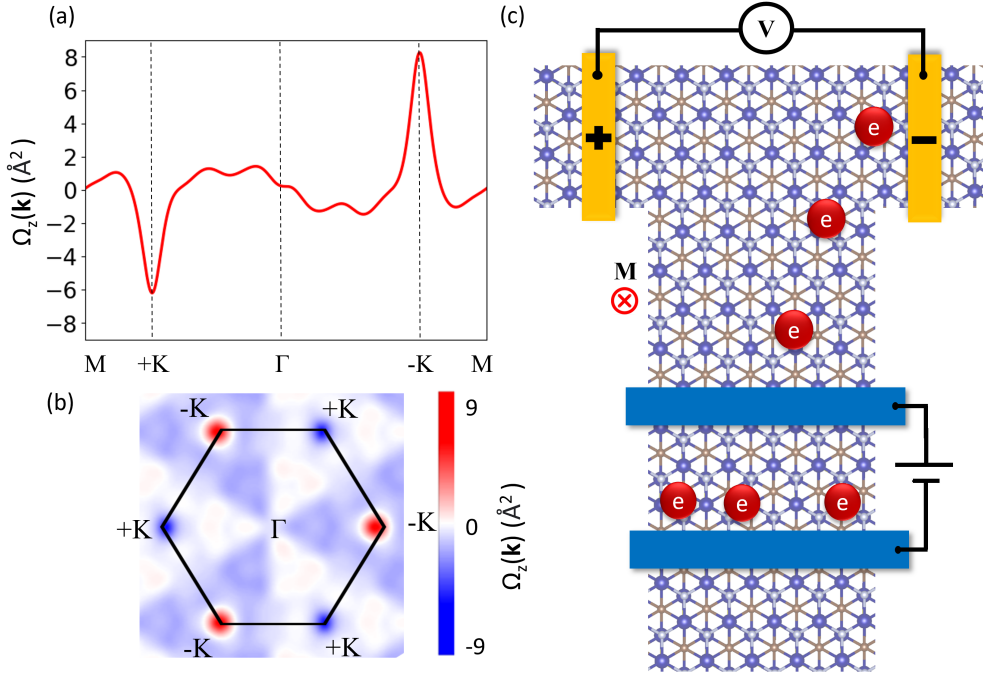


Figure 3.9: (a) Berry curvature of Cr<sub>2</sub>CSF along the high symmetry path. (b) Contour diagram of Berry curvature. (c) Schematic of AVH in Cr<sub>2</sub>CSF under the in-plane electric field and electron doping showing the movement of electrons towards right edge of the sample.

$$\Omega(\mathbf{K}) = - \sum_n \sum_{m \neq n} f_n \frac{2 \text{Im} \langle \psi_{nk} | v_x | \psi_{mk} \rangle \langle \psi_{mk} | v_y | \psi_{nk} \rangle}{(E_n - E_m)^2} \quad (3.10)$$

Here,  $f_n$  is the Fermi-Dirac distribution function,  $E_n$  represents the eigenvalue of the Bloch state  $|\psi_{nk}\rangle$  and  $\hat{v}_x/\hat{v}_y$  are the velocity operator components.

The Berry curvature of monolayer  $\text{Cr}_2\text{CSF}$  as a curve along the high-symmetry points, and as a contour map over the 2D Brillouin zone is shown in Fig. 5.4(a) and (b), respectively. At the high symmetry points  $+K$  and  $-K$ , the Berry curvature exhibits opposite signs, with absolute magnitudes of  $-6.21 \text{ \AA}^2$  and  $8.25 \text{ \AA}^2$  at  $+K$  and  $-K$ , respectively. Consequently, the integral of Berry curvature around one valley differs from that around the other, leading to measurable Hall conductivity, known as the AVH effect. The anomalous Hall effect in FV materials is termed as AVH effect because an additional component of Hall conductivity is added which occurs due to the spontaneous valley polarization. AVH can be observed in  $\text{Cr}_2\text{CSF}$  under the effect of an in-plane electric field. Under this field, the Bloch electrons will gain an anomalous velocity, which is equal to the cross product of in-plane electric field and Berry curvature i.e.,  $v \sim E \times \Omega(\mathbf{k})$  [157, 35, 158]. Now, via electron doping the Fermi level can be shifted to an energy position between  $-K$  valley and  $+K$  valley. The spin-up electrons in  $-K$  valley will start moving with anomalous velocity and get accumulated on the right side of the sample as seen in schematic Fig. 5.4(c). Further, based on the formula [146]:

$$\sigma_{xy} = -\frac{e^2}{\hbar} \int_{\text{BZ}} \frac{d^2k}{(2\pi)^2} \Omega_n(\mathbf{k}) \quad (3.11)$$

we have calculated the anomalous Hall conductivity ( $\sigma_{xy}$ ). As illustrated in Fig. 3.10, when the Fermi level is tuned between  $+K$  and  $-K$  valleys in the conduction band, a valley-polarized Hall conductivity emerges (highlighted by the shaded region), confirming the existence of AVH effect.

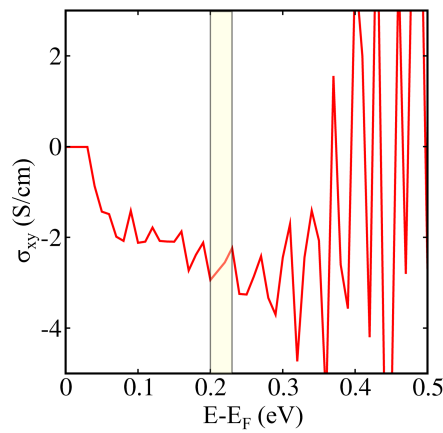


Figure 3.10: The anomalous Hall conductivity as a function of  $E_F$

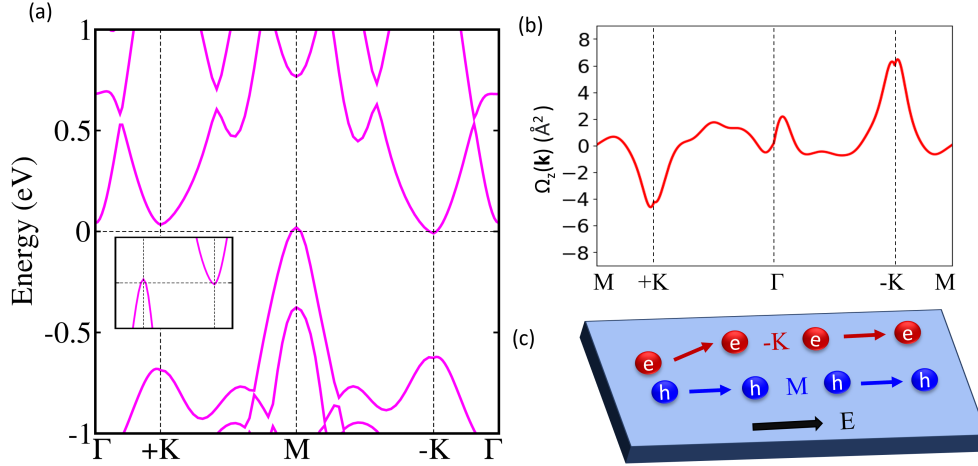


Figure 3.11: (a) Band structure of Cr<sub>2</sub>CSF under uniaxial strain of 3.5% showing QHVM phase. (b) Berry curvature of Cr<sub>2</sub>CSF along the high symmetry path. (c) Schematic of hole-electron charge carriers separation on application of in-plane electric field.

### 3.3.4 Effect of strain

The effect of external strain has been well-known in modulation of electronic properties [109, 159, 160, 161, 108, 162]. Consequently, we have applied uniaxial strain in y-direction to understand the effect of strain on valley-related properties of Cr<sub>2</sub>CSF. On reducing the y-dimension in Cr<sub>2</sub>CSF by 3.5%, an intriguing QHVM has been observed. In QHVM, the CBm and VBM slightly touch the Fermi level such that both the electron and hole carriers coexist but only one type of charge carriers are valley polarized. As seen in the electronic band structure in Fig. 5.5(a), CBm touches the Fermi level at  $-K$  while VBM touches the Fermi level at  $M$ . The Berry curvature along the 2D Brillouin zone only occurs around  $+K$  and  $-K$  valleys with opposite signs and unequal magnitudes ( $-4.21$  and  $6.15 \text{ \AA}^2$ ) as shown in Fig. 5.5(b). On application of an in-plane electric field, the electronic carriers of  $-K$  valley turn towards one edge of the sample, while the hole carriers of the  $M$  valley move in a straight line along the applied electric field (see Fig. 5.5(c)). Therefore, we can detect the QHVM phase in strained Cr<sub>2</sub>CSF by direct electric measurement, facilitating the practical valleytronic applications. The present research provides a tantalizing candidate for realizing and manipulating valley and spin physics.



## 3.4 Conclusion

To summarize, using first-principles calculations, we have studied the valley-dependent properties of  $\text{Cr}_2\text{CSX}$  MXenes. Our results reveal that monolayer  $\text{Cr}_2\text{CSF}$  is an indirect band gap FM semiconductor exhibiting an intrinsic out-of-plane magnetization with a large MAE value of 1.16 meV. This out-of-plane magnetization and time-reversal symmetry breaking leads to spontaneous valley polarization of 27.1 meV in the conduction band. The underlying physics of spontaneous valley polarization has also been discussed in detail based on the SOC Hamiltonian model. This spontaneous valley polarization causes observation of AVH effect under an in-plane electric field and electron doping, leading to a separation of charge carriers. Additionally, we have revealed that the valley-related switchable Hall effects can be effectively engineered by the application of strain. On application of uniaxial strain of 3.5% in  $\text{Cr}_2\text{CSF}$ , QHVM has been observed. The hole and electron charge carriers are separated in the presence of in-plane electric field. Existence of switchable Hall effects and presence of very high out-of plane MAE in this material makes it promising for applications in valleytronics.

# Inducing Spin Splitting and Anomalous Valley Hall Effect in A-Type AFM $\text{Fe}_2\text{C}(\text{OH})_2$ through Electric Field and Janus Engineering

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## 4.1 Introduction

In two-dimensional (2D) materials, valleys represent the local energy extrema in the conduction and valence bands, serving as an additional degree of freedom alongside charge and spin [105, 106]. Valleytronics is an emerging field that exploits this valley degree of freedom by manipulating the population of electrons in different valleys [107, 34, 108, 1, 105]. The ability to selectively populate one valley over another is known as valley polarization, and is essential for using the valleys as information carriers. This polarization creates an imbalance between the valleys, allowing for the development of low-power, high-speed information processing, and logic devices [117, 118, 119, 120]. For nonmagnetic materials, 2H-transition metal dichalcogenides have attracted extensive attention as they have a pair of degenerate valleys at a large intervalley distance [109, 110, 111, 112, 113, 114, 115]. They show opposite spin splitting at  $-\text{K}$  and  $+\text{K}$  valleys, which can be called spin-valley locking, but lack spontaneous valley polarization hindering further extension of valleytronics. To manipulate valley polarization, various external methods such as magnetic fields [113], optical excitation, [111, 112] and magnetic doping [115] have been employed, but they bring many undesirable effects [113, 121].

In most recent works, spontaneous valley polarization has been predicted in 2D hexagonal ferromagnetic (FM) materials such as  $\text{VSi}_2\text{P}_4$  [148],  $\text{Cr}_2\text{Se}_2$  [140],  $\text{Cr}_2\text{S}_2$  [149], and  $\text{Cr}_2\text{CSF}$  [163]. Compared to these FM materials, the antiferromagnetic (AFM) materials provide an intriguing alternative for valleytronic applications [164, 165, 166]. They possess zero magnetic moments, are inherently robust to external magnetic perturbations, and possess ultrafast dy-

namics, thus providing enormous potential for device applications. They have inherent valley polarization but these antiferromagnets generally lack spontaneous spin splitting in the band structures, which prevents some interesting physical phenomena [167]. AFM materials with intrinsic spin splitting are particularly important, as they allow for the realization of anomalous valley Hall effect (AVHE) without the need for external manipulation. However, in AFM materials with combined  $PT$  symmetry (where  $P$  represents spatial inversion symmetry and  $T$  is time-reversal symmetry), there is zero Berry curvature and no spin splitting, which hinders the realization of AVHE [165]. This spin degeneracy can be lifted by the application of an external electric field or by altering atomic arrangements, resulting in observable spin splitting in the electronic band structure [168]. The atomic alteration can be achieved by placing magnetic atoms with opposite spin polarizations in different environments. When these atoms experience different surrounding atomic arrangements, the symmetry that protects spin degeneracy is broken. This mechanism is known as electric-potential-difference antiferromagnetism (EPD-AFM) [169].

In this work, we have identified  $\text{Fe}_2\text{C}(\text{OH})_2$  as a promising A-type AFM valleytronic material exhibiting high spontaneous valley polarization.  $\text{Fe}_2\text{C}(\text{OH})_2$  lacks intrinsic spin splitting in its band structure due to conservation of combined  $PT$  symmetry, resulting in zero Berry curvature in the momentum space. This prevents AVHE, however, a valley layer-spin Hall effect is observed. The spin splitting is induced through the application of an external out-of-plane electric field. By combining with layer-locked Berry curvature, the layer-locked AVHE can be achieved in monolayer  $\text{Fe}_2\text{C}(\text{OH})_2$  under the external electric field. Additionally, Janus  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  is constructed to achieve EPD-AFM, which is a promising candidate material for realizing AVHE. A high out-of-plane magnetic anisotropy energy (MAE) depicted by both  $\text{Fe}_2\text{C}(\text{OH})_2$  and  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  makes them desirable for valleytronic device application.

## 4.2 Methodology

The first-principles calculations based on the density functional theory (DFT) are carried out [63, 64] using the Vienna *ab initio* Simulation Package (VASP) [136] with the projector augmented wave (PAW) [85, 86] method. The generalized gradient approximation (GGA) is used to describe the electron exchange-correlation interactions in the form of Perdew-Burke-Ernzerhof (PBE) functional [80]. The cutoff energy for the plane wave basis is set to 520 eV.

All the structures are optimized until the Hellmann-Feynman force on each ion is less than 1 meV/Å, and the self-consistent convergence criterion of the electronic iteration is set to  $10^{-5}$  eV. The vacuum space in  $z$ -direction is set to 30 Å to avoid the interactions between the periodically adjacent layers. The  $11 \times 11 \times 1$   $k$ -grid is used to sample the 2D Brillouin zone. To account for the localized nature of Fe-3d orbitals, a Hubbard correction is used by the rotationally invariant approach proposed by Dudarev et al. [138]. The linear response method is used to determine the effective  $U$  ( $U_{eff}$ ) values, and they are 5.3 and 5.5 for  $\text{Fe}_2\text{C}(\text{OH})_2$  and  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ , respectively [170]. In addition, hybrid functional Heyd-Scuseria Ernzerhof (HSE06) is also employed to confirm the results of GGA+U calculations [141]. The spin-orbit coupling (SOC) effect is considered in the calculations to address the relativistic effect, as implemented in VASP by noncollinear calculations. The Berry curvatures are computed directly from the calculated wave functions using Fukui's method, as implemented in the VASPBERRY code [171, 172].

## 4.3 Results and Discussions

### 4.3.1 Crystal structure and magnetic ground state

$\text{Fe}_2\text{C}$ -based MXenes have been reported to exhibit high Curie/Néel temperatures and dynamic stabilities [173]. We investigate the valley properties and band structures of  $\text{Fe}_2\text{C}$ -based MXenes:  $\text{Fe}_2\text{C}(\text{OH})_2$ ,  $\text{Fe}_2\text{CF}_2$ ,  $\text{Fe}_2\text{CCl}_2$ ,  $\text{Fe}_2\text{CO}_2$ , and  $\text{Fe}_2\text{CS}_2$ .  $\text{Fe}_2\text{C}(\text{OH})_2$  is explored as a prototype material in our study due to its promising valleytronic properties, which will be discussed comprehensively in subsequent sections. The crystal structure of  $\text{Fe}_2\text{C}(\text{OH})_2$ , along with the corresponding 2D Brillouin zone, is shown in Fig. 4.1(a) and (b), respectively.  $\text{Fe}_2\text{C}(\text{OH})_2$  consists of seven atomic layers arranged in the sequence H-O-Fe-C-Fe-O-H, with the central carbon layer sandwiched between two Fe-OH bilayers. This compound crystallizes in  $P3m1$  space group (No. 164), exhibiting spatial inversion symmetry in the absence of magnetic ordering. The four possible magnetic configurations namely FM, AFM1, AFM2, and AFM3 are considered as seen in Fig. 4.2. The blue and gray spheres represent spin-up and spin-down Fe atoms, respectively. The magnetic ground state of  $\text{Fe}_2\text{C}(\text{OH})_2$  is determined by comparing the energies of these magnetic configurations. Among these, AFM1 is identified as the A-type antiferromagnetic state characterized by intralayer FM and interlayer AFM couplings. The energy of AFM1 configuration is 800 meV, 700 meV, and 250 meV lower than the FM, AFM2, and

AFM3 configurations, respectively, confirming that  $\text{Fe}_2\text{C}(\text{OH})_2$  prefers A-type AFM ordering. This has also been confirmed by using more accurate HSE06 functional (see Table 4.1). The total magnetic moment per unit cell is  $0.00 \mu_B$  (where  $\mu_B$  is Bohr magneton), with the magnetic moments of the top and bottom Fe layers being  $+3.91 \mu_B$  and  $-3.91 \mu_B$ , respectively. In this A-type AFM state, the spin configuration breaks the  $P$  and  $T$  symmetry. However, the combined  $PT$  symmetry remains intact in  $\text{Fe}_2\text{C}(\text{OH})_2$  as shown in Fig. 4.1(c). The  $T$  operation reverses the spin direction of each Fe atom, followed by the  $P$  operation which swaps the top and bottom Fe atoms, resulting in symmetry conservation.

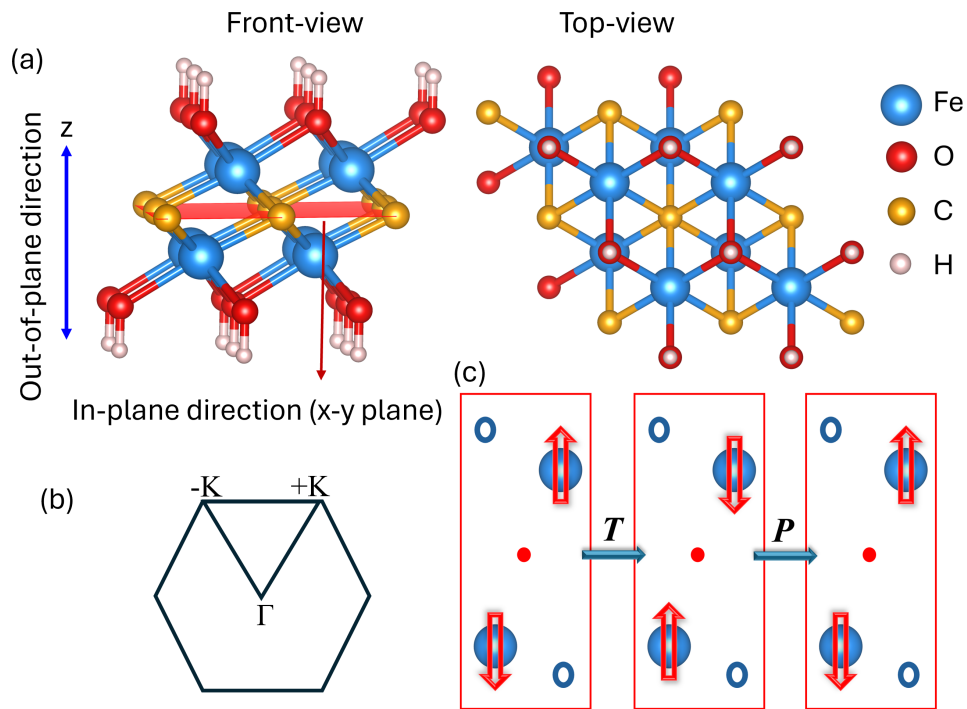


Figure 4.1: (a) Front and top views of  $\text{Fe}_2\text{C}(\text{OH})_2$  (Here,  $x-y$  plane represents the in-plane direction and the  $z$ -axis represents the out-of-plane direction). (b) Hexagonal 2D Brillouin zone. (c) A combination of  $P$  and  $T$  symmetry showing combined  $PT$  symmetry.

### 4.3.2 Valley spitting and Berry curvature

The electronic band structures for  $\text{Fe}_2\text{CF}_2$ ,  $\text{Fe}_2\text{CCl}_2$ ,  $\text{Fe}_2\text{CO}_2$ , and  $\text{Fe}_2\text{CS}_2$  are displayed in Fig. 4.3 (also see Fig. 4.4 for band structure of  $\text{Fe}_2\text{CF}_2$  with SOC) and that of  $\text{Fe}_2\text{C}(\text{OH})_2$  is shown in Fig. 4.5(a). The energy band structure shows that  $\text{Fe}_2\text{C}(\text{OH})_2$  is an indirect band-gap semiconductor with degenerate energy at  $+K$  and  $-K$  points in the conduction band. The valleys are observed at  $+K$  and  $-K$  points, but no spin splitting is observed due to the

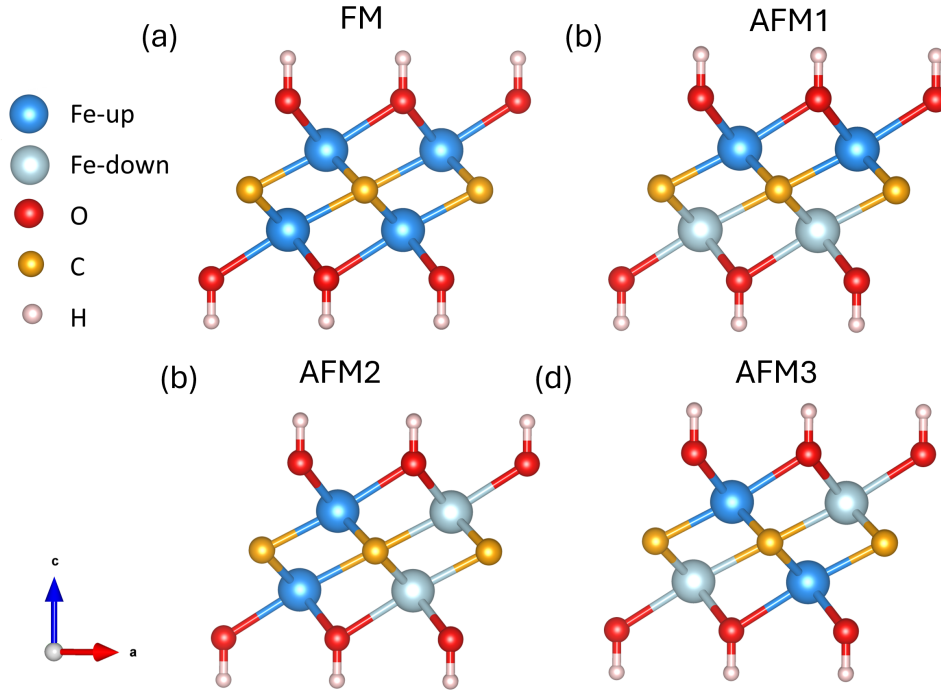


Figure 4.2: Crystal structures of (a) FM, (b) AFM1, (c) AFM2, and (d) AFM3 magnetic configurations for  $\text{Fe}_2\text{C}(\text{OH})_2$  MXene.

Table 4.1: Energy of different magnetic configurations of  $\text{Fe}_2\text{C}(\text{OH})_2$  MXene using HSE06 exchange functional. The energy of most stable configuration has been set to zero (in units of meV).

| $\text{Fe}_2\text{C}(\text{OH})_2$ MXene | HSE06 |
|------------------------------------------|-------|
| FM                                       | 100   |
| AFM1                                     | 0     |
| AFM2                                     | 620   |
| AFM3                                     | 370   |

preservation of  $PT$  symmetry. As from  $P$  symmetry:  $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \uparrow)$ , from  $T$  symmetry:  $E(-\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$ , and combining these two leads to  $PT$  symmetry:  $E(\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$ . This means that the spin-up and spin-down bands are degenerate at every  $\mathbf{k}$ , and there is no spin splitting in the band structure. When SOC is considered, as shown in Fig. 4.5(b), the energy at  $-K$  valley becomes higher than that of  $+K$  valley. The opposite spin vectors of the two sublattices in  $\text{Fe}_2\text{C}(\text{OH})_2$  break the  $P$  and  $T$  symmetry giving rise to spontaneous valley

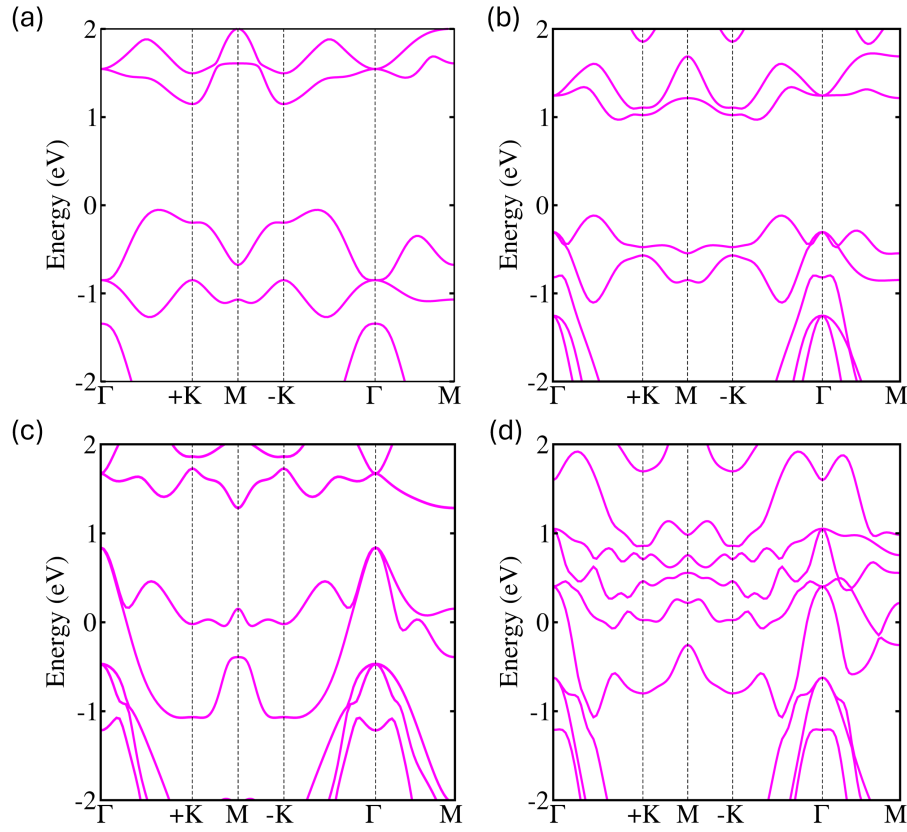


Figure 4.3: The electronic band structure of (a)  $\text{Fe}_2\text{CF}_2$  showing well defined valleys at +K and -K points in the conduction band, (b)  $\text{Fe}_2\text{CCl}_2$ , (c)  $\text{Fe}_2\text{CO}_2$ , and (d)  $\text{Fe}_2\text{CS}_2$  showing that there are no well defined valleys at high symmetry points.

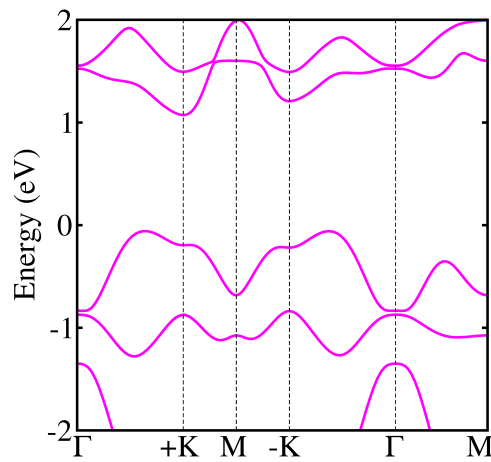


Figure 4.4: The electronic band structure of  $\text{Fe}_2\text{CF}_2$  MXene with SOC showing valley polarization of magnitude 100 meV.

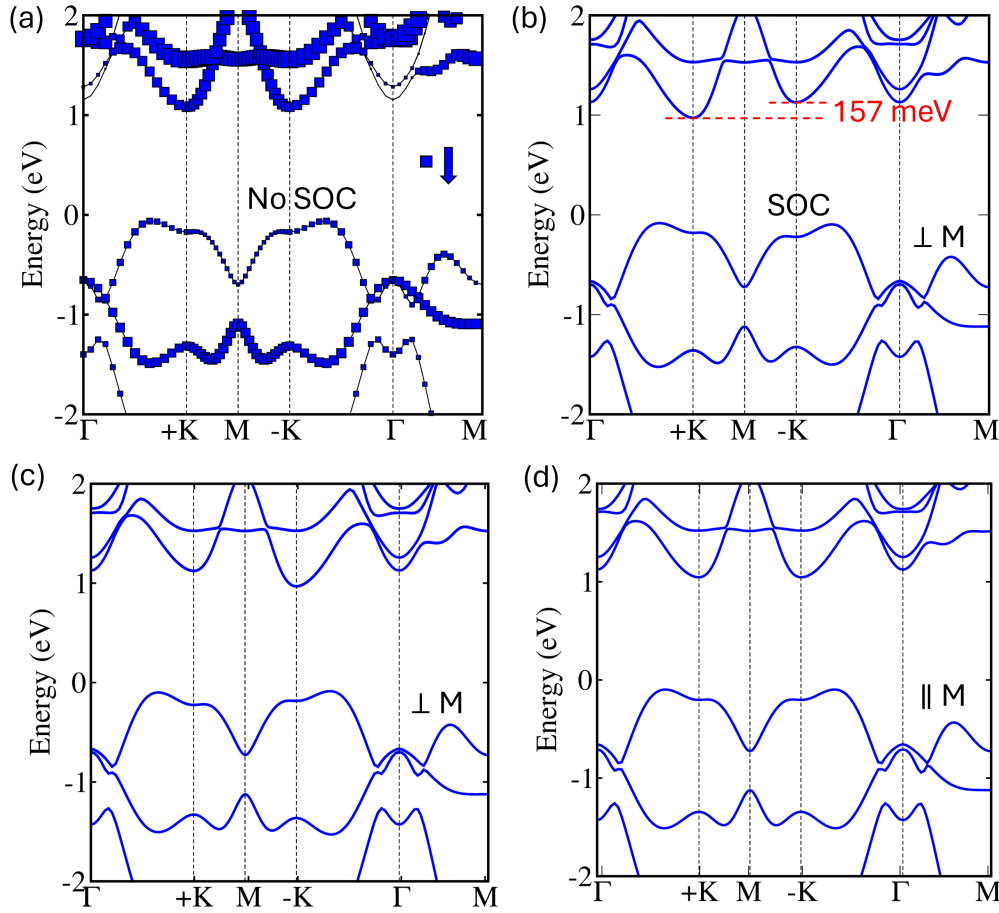


Figure 4.5: The energy band structures of  $\text{Fe}_2\text{C}(\text{OH})_2$  (a) without SOC with blue colour showing the contribution of spin-down states only, with SOC (b) for out-of-plane magnetization (i.e. along the positive  $z$ -direction) showing valley polarization, (c) with opposite out-of-plane magnetization (along the negative  $z$ -direction), and (d) for in-plane magnetization, showing absence of valley polarization.

polarization. A notable valley polarization is induced with a sizable valley splitting of 157 meV ( $\Delta E_C = E_{-K} - E_{+K}$ ). This magnitude of valley splitting is higher than many reported magnetic valley materials [122, 174, 175, 165]. Further, when the direction of magnetization is reversed, the valley polarization gets switched with the energy at +K valley becoming higher than that of -K valley with the same magnitude of valley splitting (see Fig. 4.5(c)). When the magnetization direction is in-plane, no valley polarization is observed as shown in Fig. 4.5(d). Even with SOC included, the spin degeneracy is maintained for both in-plane and out-of-plane magnetization directions. This indicates that  $\text{Fe}_2\text{C}(\text{OH})_2$  exhibits robust valleytronic behavior. Furthermore, the MAE, which determines the preferred magnetization direction, is calculated using the equation:  $\text{MAE} = E_{x/y} - E_z$ , where  $E_{x/y}$  and  $E_z$  denote the in-plane and out-of-plane spin orientations, respectively. The MAE value is 174  $\mu\text{eV}/\text{unit cell}$ , confirming



that  $\text{Fe}_2\text{C}(\text{OH})_2$  has an out-of-plane easy magnetization axis. This out-of-plane magnetization leads to spontaneous valley polarization, supporting the realization of valleytronic applications. The SOC-induced valley polarization primarily arises from the intra-atomic interaction  $\hat{H}_{\text{SOC}}^0$ ,

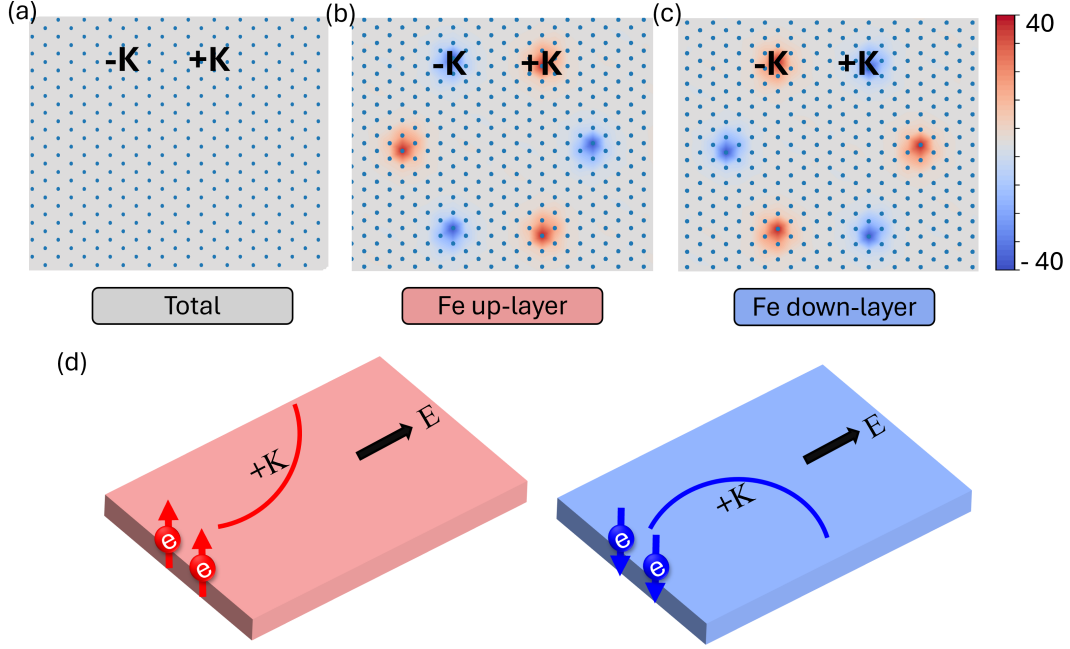


Figure 4.6: The distribution of (a) total, (b) spin-up, and (c) spin-down Berry curvatures for  $\text{Fe}_2\text{C}(\text{OH})_2$ . (d) A schematic of valley layer-spin Hall effect under the application of a longitudinal in-plane electric field and appropriate electron doping. The left and right planes represent the top and bottom Fe layers, respectively.

which affects the states with the same spin orientation and is given by: [153, 154].

$$\hat{H}_{\text{SOC}}^0 = \lambda \hat{S}_{z'} \left( \hat{L}_z \cos \theta + \frac{1}{2} \hat{L}_+ e^{-i\phi} \sin \theta + \frac{1}{2} \hat{L}_- e^{i\phi} \sin \theta \right) \quad (4.1)$$

Here, the magnetization is out-of-plane, i.e.,  $\theta = 0$  (see Fig. 4.7(a)). Therefore, the above equation is simplified to:

$$\hat{H}_{\text{SOC}}^0 = \lambda \hat{S}_{z'} \hat{L}_z \quad (4.2)$$

To proceed further, we have observed that the conduction band valleys are primarily composed of  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals of the Fe atoms (see Fig. 4.7(b)). Therefore, the basis wave vectors are chosen in the following form:

$$|\phi_c^\tau\rangle = \frac{1}{\sqrt{2}} (|d_{x^2-y^2}\rangle + i\tau |d_{xy}\rangle) \quad (4.3)$$

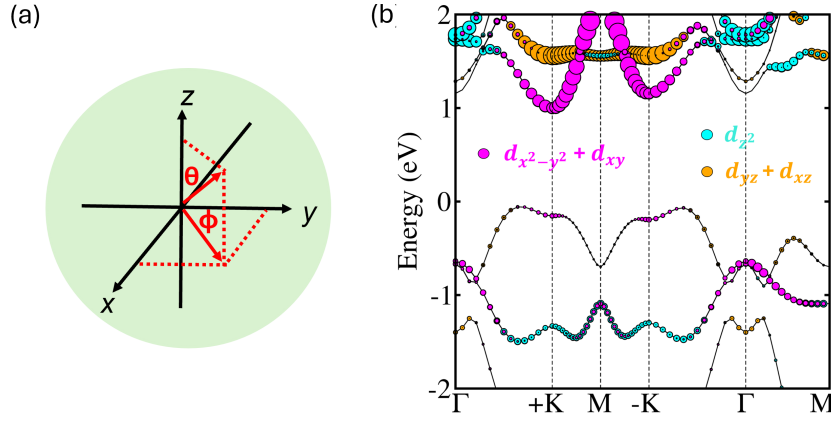


Figure 4.7: (a) Representation of polar angles. (b) Orbital projected band structure of  $\text{Fe}_2\text{C}(\text{OH})_2$  in the presence of SOC.

where  $c$  represents the conduction band and  $\tau = \pm 1$  corresponds to  $+K/-K$  valley. The energy level at  $+K/-K$  can be denoted by following formula:

$$\begin{aligned}
 E_c^{+K/-K} &= \langle \phi_c^\tau | \hat{H}_{\text{SOC}}^0 | \phi_c^\tau \rangle \\
 &= \frac{i\tau}{2} (\langle d_{x^2-y^2} | \hat{H}_{\text{SOC}}^0 | d_{xy} \rangle \\
 &\quad - \langle d_{xy} | \hat{H}_{\text{SOC}}^0 | d_{x^2-y^2} \rangle) \\
 &= \frac{i\tau}{2} \lambda (\langle d_{x^2-y^2} | \hat{L}_z | d_{xy} \rangle - \langle d_{xy} | \hat{L}_z | d_{x^2-y^2} \rangle)
 \end{aligned} \tag{4.4}$$

where  $\hat{L}_z |d_{x^2-y^2}\rangle = 2i |d_{xy}\rangle$ ,  $\hat{L}_z |d_{xy}\rangle = -2i |d_{x^2-y^2}\rangle$  and  $\alpha = \langle \uparrow | \hat{S}_z | \uparrow \rangle \langle \uparrow | \hat{S}_z | \uparrow \rangle$ . The valley polarization in the conduction band is obtained through

$$\begin{aligned}
 \Delta E_c &= E_c^{+K} - E_c^{-K} \\
 &= i\lambda\alpha \langle d_{x^2-y^2} | \hat{L}_z | d_{xy} \rangle - i\lambda\alpha \langle d_{xy} | \hat{L}_z | d_{x^2-y^2} \rangle \\
 &= 4\lambda\alpha
 \end{aligned} \tag{4.5}$$

When the magnetocrystalline direction is along an out-of-plane, the valley splitting of  $\text{Fe}_2\text{C}(\text{OH})_2$  will be  $4\lambda\alpha$ .

On the other hand, if magnetic orientation is in-plane, i.e.,  $\theta = \frac{\pi}{2}$ , we get:

$$\hat{H}_{\text{SOC}}^0 = \lambda \hat{S}_{z'} \left( \frac{1}{2} \hat{L}_+ e^{-i\phi} + \frac{1}{2} \hat{L}_- e^{i\phi} \right) \tag{4.6}$$

In this case,  $\Delta E_c = 0$ , i.e., no spontaneous valley polarization (Fig. 4.5(d)).

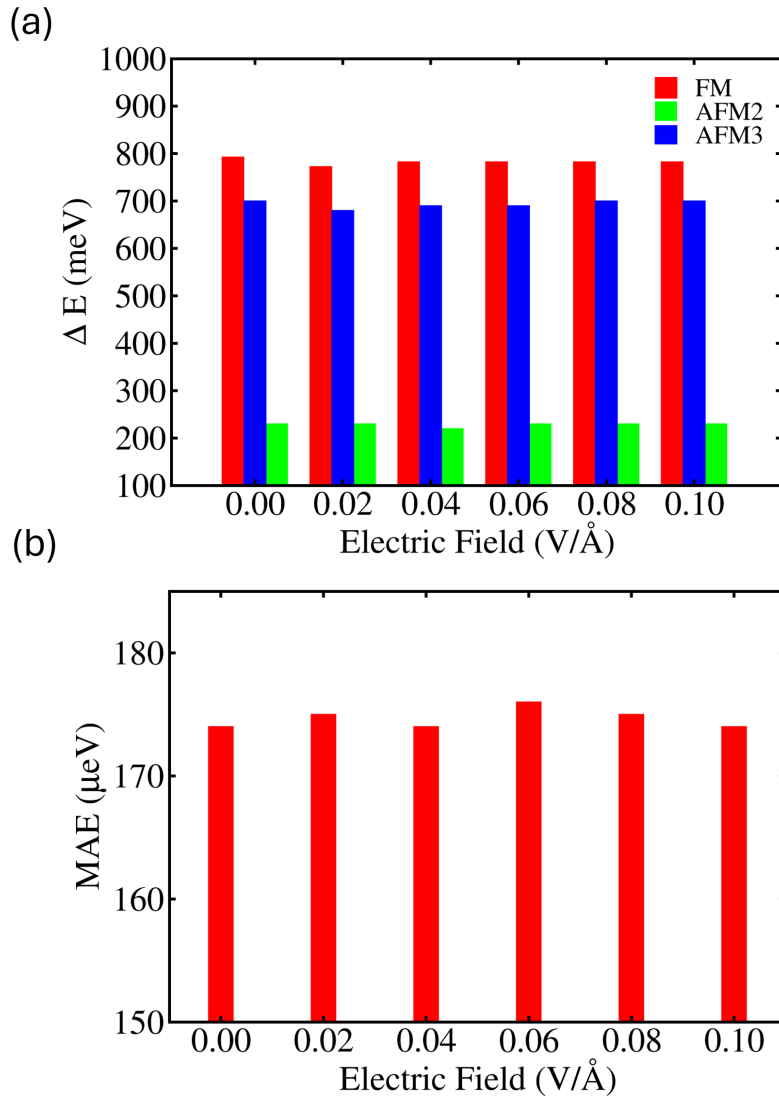


Figure 4.8: For  $\text{Fe}_2\text{C}(\text{OH})_2$ , (a) the energy difference between FM/AFM2/AFM3 and AFM1 magnetic orderings as a function of electric field, and (b) the variation of MAE as a function of electric field.

### 4.3.3 Spin spitting caused by electric field

The distribution of total Berry curvature for  $\text{Fe}_2\text{C}(\text{OH})_2$  is shown in Fig. 4.6(a). Due to the conserved  $PT$  symmetry, the total Berry curvature is zero throughout the momentum space. Therefore,  $\text{Fe}_2\text{C}(\text{OH})_2$  cannot show AVHE but it can show valley layer-spin Hall effect. Figure 4.6(b) and (c) show the Berry curvatures of spin-up and spin-down channels. The Berry curvatures show opposite signs for different valleys of the same spin channel and the same valley of different spin channels, producing a layer-locked hidden Berry curvature. This Berry curvature arises because each layer unit (C-Fe-OH) breaks the local  $PT$  symmetry. When the Fermi level is shifted between the  $+K$  and  $-K$  valleys in the conduction band via electron doping, the

spin-up and spin-down electrons from  $+K$  valley will accumulate along the opposite sides of the specimen under the effect of an in-plane electric field. Under this field, the Bloch electrons will gain an anomalous velocity, equal to the cross product of in-plane electric field and Berry curvature i.e.,  $v \sim E \times \Omega(\mathbf{k})$  [157, 35, 158]. This results in the valley layer-spin Hall effect (Fig. 4.6(d)).

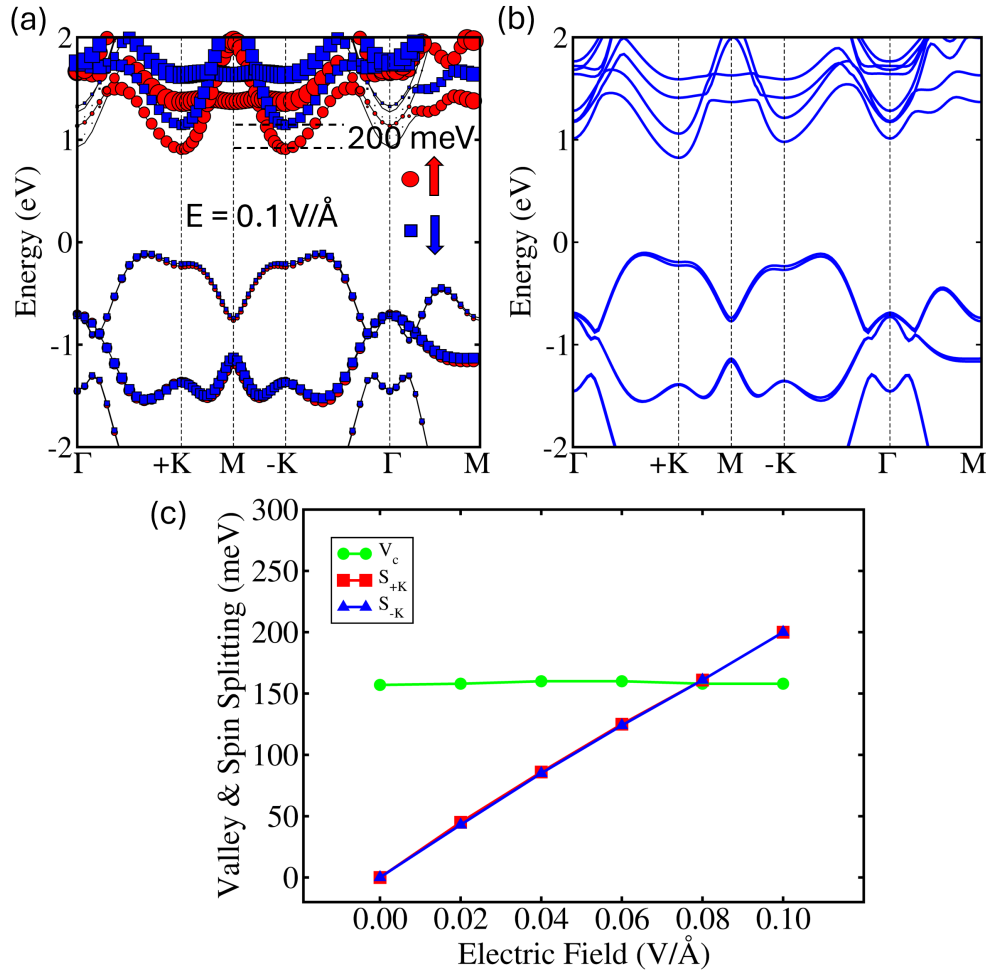


Figure 4.9: For  $\text{Fe}_2\text{C}(\text{OH})_2$ , the spin-resolved electronic band structure at representative electric field:  $E = 0.10 \text{ V/\AA}$  (a) in absence of SOC showing spin splitting, and (b) in presence of SOC, showing spin split bands along with valley polarization. (c) The magnitude of valley splitting ( $V_c$ ), and spin splitting ( $S_{+K}$  and  $S_{-K}$  at  $+K$  and  $-K$  valleys, respectively) in the conduction band as a function of electric field.

Further, an out-of-plane electric field is employed to break the  $PT$  symmetry [164]. This removal subsequently leads to the lifting of spin degeneracy in the band structure. A layer-dependent electrostatic potential induced by the out-of-plane electric field results in the spin splitting effect. An out-of-plane electric field ranging from 0.00 to 0.10  $\text{V/\AA}$  is applied. Firstly, we have determined the magnetic ground state by calculating the energy of FM, AFM1, AFM2,

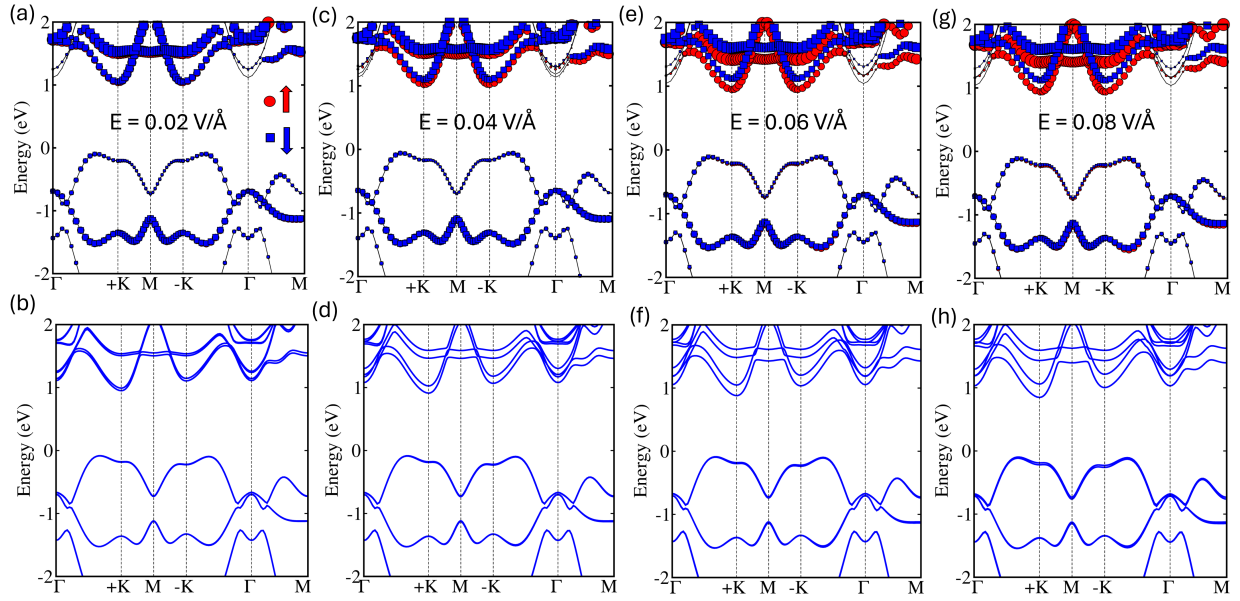


Figure 4.10: Band structure of  $\text{Fe}_2\text{C}(\text{OH})_2$  under an electric field (a)  $E = 0.02 \text{ V/\AA}$ , (c)  $E = 0.04 \text{ V/\AA}$ , (e)  $E = 0.06 \text{ V/\AA}$ , (g)  $E = 0.08 \text{ V/\AA}$  in the absence of SOC, and (b), (d), (f), and (h) at corresponding electric fields in the presence of SOC.

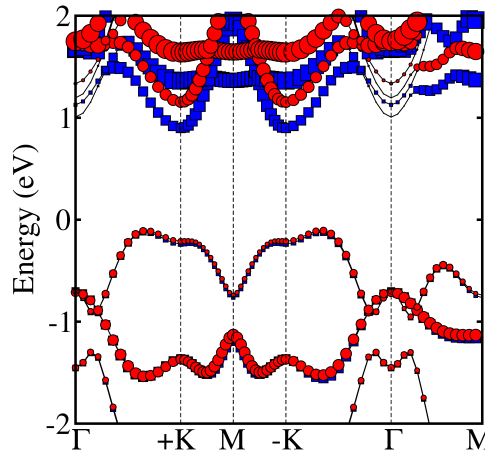


Figure 4.11: Reversal of the spin order of spin splitting on reversing the direction of electric field.

and AFM3 configurations under the applied range of electric field. As shown in Fig. 4.8(a), AFM1 state remains the preferred magnetic ground state at all the electric fields and the energy does not vary much over this range. Subsequently, we have calculated the MAE vs. electric field and concluded that the MAE consistently favors the out-of-plane direction and shows minimal variation under the applied electric field (Fig. 4.8(b)). The electronic band structures, without and with SOC are computed for various electric field values (0.02, 0.04, 0.06, 0.08  $\text{V/\AA}$ ) as shown in Fig. 4.10. Figure 4.9(a) shows the energy band structure at a representative electric field  $0.10 \text{ V/\AA}$  without including SOC. It is evident from the plots that spin splitting

begins to occur upon the application of electric field. When an electric field of  $0.02 \text{ V/\AA}$  is applied a spin splitting of magnitude of 45 meV is observed. Theoretically, the magnitude of spin splitting  $\propto eEd$ , where  $E$  is the applied electric field and  $d$  is the separation over which the potential difference acts [164]. For  $\text{Fe}_2\text{C}(\text{OH})_2$ ,  $d = 2.55 \text{ \AA}$ , and the calculated splitting is 51 meV, which is close to our first-principles value. At a representative value of  $E = 0.10 \text{ V/\AA}$  the spin splitting of magnitude 200 meV is observed as shown in Fig. 4.9(a). When SOC is applied, the valley polarization appears along with the spin splitting as shown in Fig. 4.9(b). As seen from Fig. 4.9 (c), the magnitude of valley polarization is least impacted by the magnitude of electric field. Although the magnitude of spin splitting as expected varies linearly with the electric field. Moreover, the spin splitting has the same value at  $+K$  and  $-K$  valleys. The coexistence of valley polarization and spin splitting is needed for the realization of AVHE. When the direction of electric field is reversed from  $+E$  to  $-E$ , the layer-dependent electrostatic potential is also reversed, reversing the spin order of spin splitting (see Fig. 4.11). However, the size of spin splitting and valley polarization remain unchanged. This happens due to the relationship between two Fe layers, which possess opposite magnetic moments and are connected by a glide mirror symmetry  $G_z$ .

Further, the distribution of Berry curvatures for up, and down spins under the electric field of magnitude  $0.10 \text{ V/\AA}$  are plotted in Fig. 4.12(a) and (b). It is seen that the Berry curvature is opposite at  $+K$  and  $-K$  points. Upon shifting the Fermi level between  $+K$  and  $-K$  valley of the conduction band and application of an in-plane electric field, the spin-up electrons in the conduction band at  $+K$  move under the action of an anomalous velocity. The electrons get concentrated at the top edge of the sample as illustrated in Fig. 4.12(c). This leads to a layer-locked AVHE. When the direction of electric field is reversed, the valleys in the conduction band are formed of spin-down electrons. Under the action of negative Berry curvature and an in-plane electric field, the spin-down electrons at  $+K$  move to the lower edge of the sample. This accumulation of spin-polarized electrons produces a net spin current, and a voltage is generated.

#### 4.3.4 Spin splitting caused by Janus structure

The two Fe atoms in  $\text{Fe}_2\text{C}(\text{OH})_2$  have the same surrounding atomic environment of C and OH, which gives rise to degeneration of electron spin. To break this degeneracy, a Janus monolayer can be constructed by replacing the OH layer with the F element, forming  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ .

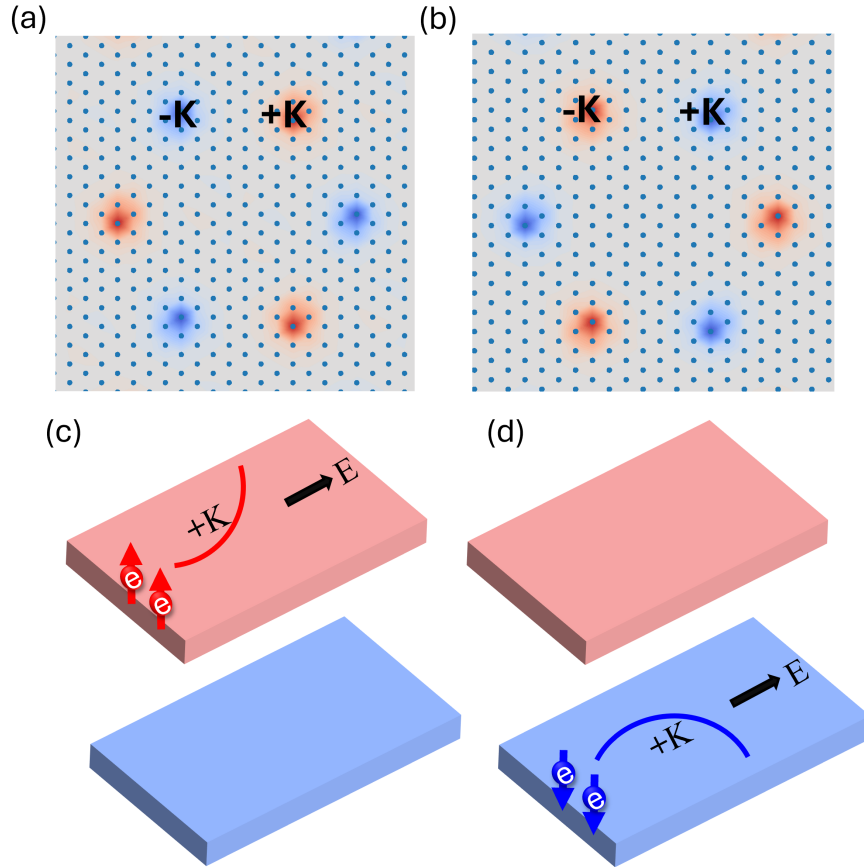


Figure 4.12: The distribution of (a) spin-up, and (b) spin-down Berry curvatures for  $\text{Fe}_2\text{C}(\text{OH})_2$  under an electric field of  $0.10 \text{ V/\AA}$ . (c), (d) The in-plane electric field and electron doping produce layer-locked AVHE. The top and bottom planes represent the top and bottom Fe layers, respectively.

The front and top views of  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  are shown in Fig. 4.13(a). The structure consists of six atomic layers arranged in the sequence H-O-Fe-C-Fe-F, where each Fe atom now experiences a different surrounding atomic environment. The difference in electronegativity of OH and F induces an intrinsic polar electric field along the  $z$ -direction, enabling the realization of EPD-AFM. The energy of FM and three AFM configurations (AFM1, AFM2 and AFM3) is calculated to determine the magnetic ground state of  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ . The AFM1 ordering is found to be the magnetic ground state with energies 1.02 eV, 232 meV, and 713 meV less than FM, AFM2, and AFM3 configurations, respectively. The total magnetic moment of  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  per unit cell is  $0.00 \mu_B$ , with individual magnetic moments of  $3.90 \mu_B$  and  $-3.85 \mu_B$  for the top and bottom Fe layers, respectively. To confirm the spontaneous valley polarization of  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ , the MAE is calculated, and the predicted value is  $169 \mu\text{eV/unit cell}$ , which means that the easy magnetization axis is out-of-plane. As seen in Fig. 4.13(b), due to the broken  $PT$  symmetry, the spin splitting of magnitude 152 meV is observed in the energy band structure. When SOC



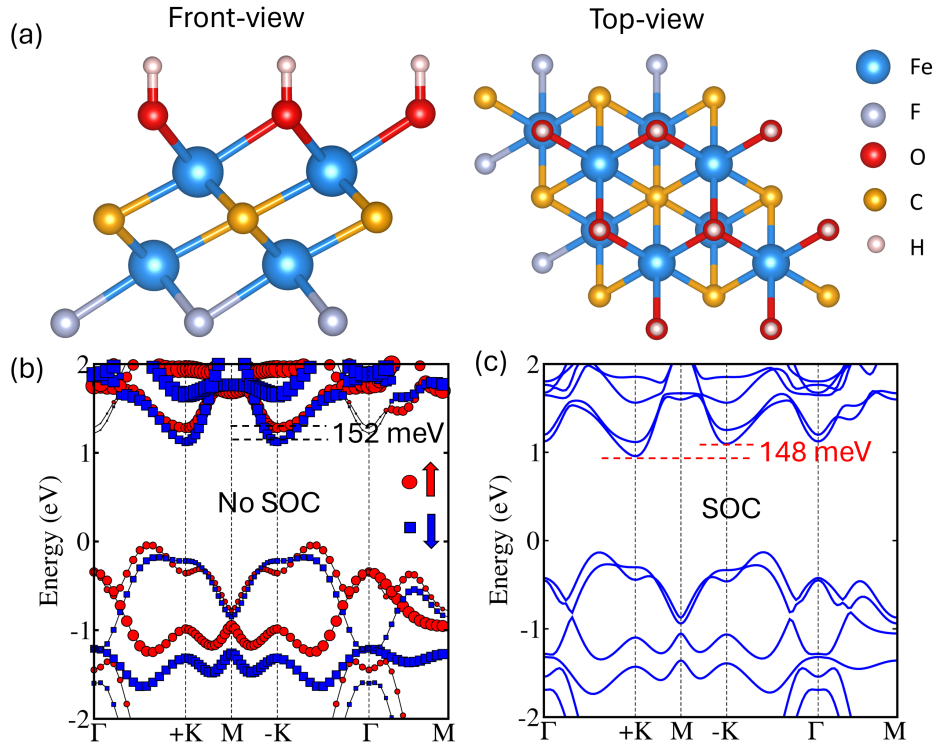


Figure 4.13: (a) The top and (b) side views of the crystal structure of Janus monolayer  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ . The energy band structure (c) without SOC with red (blue) circles (squares) representing the spin-up (spin-down) states, and (d) with SOC for magnetization direction along the positive  $z$ -direction.

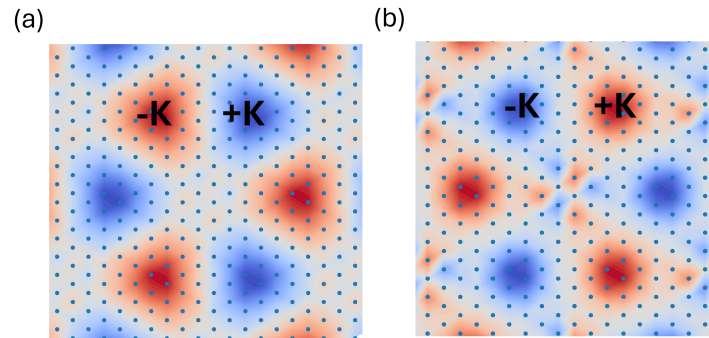


Figure 4.14: The distribution of (a) spin-up, and (b) spin-down Berry curvatures for  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ .

is included with the magnetization direction along positive  $z$ -direction, the spontaneous valley polarization of magnitude 148 meV appears (Fig. 4.13(c)). The Berry curvatures for up and down spins are calculated as seen in Fig. 4.14. The Berry curvatures are peaked at  $+K$  and  $-K$  valleys. It is seen that the Berry curvatures are opposite for  $+K$  and  $-K$  valleys. Moreover, the Berry curvatures at the same valley are also opposite for different spin channels. AVHE can be observed in  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  under the effect of an in-plane electric field. By shifting the



Fermi level between the  $+K$  and  $-K$  valleys in the conduction band, the spin-down carriers from the  $+K$  valley will accumulate along the bottom boundary of the sample, resulting in the layer-locked AVHE.

## 4.4 Conclusion

To summarize, using first-principles calculations, we have studied the valley-dependent properties of  $\text{Fe}_2\text{C}(\text{OH})_2$ . It is an A-type AFM monolayer with a large spontaneous valley polarization of 157 meV in the conduction band. The combined  $PT$  symmetry in  $\text{Fe}_2\text{C}(\text{OH})_2$  ensures spin degeneracy, resulting in zero Berry curvature in the momentum space, and consequently suppressing the AVHE. However, a nonzero layer-locked hidden Berry curvature emerges in real space, leading to the observation of valley layer-spin Hall effect. Further, by applying an out-of-plane electric field, a layer-dependent electrostatic potential is introduced, inducing spin splitting and enabling a layer-locked AVHE in  $\text{Fe}_2\text{C}(\text{OH})_2$ . Notably, the order of spin splitting can be reversed by changing the direction of the applied electric field. Furthermore, AVHE can be intrinsically realized in Janus  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  without the need for an external electric field, owing to its built-in electric potential. These findings demonstrate that AFM monolayers  $\text{Fe}_2\text{C}(\text{OH})_2$  and  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ , possess exceptional properties for achieving AVHE, offering significant potential for spintronic and valleytronic applications.

# Unlocking reversible and nonvolatile anomalous valley Hall control through multiferroic van der Waals heterostructures

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## 5.1 Introduction

The quest for novel quantum degrees of freedom and robust control mechanisms is driving the development of next-generation nanoelectronic devices. Among these, the valley degree of freedom, an energy extremum in the band dispersion of two-dimensional (2D) materials, has emerged as a promising information carrier. These binary valley states, found in energy-degenerate but inequivalent valleys at the Brillouin zone corners, form the foundation for valleytronic devices aimed at information storage and logical operations [34, 176, 107, 177]. Pioneering studies on 2D graphene and transition metal disulfides have revealed intriguing phenomena. These include the valley Hall effect and valley-dependent optical selection rules, paving the way for theoretical predictions and experimental realizations of applications such as valley spin valves and filters [178, 179, 180, 181].

However, the widespread application of valley signals and the advancement of valleytronics for binary information encoding are often hindered by valley degeneracy. Various strategies have been proposed to overcome this by breaking time-reversal symmetry, including external electromagnetic fields, optical pumping, magnetic doping, or magnetic proximity effects [182, 183, 184, 185, 186, 187]. Unfortunately, many of these methods are either volatile, difficult to control, introduce undesirable impurity scattering, or yield only minuscule valley splitting, making them impractical for real-world applications [183, 187]. Crucially, achieving significant valley splitting through external means or magnetic substrates often presents experimental challenges. Thus, the central challenge for practical valleytronic devices lies in develop-

ing tunable and nonvolatile valley splitting. To address this, the search for materials exhibiting intrinsic valley splitting is paramount. Inspired by the magnetic proximity effect, the coupled interplay of an intrinsic magnetic exchange field with spin-orbit coupling (SOC) is a highly desirable route to achieve nonvolatile intrinsic valley splitting. The breaking of both spatial inversion and time-reversal asymmetries in such systems leads to a nonzero valley magnetic moment and Berry curvature with unequal magnitudes and opposite signs, resulting in discernible valley splitting. Consequently, when a transverse voltage is applied, Bloch electrons acquire anomalous velocities, generating the anomalous valley Hall (AVH) effect. The coexistence of intrinsic magnetic exchange fields and SOC in ferromagnetic semiconductors makes them a focal point for research into nonvolatile valley splitting and the AVH effect. While explorations have spanned various 2D materials, including graphene, transition metal disulfides, and intrinsic ferrovalley materials like  $\text{FeCl}_2$ ,  $\text{GdI}_2$  and  $\text{NdX}_2$  [188, 189, 190]. Recent advancements have focused on heterostructures, such as electrical tuning of the AVH effect in antiferrovalley bilayer  $\text{VSe}_2$ , ferroelectric switching in inversion-symmetric bilayer  $\text{T-FeCl}_2$  structures [191], stacking-dependent AVH behavior in  $\text{MnPSe}_3/\text{Sc}_2\text{CO}_2$  [174], and multiferroic systems like  $\text{CrOX}/\text{In}_2\text{Se}_3$  [192],  $\text{AgBiP}_2\text{S}_6/\text{CrBr}_3$  [193] and  $\text{WSe}_2/\text{VSe}_2$  [194]. Despite these advances, achieving reversible and nonvolatile control over valley and spin degrees of freedom in a unified material platform remains a significant challenge. In this work, we propose a concrete realization of such control using multiferroic van der Waals heterostructures. Specifically, we demonstrate through first-principles calculations that a heterostructure composed of ferromagnetic monolayer  $\text{VSSe}$  stacked on a ferroelectric monolayer  $\text{Al}_2\text{S}_3$  enables precise, reversible modulation of the AVH response. By switching the ferroelectric polarization direction in  $\text{Al}_2\text{S}_3$  via a transient electric field, the intrinsic valley polarization in  $\text{VSSe}$  can be flipped between the valence and conduction bands. This switch leads to an inversion of the AVH Hall voltage sign, providing a platform for electrically controllable, nonvolatile valleytronic functionalities. Our findings present a viable pathway toward practical and energy-efficient valley-based electronics.

## 5.2 Methodology

The calculations are performed at density functional theory (DFT) [63, 64] level with the projector augmented wave (PAW) [85, 86] method implemented in Vienna *ab initio* Simulation

Package (VASP) [136] code. The exchange-correlation interactions are treated by generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional [80]. The cutoff energy of 520 eV is used for the plane wave basis set such that the total energy calculations are converged within  $10^{-5}$  eV. The vacuum in  $z$ -direction is set to 30 Å to avoid artificial interactions caused by the periodic boundary conditions. The  $11 \times 11 \times 1$   $k$ -grid is used to sample the 2D Brillouin zone. All the structural parameters are fully optimized until the Hellmann-Feynman forces are smaller than 1 meV/Å. A dipole correction [195] was considered. The interlayer van der Waals interaction was described by the DFT-D2 [196] method. Hybrid functional Heyd-Scuseria Ernzerhof (HSE06) employed to obtain accurate band structures [141]. The Berry curvatures are computed directly from the calculated wave functions using Fukui's method, as implemented in the VASPBERRY code [171, 172].

## 5.3 Results and Discussions

### 5.3.1 Crystal structure and magnetic ground state

The advent of Janus materials, has opened new avenues in materials science due to their unique properties arising from broken out-of-plane mirror symmetry. The successful experimental synthesis of Janus MoSSe via modified chemical vapor deposition (CVD) methods has validated their practical realization [197, 198]. This exciting progress, particularly the experimental synthesis of 2D ferrovalley materials like the 2H-VSe<sub>2</sub> monolayer, paves the way for a new class of Janus structures with intrinsic ferromagnetic semiconductor properties [199]. Notably, the Janus 2H-VSSe monolayer was first predicted by Zhang et al., who thoroughly investigated its piezoelectricity, ferroelasticity, and valley polarization [200]. Given the success with similar materials, it is highly anticipated that ordered Janus 2H-VSSe can also be grown using modified CVD techniques. This prospect underscores the significance of gaining deeper insights into the intrinsic physical properties of the Janus 2H-VSSe monolayer. Our investigations reveal that VSSe is a ferromagnetic semiconductor exhibiting strong SOC. The loss of mirror symmetry in VSSe enables bidirectional modulation of the band gap simply by altering the direction of an applied electric field. With the simultaneous breaking of time-reversal, inversion, and mirror symmetries, VSSe promises enhanced tunability under external fields, making it an ideal candidate for exploring advanced valley control mechanisms [146, 201].

The crystal structure and electronic band structure of VSSe is shown in Fig. 5.1(a) and

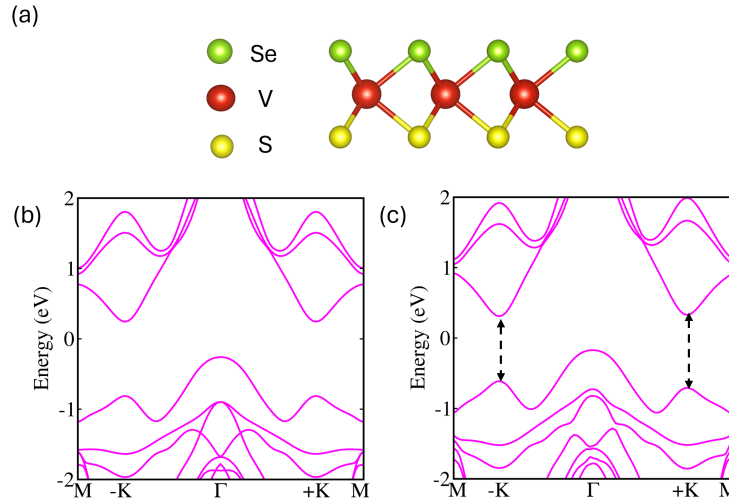


Figure 5.1: (a) Crystal structures of monolayer VSSe. (b) Band structures of monolayer VSSe without SOC. (c) Band structures of monolayer VSSe with SOC. The Fermi level is set to zero.

(b), respectively. As depicted in its band structure Fig. 5.1(c), the coexistence of SOC and inherent exchange interaction in monolayer VSSe lifts the energy degeneracy between these two valleys, leading to valley polarization. When an external in-plane electric field is applied, Bloch electrons from either the  $+K$  and  $-K$  valley acquire transverse velocities. This occurs under the influence of an effective magnetic field generated by the Berry curvature in that respective valley, which in turn gives rise to the AVH effect. While the valley polarization in monolayer VSSe can be tuned by an external magnetic field, thereby controlling the sign of the AVH effect. However the magnetic approach is generally energy-intensive. Therefore, an alternative, reversible, and nonvolatile electrical method for manipulating valley polarization is highly desirable.

To achieve this electrical control, 2D ferroelectric materials emerge as ideal candidates. These materials possess two stable, electrically switchable polarized states that are nonvolatile, meaning the chosen polarization direction persists even after the external electrical stimulus is removed. For this we chose two-dimensional (2D)  $\text{Al}_2\text{S}_3$  as a ferroelectric substrate. This material's crystal structure, with its distinct polarization states, is detailed in Fig. 5.2(a) and (b). The stable 2D  $\text{Al}_2\text{S}_3$  monolayer features a quintuple-layer structure, specifically S-Al-S-Al-S, characterized by the  $P3m1$  space group. Our calculated lattice parameter of  $3.59 \text{ \AA}$  aligns well with previous findings [202]. The material's ferroelectricity stems from the asymmetric displacement of atoms in its central sulfur layer, enabling reversible spontaneous electric polarization in out-of-plane orientations. We denote these ferroelectric polarization states as  $P_{up}$

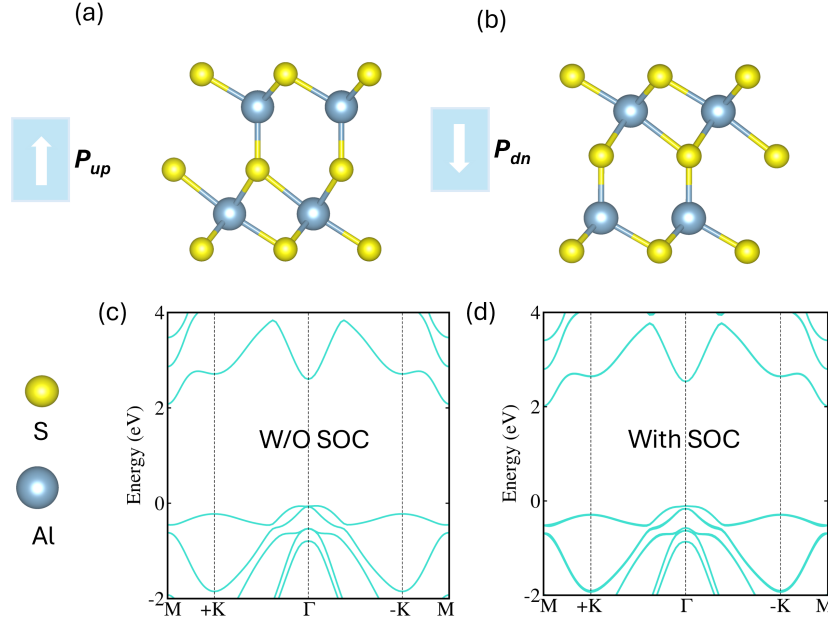


Figure 5.2: (a), (b) Crystal structures of monolayer  $\text{Al}_2\text{S}_3$  from side views with different ferroelectric polarization. (c) Band structures of monolayer  $\text{Al}_2\text{S}_3$  without SOC. (d) Band structures of monolayer  $\text{Al}_2\text{S}_3$  with SOC. The Fermi level is set to zero.

and  $P_{dn}$ , corresponding to the middle sulfur atom's vertical alignment with the upper and lower aluminum layers, respectively.  $\text{Al}_2\text{S}_3$  is part of the well-established  $\text{In}_2\text{Se}_3$  family of ferroelectrics, which are known to exhibit room-temperature ferroelectric properties experimentally [203, 204]. Our analysis of the band structure for 2D  $\text{Al}_2\text{S}_3$  as shown in Fig. 5.2(a) confirms its semiconductor nature with an indirect band gap of 2.97 eV. Here, the valence band maximum (VBM) is situated along the  $K$ - $\Gamma$  line of the Brillouin zone, while the conduction band minimum (CBM) is at the  $\Gamma$  point. While we also considered the impact of SOC, it introduced only minor modifications to the overall band structure as shown in Fig. 5.2(c) and (d).

Placing a ferrovalley VSSe monolayer on a ferroelectric substrate allows for electrically controlled modulation of both valley polarization and the AVH effect. Our design principle, visually represented in Fig. 5.3, demonstrates that reversing the ferroelectric substrate's polarization can switch the VSSe valley polarization from the VBM to the CBM. This transition can even submerge the VBM or CBM valley into trivial bands, a distinct feature not achievable through doping. Crucially, this ferroelectric substrate provides reversible and nonvolatile tuning of the AVH effect's sign, a capability doping alone cannot match.

To engineer the VSSe/ $\text{Al}_2\text{S}_3$  multiferroic heterostructure, we aligned the unit cells of 2D  $\text{Al}_2\text{S}_3$  and 2D VSe<sub>2</sub>. The minimal lattice mismatch of 3.6% between these materials suggests

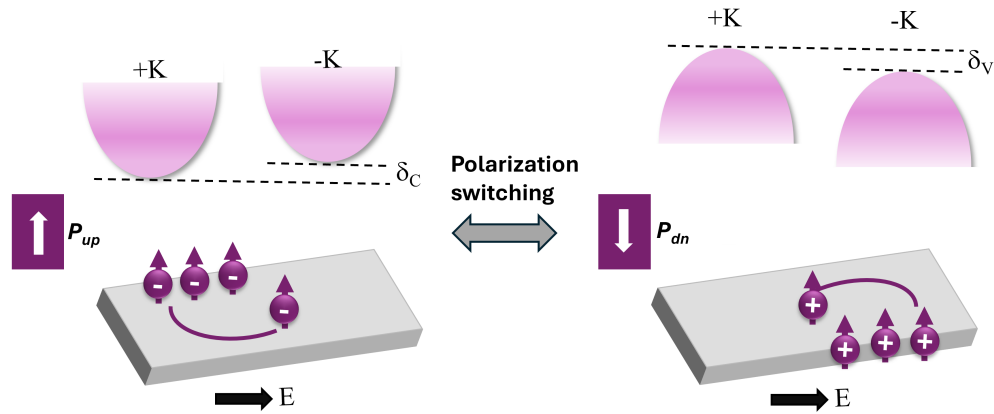


Figure 5.3: Design principle based on multiferroic heterostructure. Diagrams of band structures around the  $+K$  and  $-K$  valleys and FE-controlled AVH effect under in-plane electric field.

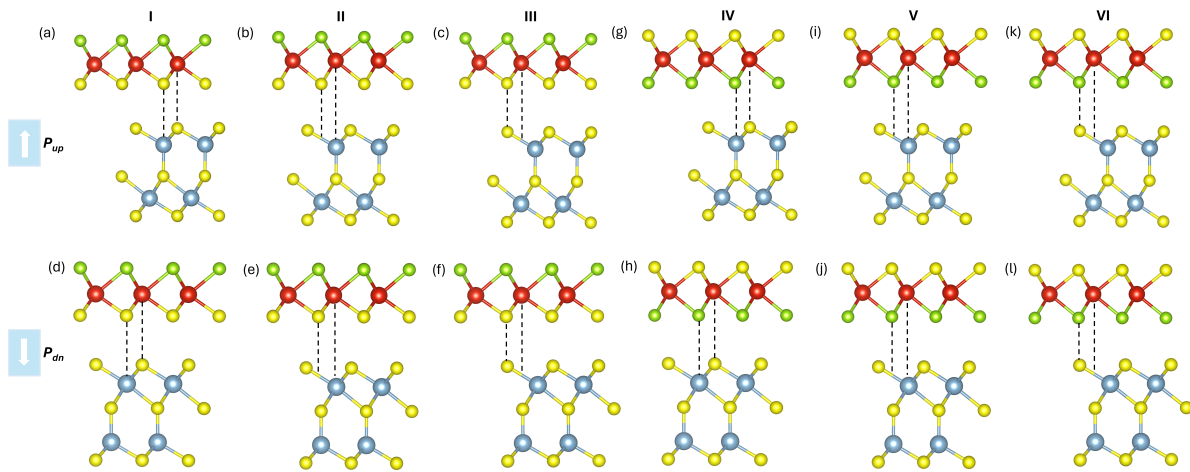


Figure 5.4: Crystal structures of different stacking configurations of the VSSe/Al<sub>2</sub>S<sub>3</sub> heterostructures with (a), (c), (e), (g), (i), (k)  $P_{up}$  and (b), (d), (f), (h), (j), (l)  $P_{dn}$  polarization.

that experimental fabrication of this heterostructure should be readily achievable. We investigated six potential stacking configurations for both polarization states ( $P_{up}$  and  $P_{dn}$ ) each, as shown in Fig. 5.4. Our calculations of the relative energies for these various structures (Table 5.1) indicate that the type-I configuration is energetically the most stable for both polarization directions. Subsequently, we have calculated the energies of type-I configuration in different magnetic states namely FM, AFM1, AFM2, and AFM3. The up and down arrows represent spin-up and spin-down Vanadium atoms, respectively as shown in Fig. 5.5. Crucially, the ferromagnetic (FM) ground state of VSSe is preserved within this multiferroic heterostructure, as confirmed by the energies of various magnetic configurations listed in Table 5.2. All the energies have been calculated using HSE06 functional.

Table 5.1: Energy of different stacking configurations of VSSe/Al<sub>2</sub>S<sub>3</sub> heterostructure in units of eV.

| Configuration-VSSe/Al <sub>2</sub> S <sub>3</sub> | $P_{up}$ | $P_{dn}$ |
|---------------------------------------------------|----------|----------|
| I                                                 | 0        | 0        |
| II                                                | 0.250    | 0.232    |
| III                                               | 0.255    | 0.234    |
| IV                                                | 0.342    | 0.333    |
| V                                                 | 0.345    | 0.334    |
| VI                                                | 0.344    | 0.330    |

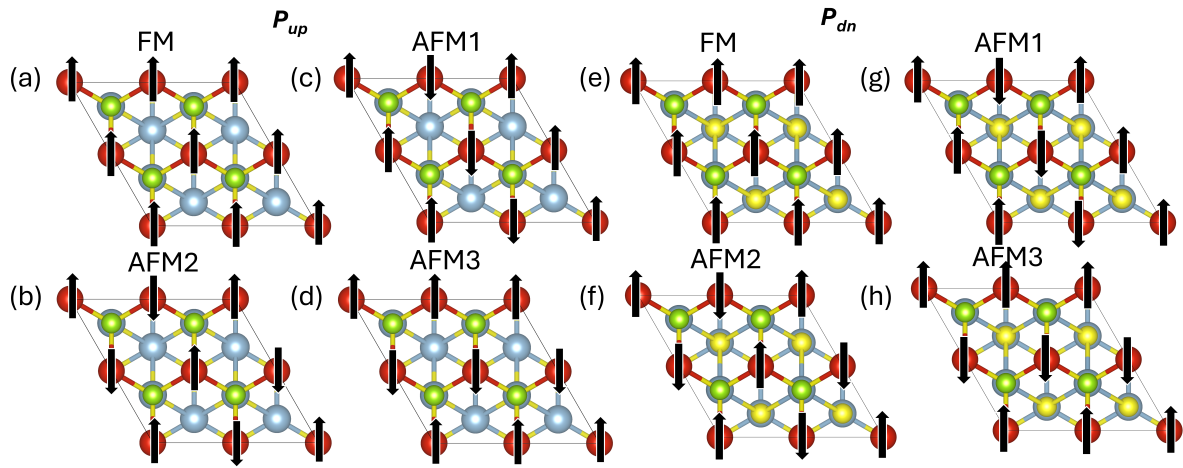


Figure 5.5: Structure of (a-d) type-I  $P_{up}$  and (e-h) type-I  $P_{dn}$  with FM and AFM configurations.

Table 5.2: Energy of different magnetic configurations of VSSe/Al<sub>2</sub>S<sub>3</sub> heterostructure in units of eV.

| Type-I VSSe/Al <sub>2</sub> S <sub>3</sub> | $P_{up}$ | $P_{dn}$ |
|--------------------------------------------|----------|----------|
| FM                                         | 0        | 0        |
| AFM1                                       | 0.475    | 0.328    |
| AFM2                                       | 0.475    | 0.327    |
| AFM3                                       | 0.474    | 0.327    |

### 5.3.2 Valley spitting and Berry curvature

Further, the electronic band structures for type-I  $P_{up}$  is displayed in Fig. 5.6(a). The energy band structure shows an indirect band-gap semiconductor with 0.29 eV band gap. Here, the



VBM is located at the  $\Gamma$  point, while the CBM resides at the  $+K/-K$  point. This arrangement creates a typical staggered-gap (Type-II) band alignment, where the VBM is primarily contributed by  $\text{Al}_2\text{S}_3$  and the CBM by the spin-up channel of  $\text{VSSe}$ . Moreover, both the conduction and valence bands have degenerate valleys at  $+K$  and  $-K$  points. The valleys of the valence band are submerged within the trivial bands of ferroelectric substrate.

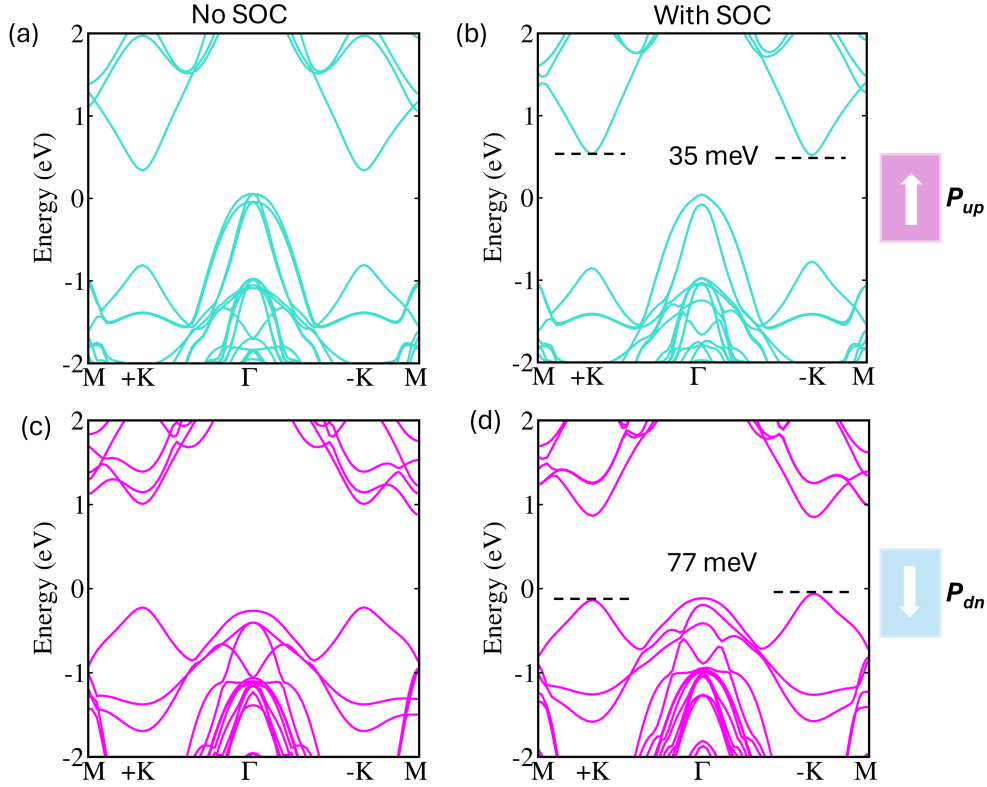


Figure 5.6: Band structures of (a) type-I  $P_{up}$  and (c) type-I  $P_{dn}$  configurations without SOC. Band structures of (b) type-I  $P_{up}$  and (d) type-I  $P_{dn}$  configurations with SOC. White arrows show the FE polarization direction. The Fermi level is set to zero.

In contrast, the type-I  $P_{dn}$  configuration undergoes a significant transformation in its band structure. Its indirect band gap expands to 0.88 eV, notably wider than that of the type-I  $P_{up}$  state. As depicted in Fig. 5.6(c), the VBM shifts to the  $+K/-K$  point, while the CBM moves to the M point. Although the Type-II band alignment is maintained, the dominant contributions to the band edges are effectively inverted compared to the type-I  $P_{up}$  configuration. Specifically, the VBM is now primarily governed by the spin-up channel of  $\text{VSSe}$ , with the CBM being dominated by  $\text{Al}_2\text{S}_3$ . Crucially, unlike the type-I  $P_{up}$  case, the valleys within the VBM remain well-preserved at the  $+K$  and  $-K$  points, whereas the valleys in the lowest conduction band become submerged.

When we include the SOC effect, as illustrated in Fig. 5.6(b) and (d), valleys become non-degenerate, resulting in spontaneous valley polarization. We calculated the spontaneous valley polarization for type-I  $P_{up}$  case in the CBM to be  $\Delta E_c = 35$  meV, and for type-I  $P_{dn}$  in the VBM, to be  $\Delta E_v = 77$  meV, which is a substantial. These values significantly surpass those found in some experimentally demonstrated magnetic proximity systems (0.3-1.0 meV) [205] and existing ferrovalley materials [140]. Such robust polarization can effectively resist the annihilation of valley polarization caused by kinetic energy near room temperature (25 meV). It is important to note that in the type-I  $P_{up}$  heterostructure, the VSSe valleys in the VBM become submerged in the trivial bands of  $Al_2S_3$ , which limit their potential utilization. Conversely, for the type-I  $P_{dn}$  configuration, the VSSe valleys in the CBM are similarly submerged. Consequently, the effective response driven by valley polarization switches from the CBM to the VBM simply by flipping the ferroelectric polarization. This transition is accompanied by a fundamental change in valley physics and the AVH effect. This means the AVH effect becomes highly controllable by reversing the electric polarization of  $Al_2S_3$ , which greatly benefits the development of reversible and nonvolatile controllable valleytronic devices. This approach stands apart from heterostructures like  $VSe_2/Sc_2CO_2$  [206], where ferroelectricity primarily enables only an on-off switching of the AVH effect. Furthermore, a detailed examination of the spin-polarized electronic band structures, presented in Fig. 5.7(a) and (b), reveals distinct spin contributions for both type-I  $P_{up}$  and type-I  $P_{dn}$  configurations. These plots indicate that in the type-I  $P_{up}$  configuration, valleys near the Fermi level in conduction band are primarily contributed by spin-up electrons of Vanadium. Conversely, in type-I  $P_{dn}$  configuration, the dominant contribution near the Fermi level in valence band comes from spin-up holes of Vanadium. Furthermore, Berry

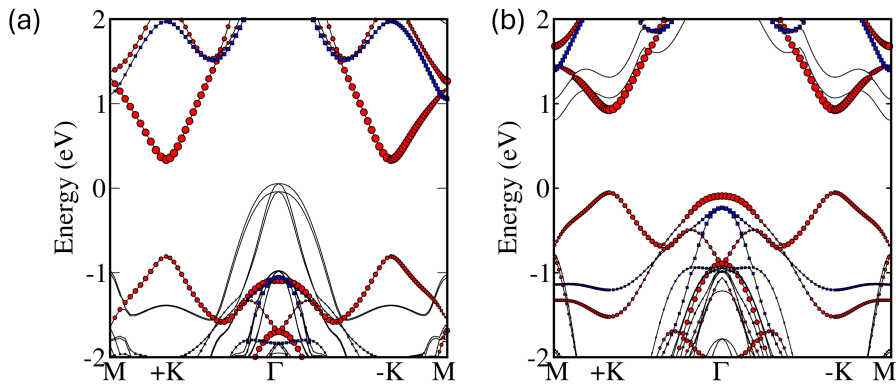


Figure 5.7: Spin projected band structures of (a) type-I  $P_{up}$  and (c) type-I  $P_{dn}$  configurations without SOC. Red and blue symbols show spin-up and spin-down charge carriers, respectively.

curvature has been an invaluable tool for examining the Hall effect. Particularly in systems where space inversion symmetry is broken, it has been observed that charge carriers within the  $+K$  and  $-K$  valleys tend to acquire a non-zero Berry curvature. Consequently, when time-reversal symmetry is also broken, an interesting characteristic emerges: a contrasting feature between valleys becomes apparent. Therefore, to understand the valley-related properties of heterostructure we have calculated the Berry curvature using Kubo formula [156]:

$$\Omega(K) = - \sum_n \sum_{m \neq n} f_n \frac{2Im \langle \psi_{nk} | v_x | \psi_{mk} \rangle \langle \psi_{mk} | v_y | \psi_{nk} \rangle}{(E_n - E_m)^2} \quad (5.1)$$

Here,  $f_n$  is the Fermi-Dirac distribution function,  $E_n$  represents the eigenvalue of the Bloch state  $|\psi_{nk}\rangle$  and  $\hat{v}_x/\hat{v}_y$  are the velocity operator components. As depicted in Fig. 5.8(a) and (b), the Berry curvatures around the  $+K$  and  $-K$  valleys exhibit distinct absolute values and opposite signs, a clear indication of a robust valley-contrasting feature. A key finding is the ability to switch the valley polarization from the CBM to the VBM simply by reversing the ferroelectric polarization of the  $Al_2S_3$  substrate. This phenomenon occurs because the time-reversal operator, which transforms the orbital part of the Bloch function to its complex conjugate and flips the spin, causes the VBM and CBM at both the  $+K$  and  $-K$  points to display Berry curvatures with opposing signs. Consequently, we observe a complete reversal of the Berry curvature signs in response to ferroelectric polarization switching.

Since, the anomalous Hall conductivity is directly proportional to the integral of the Berry curvature over the Brillouin zone, the net Hall currents generated in the type- $I_{up}$  and type- $I_{dn}$  states are clearly distinguishable. The ability to switch valley physics between the conduction and valence bands via ferroelectricity allows for an on-off control in both electron-doped and hole-doped scenarios. This demonstrates that the anomalous valley Hall effect is significantly realized and effectively controlled through ferroelectric switching.

### 5.3.3 Valleytronic memory device

These findings highlight the promising potential of the  $VSSe/Al_2S_3$  heterostructure for designing valleytronic memory devices. We have developed a prototype device based on this heterostructure, depicted in Fig. 5.8(c) and (d). In this prototype, the electric polarization in the  $Al_2S_3$  is toggled by a vertical external voltage. When the ferroelectric substrate's polarization is in the  $P_{up}$  configuration (Fig. 5.8(c)), spin-up electrons accumulate on the up side of the  $VSSe$  monolayer due to valley polarization at the CBM, yielding a measurable transverse

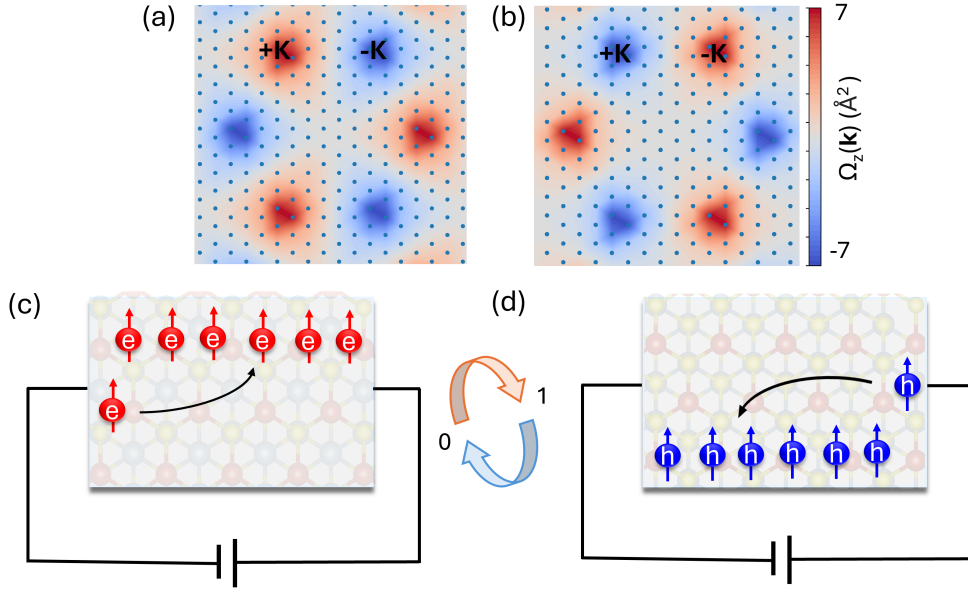


Figure 5.8: Contour maps of the Berry curvatures across the 2D Brillouin zone for the (a) type-I  $P_{up}$  and (b) type-I  $P_{dn}$  configurations. (c) Schematic of the AVH effect and memory device in (c) type-I  $P_{up}$  and (d) type-I  $P_{dn}$  configurations.

Hall voltage. We define this as the "0" state of the device. Conversely, when the ferroelectric substrate's polarization direction is reversed to  $P_{dn}$  (Fig. 5.8(d)), spin-up holes become the majority carriers, resulting in a different transverse Hall voltage signal strength, which we identify as the "1" state. This design allows for a damage-free data reading process by simply checking the differences in the ferroelectric coupling-induced Hall voltage signal strength, effectively avoiding the destructive effects often associated with directly sensing polarized states in memory devices.

## 5.4 Conclusion

We have theoretically developed a design principle for achieving reversible and nonvolatile control of the AVH effect. Our first-principles calculations confirm that stacking ferrovalley VSSe on a ferroelectric  $\text{Al}_2\text{S}_3$  monolayer allows for effective tuning of the AVH effect. We can electrically control the VSSe valley polarization, switching it from the VBM to the CBM by simply reversing the electric polarization of ferroelectric substrate. The electrical control offers a highly desirable, energy-efficient alternative to the more intensive magnetic methods typically used for controlling valley polarization. Critically, the sign of transverse Hall voltage

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is directly controlled by the ferroelectric polarization. This ferroelectric-driven and tunable AVH effect in such a multiferroic heterostructure presents a promising avenue for all-electric data memory devices.

# Exploring strong and weak topological states on isostructural substitutions in $\text{TlBiSe}_2$

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## 6.1 Introduction

Since the discovery of Topological Insulators (TIs) about a decade ago, there has been an enormous increase in interest towards topological condensed matter systems[207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 12, 217, 13]. TIs show great potential applications in quantum computing and spintronics due to the insensitivity of the transport property towards non-magnetic perturbations[218, 13]. TIs also pave the way for realizing advanced quantum phenomena such as Weyl semimetals[219], Majorana-fermions[220] and Higgs mechanism[221]. These alluring materials are insulating in bulk but support the flow of electrons on their surface. As a result, their surface consists of linear states that are protected by the Time-Reversal Symmetry (TRS)[222]. A necessary condition for the appearance of these states is the inversion of bands, which takes place at the Time-Reversal Invariant Momenta (TRIM) in the bulk Brillouin Zone (BZ)[223, 224]. The natural ordering of the energy levels forming the edges of the gap is inverted owing to the strong Spin-Orbit Coupling (SOC) associated with heavy elements. The topology of TRS invariant insulators is characterized by the  $Z_2$  index,  $\nu_0$ , which can either be 0 or 1, depicting a topologically trivial or non-trivial phase, respectively. However, it has been recently reported that even when  $\nu_0 = 0$ , the system can show non-trivial characteristics[225]. Based on whether the material hosts odd or even number of Dirac cones in the electronic structure of its surface, TIs are further classified as Strong Topological Insulator (STI) having  $Z_2$  invariant,  $\nu_0 = 1$  or Weak Topological Insulator (WTI) with  $Z_2$  invariant,  $\nu_0 = 0$ [226, 227]. Nevertheless, the complete characterization of 3D TIs requires a set of, in total, four  $Z_2$  numbers:  $(\nu_0; \nu_1 \nu_2 \nu_3)$ . The indices  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  are called weak indices and are believed to be

nonrobust quantities[228, 229]. Therefore, the calculation of surface states and  $Z_2$  invariant gives complete information about the topological nature of material.

First-principles calculations led to the prediction of a large number of 2D and 3D TIs[230, 231, 232, 226, 233, 234, 235, 236, 237, 238]. Among the various well established families of 3D TIs,  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$  have been most widely studied for investigating topological states and their properties[239, 240, 53]. Their crystal structures consist of quintuple layers held together by weak van der Waals (vdW) forces, providing natural cleavage planes without breaking strong bonds. The band structure calculations in  $\text{Bi}_2\text{Se}_3$  have shown that the Dirac point of surface state lies close to the valence band maximum (VBM)[241]. This leads to the opening of electron scattering channel from surface states to bulk continuum states, and the topological transport regime begins to collapse. Therefore, there is a strong need for materials with ideal and relatively isolated Dirac cones. A variety of candidates with non-trivial electronic states including,  $\text{HgTe}$ [242],  $\text{InAs}$ [243], ternary tetramytes  $\text{Ge}_m\text{Bi}_{2n}\text{Te}_{(m+3n)}$ , half-Huesler compounds[244, 245],  $\text{LiAuSe}$  honeycomb lattice[246],  $\beta\text{-Ag}_2\text{Te}$ [247] to non-centrosymmetric  $\text{BiTeX}$  ( $X=\text{Cl, Br, I}$ )[248] have been suggested. Theoretical studies have shown that Tl-based ternary chalcogenides, viz.,  $\text{TlSbTe}_2$ ,  $\text{TlBiSe}_2$  and  $\text{TlBiTe}_2$  are 3D TIs with a single Dirac cone surface state at the  $\Gamma$  point, which is well isolated from the bulk continuum[249]. Tl-based materials have a 3D character because each Tl (Bi) layer is sandwiched between two Se layers with strong coupling between neighboring atomic layers instead of weak vdW forces as in  $\text{Bi}_2\text{Se}_3$ . The electronic structure of many Tl-based TIs, viz.,  $\text{TlAB}_2$  ( $A = \text{Sb, Bi}$  and  $B = \text{Se, Te, S}$ ) have been investigated by Density Functional Theory (DFT) calculations[224, 250]. The role of surface termination has also been explored in  $\text{TlBiSe}_2$  and  $\text{TlBiTe}_2$ [251]. Following this, the isostructural substitution of the above base material is been endeavoured to retain its topological properties. For example, In-based compounds like  $\text{InBiTe}_2$  and  $\text{InSbTe}_2$ , crystallizing in the  $\text{TlBiSe}_2$  like crystal structure have been studied. Intriguingly, these materials lack the Dirac cone feature, which depicts their topologically trivial nature[252]. Therefore, despite  $\text{TlAB}_2$  ( $A = \text{Sb, Bi}$  and  $B = \text{Se, Te, S}$ ) showing topologically non-trivial band structure, any other isostructural substitution to retain its topological nature is hitherto unknown.

Motivated with this idea, in this article, we have explored the possibility of having materials belonging to same class of ternary chalcogenides via a thorough isostructural substitution approach. First, we have performed substitution at suitable sites of  $\text{TlBiSe}_2$  and

scanned for those materials whose band structure shows band inversion at odd/even number of TRIMs. After that, to determine the accurate band gap of TlBiSe<sub>2</sub>, we have employed various exchange-correlation ( $\epsilon_{xc}$ ) functionals, viz., PBE+SOC, HSE06+SOC,  $G_0W_0$ @PBE+SOC and  $G_0W_0$ @HSE06+SOC. The band gap obtained from  $G_0W_0$ @PBE+SOC functional is in close agreement with the experimental value. Therefore, we have further calculated the band gap of all materials using  $G_0W_0$ @PBE+SOC. Subsequently, we have examined the potential materials for their dynamical stability. The stable materials are then characterized as STI/WTI depending on whether they show odd/even number of surface states, respectively. To confirm their topological nature, we have also calculated the  $Z_2$  topological invariants.

## 6.2 Methodology

The calculations are performed using DFT[63, 64] with the Projected Augmented Wave (PAW)[85, 86] method implemented in Vienna *Ab initio* Simulation Package (VASP)[136] code. All the structures are optimized with the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[80] until the Hellmann-Feynman forces are smaller than 0.001 eV/Å. The plane wave basis is used with 400 eV cutoff energy. The  $\Gamma$ -centered  $6 \times 6 \times 4$   $k$ -grid is used to sample the irreducible BZ of rhombohedral phase with the  $R\bar{3}m$  space group. SOC is included in all calculations except in ionic optimization. The advanced hybrid  $\epsilon_{xc}$  functional (HSE06) including SOC and many-body perturbation methods,  $G_0W_0$ @PBE+SOC and  $G_0W_0$ @HSE06+SOC are used for the better estimation of the band gap[253]. For this, we have used  $4 \times 4 \times 4$   $k$ -grid, and the number of bands is set to six times the number of occupied bands. The phonon calculations are performed with  $4 \times 4 \times 4$  supercells using the PHONOPY package[254, 255]. In order to investigate the topological properties of the materials, we have performed DFT calculations using fully relativistic norm-conserving pseudopotentials as implemented in the QUANTUM ESPRESSO code[87]. The results of these DFT calculations are then fed as input to WANNIER90[101] for constructing a tight-binding model based on Maximally Localized Wannier Functions (MLWFs) with  $p$  orbitals of Se, Bi and  $sp$  orbitals of Ga, Tl, Sn, Sb, Pb. The surface states and topological invariants are then calculated using the Green's function method as implemented in the Wannier-TOOLS package[256].



## 6.3 Results and Discussions

### 6.3.1 Bulk electronic structure and band inversion

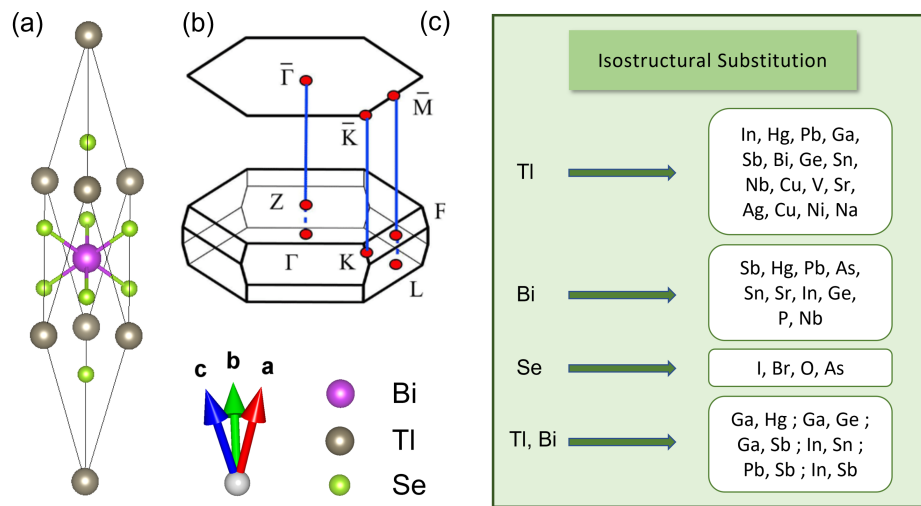


Figure 6.1: (a) Primitive crystal structure of TlBiSe<sub>2</sub>, (b) 3D BZ for primitive unit cell with four time-reversal invariant points  $\Gamma$ , Z, F and L along with the projected surface BZ, and (c) Complete substitution with various elements at Tl, Bi, Se and Tl, Bi sites simultaneously.

TlBiSe<sub>2</sub> belongs to the Tl-family of compounds having a rhombohedral crystal structure with space group  $R\bar{3}m$ [249]. There are four atoms in the primitive unit cell which are placed in layers normal to the three-fold axis with the sequence -Tl-Se-Bi-Se-, i.e., along [111] axis of rhombohedral unit cell (see Figure 6.1(a)). The 3D BZ for rhombohedral unit cell having high symmetry points F,  $\Gamma$ , L and Z, along with its projected (111) surface BZ is shown in Figure 6.1(b). The structure has inversion symmetry where both Bi and Tl act as inversion centers. We have first estimated the band gap of TlBiSe<sub>2</sub> using PBE+SOC. The calculated band gap is 215 meV (Direct), whereas the experimental band gap is 350 meV[257]. The band gap is thus underestimated due to the DFT limitation arising from the approximations used in the  $\epsilon_{xc}$  functional. Therefore, we have used hybrid  $\epsilon_{xc}$  functional (HSE06) with default  $\alpha = 0.25$ , i.e., incorporating 25% of Hartree-Fock exact exchange to capture the electron's self-interaction error along with SOC. It gives a direct band gap of 85 meV, which is also not in accordance with previously reported theoretical calculations[251]. Therefore, we have performed  $G_0W_0$  calculations on top of the orbitals obtained from the PBE+SOC ( $G_0W_0$ @PBE+SOC) and HSE06+SOC ( $G_0W_0$ @HSE06+SOC). The respective band gaps are 280 meV and 249 meV

(see Table 6.1).  $G_0W_0@PBE+SOC$  gives the most accurate band gap, however, the band profile is not much affected by the choice of  $\epsilon_{xc}$  functional (see Fig. 6.2). Therefore, we have used PBE  $\epsilon_{xc}$  functional to plot the band structures in view of its low computational cost. The band structure of TlBiSe<sub>2</sub> with the projected wavefunctions to atomic orbitals is shown in Figure 6.3(a). The Conduction Band (CB) is dominated by Bi- $p$  and Tl- $p$  orbitals, while Se- $p$  orbitals dominate the Valence Band (VB). The inclusion of SOC has led to an increase in the band gap around the  $\Gamma$  point. The valence and conduction band edges switch their orbital character around this point, indicating the band inversion. The  $p$  orbitals of Se and Bi are involved in this band inversion, as can be clearly seen from Figure 6.3(b).

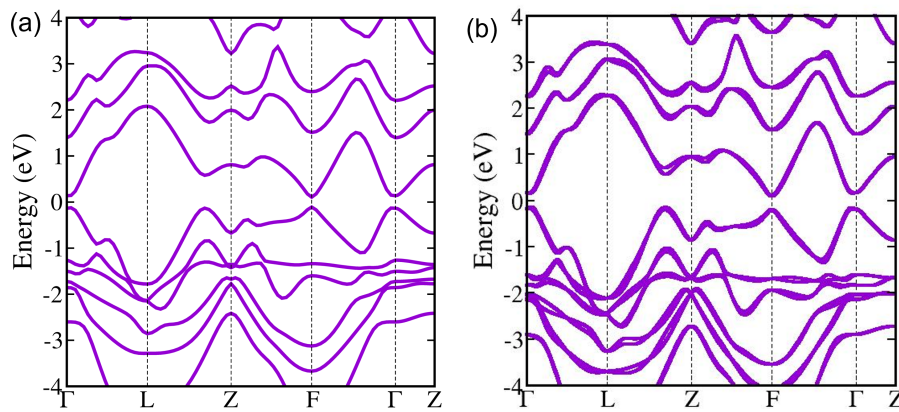


Figure 6.2: Band structure of TlBiSe<sub>2</sub> calculated using (a) PBE+SOC (b)  $G_0W_0@PBE+SOC$ .

Table 6.1: Band gap (in meV) of TlBiSe<sub>2</sub> using different  $\epsilon_{xc}$  functionals.

| PBE+SOC | HSE06+SOC | $G_0W_0@PBE+SOC$ | $G_0W_0@HSE06+SOC$ |
|---------|-----------|------------------|--------------------|
| 215     | 85        | 280              | 249                |

The similar band inversion has also been observed in TlBiTe<sub>2</sub> and TlSbSe<sub>2</sub>[251]. Following the trend, we have carried out complete substitution in TlBiSe<sub>2</sub> at Tl, Bi or Se sites and Tl, Bi sites simultaneously to obtain different materials belonging to the same class (see Figure 6.1(c)). The band structures of these materials are plotted to see the effect of SOC on the orbital contribution projected on the bands lying near Fermi level. Firstly, Ga is substituted at the Tl site ( $Ga_{Tl}$ ) to form GaBiSe<sub>2</sub>. It also crystallizes in  $R\bar{3}m$  phase with lattice parameters given as  $a = b = c = 7.18 \text{ \AA}$  (in rhombohedral setting) and yields the band structure shown in Figure 6.3(c). SOC driven inversion of energy levels along with opening of band gap takes place at

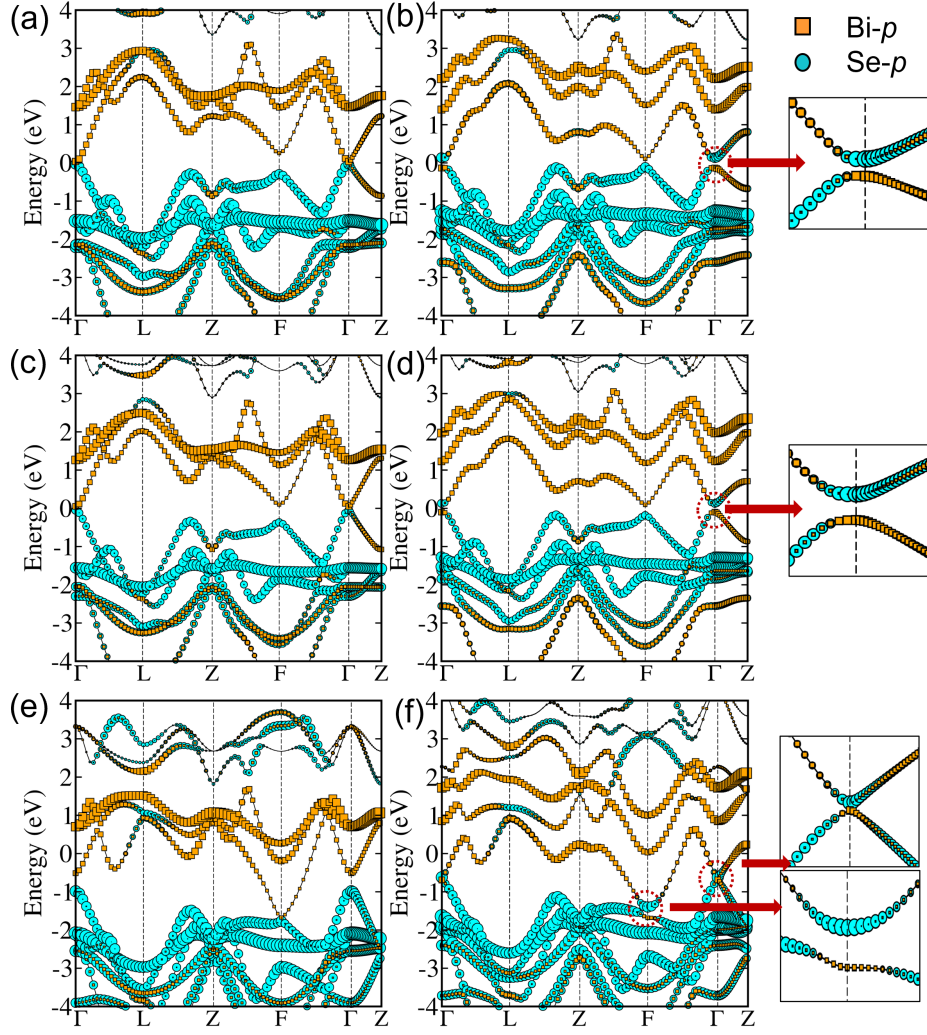


Figure 6.3: The band structures for  $\text{TlBiSe}_2$ ,  $\text{GaBiSe}_2$  and  $\text{PbBiSe}_2$  without SOC are shown in (a), (c), (e) and with SOC are shown in (b), (d), (f), respectively. Insets show band inversion at respective high symmetry points.

high symmetry point  $\Gamma$  (Figure 6.3(d)). The projected wavefunctions to atomic orbitals show that  $p$  orbitals of all atoms contribute near the Fermi level. The inversion involves Bi- $p$  and Se- $p$  orbitals (similar to the case of  $\text{TlBiSe}_2$ ), giving an initial indication that the material can harbor non-trivial topological phase. The indirect band gap as calculated by  $G_0W_0@PBE+SOC$  is 183 meV.

After  $\text{GaBiSe}_2$ , we have substituted  $\text{Pb}_{\text{Tl}}$  to get  $\text{PbBiSe}_2$  having lattice parameters as  $a = b = c = 8.27 \text{ \AA}$ , and crystallizing in the  $R\bar{3}m$  phase.  $G_0W_0@PBE+SOC$  yields an indirect band gap of 3 meV. The VB and CB are mainly composed of  $p$  orbitals of Pb, Bi and Se, as shown in Figure 6.3(e) and 6.3(f). The parity inversion occurs at  $\Gamma$  and F points, unlike the former. In this BZ, there are 8 TRIMs, i.e.,  $\Gamma$ , Z (non-degenerate) and F, L (triply-degenerate). Therefore,

the inversion is occurring at even number of TRIMs, which means that the system should be in trivial state. However, it has been found that if even number of band inversions occur in the first quadrant, but if one or more BZ sides possess odd number of band inversions, then a WTI can be obtained[235].

Table 6.2: Band gap (in meV) of different materials using  $G_0W_0$ @PBE+SOC.

| Material                            | Indirect Band Gap |
|-------------------------------------|-------------------|
| <b>GaBiSe<sub>2</sub></b>           | 183               |
| <b>PbBiSe<sub>2</sub></b>           | 3                 |
| <b>SnBiSe<sub>2</sub></b>           | 20                |
| <b>SbBiSe<sub>2</sub></b>           | 118               |
| <b>Bi<sub>2</sub>Se<sub>2</sub></b> | 327               |
| <b>TlSnSe<sub>2</sub></b>           | 44                |
| <b>PbSbSe<sub>2</sub></b>           | 41                |

Table 6.3: Optimized lattice parameters for  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$  and  $\text{PbSbSe}_2$ .

| Material                            | Lattice Parameters( $\text{\AA}$ ) |
|-------------------------------------|------------------------------------|
| <b>SnBiSe<sub>2</sub></b>           | 8.254                              |
| <b>SbBiSe<sub>2</sub></b>           | 8.059                              |
| <b>Bi<sub>2</sub>Se<sub>2</sub></b> | 8.163                              |
| <b>TlSnSe<sub>2</sub></b>           | 7.747                              |
| <b>PbSbSe<sub>2</sub></b>           | 8.166                              |

A similar type of parity inversion at even number of TRIMs is obtained for  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$  and  $\text{PbSbSe}_2$  (refer Fig. 6.4 and 6.5 for band structures and Table 6.3 for optimized lattice parameters, respectively). The band gaps of all these materials calculated using  $G_0W_0$ @PBE+SOC are given in Table 6.2. After screening the systems for SOC-induced inversion in the band structures, we have analyzed them for dynamical stability. Figure 6.6 shows the phonon band structures for  $\text{GaBiSe}_2$  and  $\text{PbBiSe}_2$ . The absence of negative frequencies confirms the dynamical stability of these materials. For other systems, viz.,

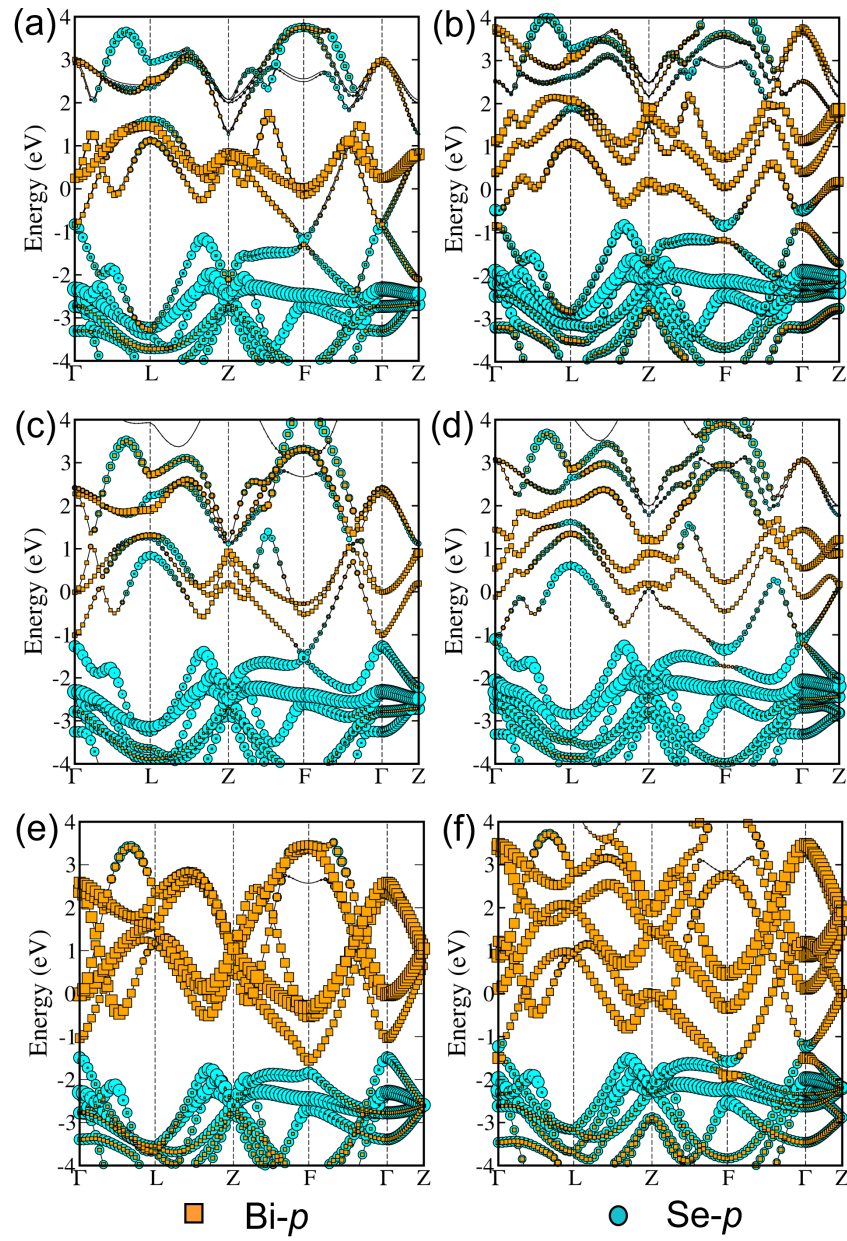


Figure 6.4: The band structures for  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$  and  $\text{Bi}_2\text{Se}_2$  without SOC are shown in (a), (c), (e) and with SOC are shown in (b), (d), (f), respectively.



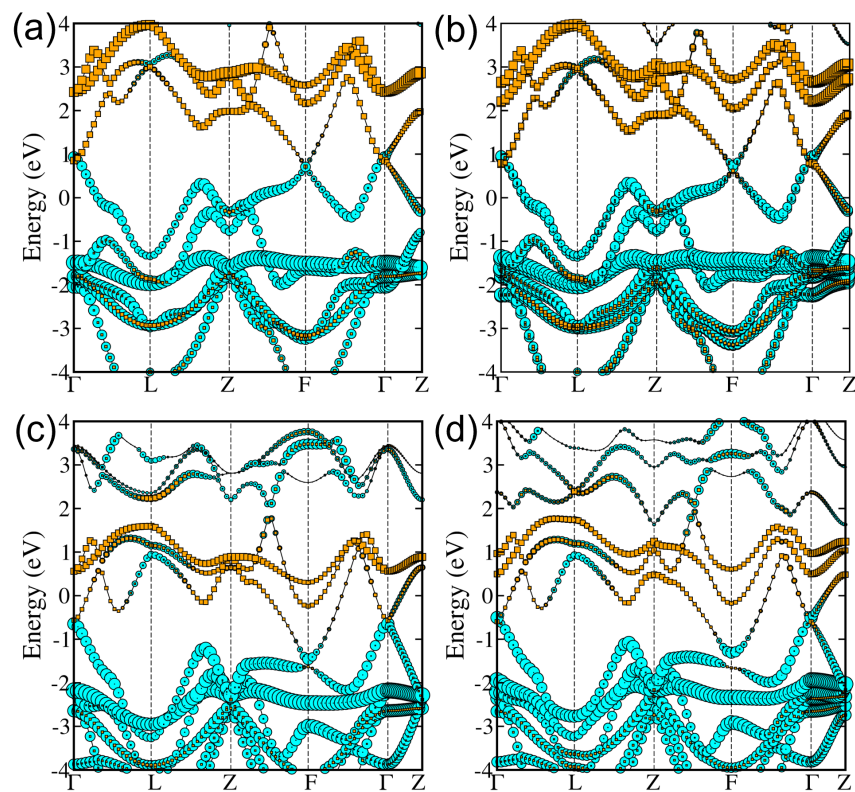


Figure 6.5: The band structures for  $\text{TlSnSe}_2$  and  $\text{PbSbSe}_2$  without SOC are shown in (a), (c) and with SOC are shown in (b), (d), respectively.

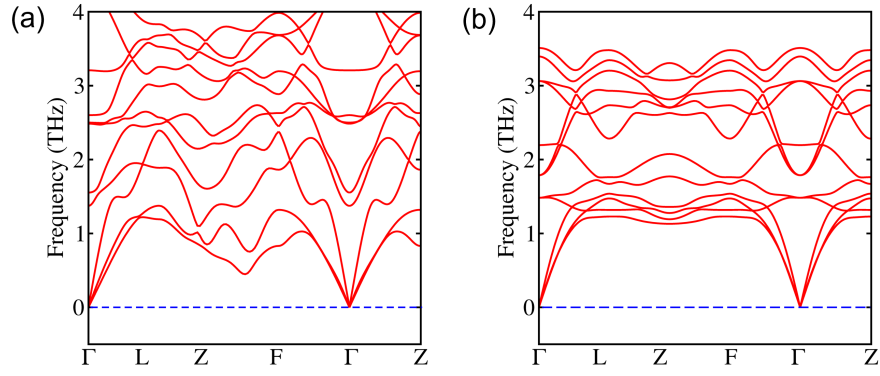


Figure 6.6: Phonon band structures of (a) GaBiSe<sub>2</sub> and (b) PbBiSe<sub>2</sub>.

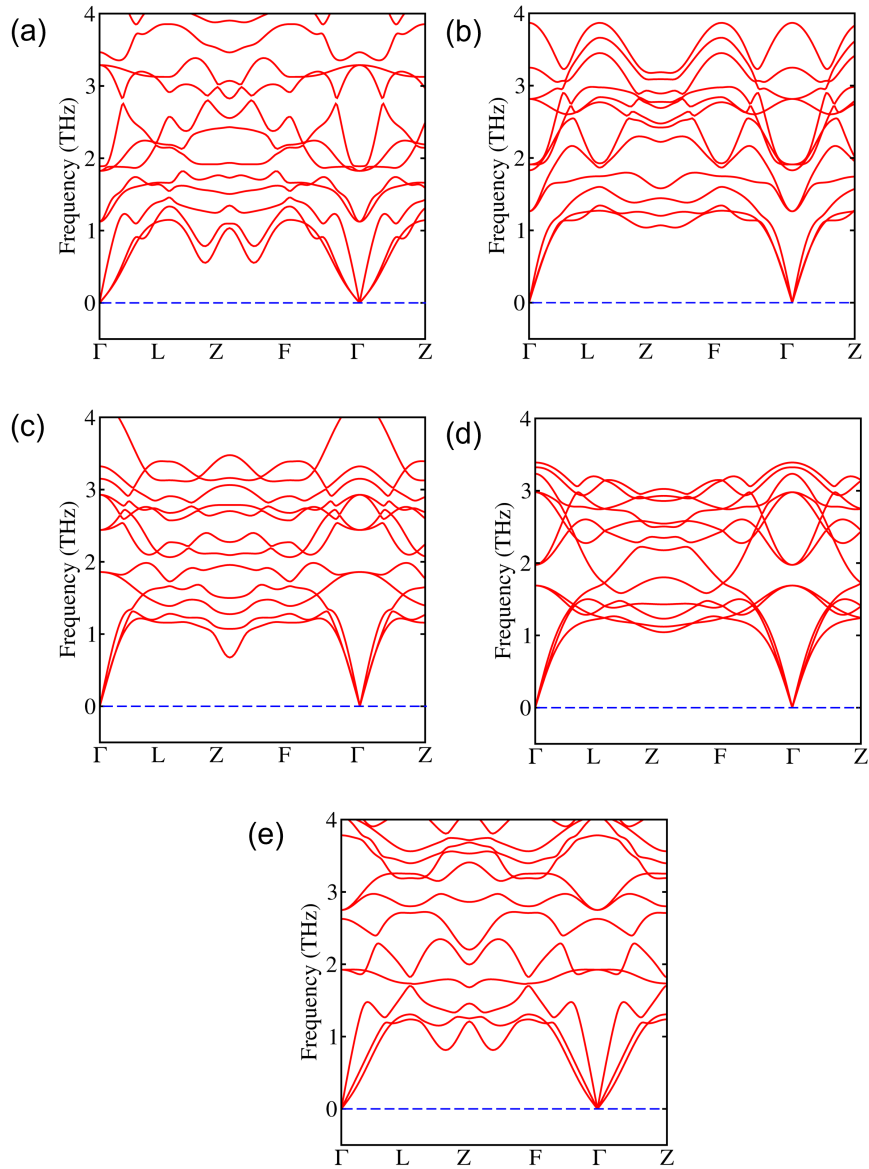


Figure 6.7: Phonon band structures of (a) SnBiSe<sub>2</sub>, (b) SbBiSe<sub>2</sub>, (c) Bi<sub>2</sub>Se<sub>2</sub>, (d) TlSnSe<sub>2</sub> and (e) PbSbSe<sub>2</sub>.

SnBiSe<sub>2</sub>, SbBiSe<sub>2</sub>, Bi<sub>2</sub>Se<sub>2</sub>, TlSnSe<sub>2</sub> and PbSbSe<sub>2</sub>, see Fig. 6.7.

### 6.3.2 Topological surface states and $Z_2$ invariant

The presence of band inversion on inclusion of SOC is a telltale signature of possibility of non-trivial phase. However, an inverted band structure cannot be considered as a sole criterion to assure the existence of a non-trivial phase. Therefore, further analysis is required to establish its topological nature. Previous studies have reported that non-trivial band topology generates metallic surface states, which are the hallmark of TIs[55]. In view of this, we have computed the spectrum of surface states by considering a semi infinite slab of 3D material. These lattice surfaces possess Dirac cones, lying at the same  $k$ -point where the band inversion has occurred in the corresponding bulk band structure. Furthermore, to elucidate the topological nature of the materials,  $Z_2$  topological invariants are calculated. TRS yields four distinct  $Z_2$  invariants ( $\nu_0; \nu_1 \nu_2 \nu_3$ ) in 3D case. Each of these four invariants takes up value either 0 or 1, indicating a total of 16 phases with three general classes: a normal insulator, an STI and a WTI[229]. An ordinary or trivial insulator is obtained when all four invariants are zero, i.e., (0;000), while an STI is obtained when  $\nu_0 = 1$ . This type of system is robust against weak time-reversal invariant perturbations. However, when  $\nu_0 = 0$ , and at least one of the indices out of  $\nu_1$ ,  $\nu_2$  or  $\nu_3$  is nonzero, then the material is WTI. It can be viewed as a stacking of 2D TIs, and is less robust against perturbations.

It has already been established that TlBiSe<sub>2</sub> is a strong 3D TI[258]. On that account, we first obtain its surface band structure. For this, a tight-binding Hamiltonian with MLWFs considering the projection of  $p$  orbitals of Bi/Se and  $sp$  orbitals of Tl is constructed. Since the left and right surface for TlBiSe<sub>2</sub> terminates with different atoms (Tl and Se, respectively), therefore, we have plotted surface state spectra of (111) surface for both the surface terminations. Figure 6.8(a) and 6.8(b) show a single surface state protected by TRS at the  $\Gamma$  point in the projected 2D BZ. Alongside, we have calculated the topological invariant,  $\nu_0$ , which comes out to be 1, confirming that TlBiSe<sub>2</sub> is an STI. Following this, we have explored GaBiSe<sub>2</sub> for topological properties. In this case, the  $p$  orbitals of Bi/Se and  $sp$  orbitals of Ga are considered in constructing the tight-binding Hamiltonian. A single Dirac cone protected by TRS has been observed for (111) surface (see Figure 6.8(c) and 6.8(d)), and the corresponding topological invariant is (1;000), which is a signature of non-trivial topology. This validates that GaBiSe<sub>2</sub> is an STI.

Afterwards, we have performed surface band structure calculation for PbBiSe<sub>2</sub>. We have



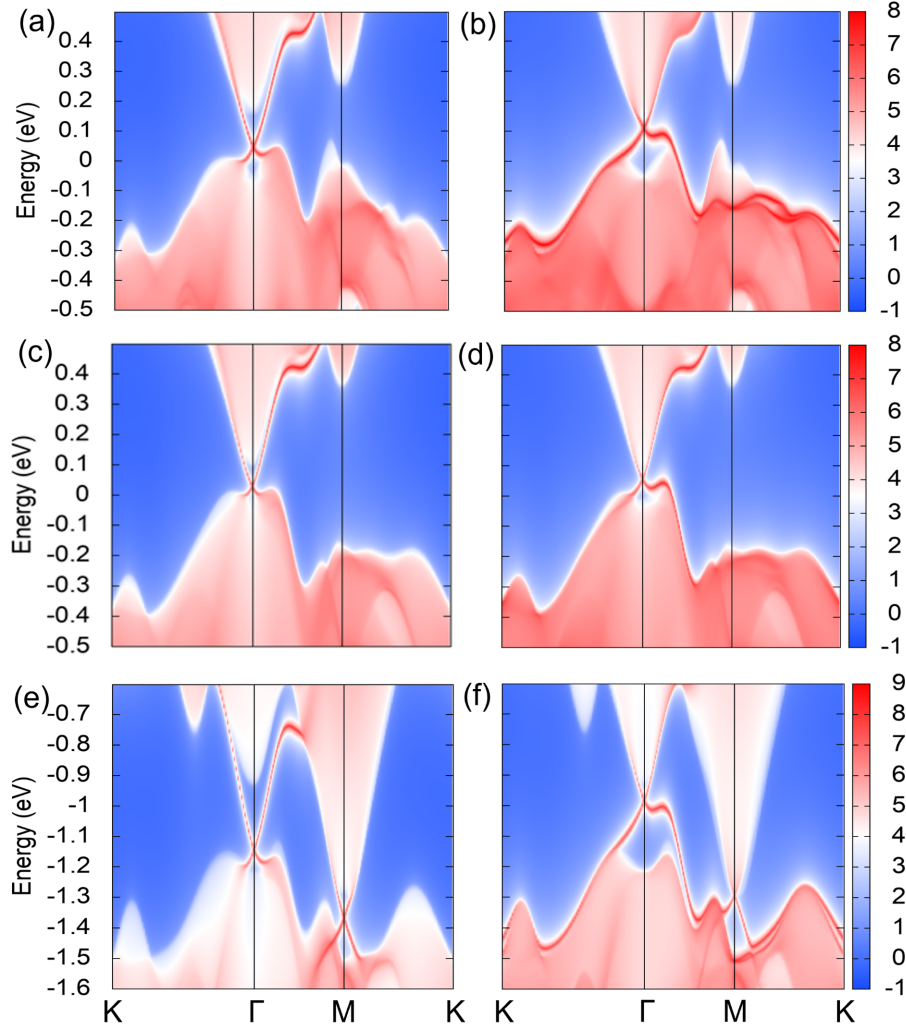


Figure 6.8: Surface states for the left surface of  $\text{TlBiSe}_2$ ,  $\text{GaBiSe}_2$  and  $\text{PbBiSe}_2$  are shown in (a), (c), (e) and for the right surface are shown in (b), (d), (f), respectively. Here, the sharp red curves represent surface states, whereas, the shaded regions show the spectral weight of projected bulk bands.

obtained even (two) number of surface states lying at  $\Gamma$  and  $M$  (see Figure 6.8(e) and 6.8(f)). The presence of even number of surface states yields  $\nu_0 = 0$ , and the weak indices come out to be  $\nu_1 = 0$ ,  $\nu_2 = 0$  and  $\nu_3 = 1$ . As even number of surface states lead to scattering and are not topologically protected, hence this material is categorized as a WTI. The similar calculations are performed for  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$  and  $\text{PbSbSe}_2$ . All of them show even number of surface states, as shown in Fig. 6.9 and 6.10, and corresponding  $Z_2$  invariants are given in Table 6.4. These materials belong to the class of  $Z_2$  WTI. Nowadays, WTIs are also getting attention as it has been found that their surface states are robust against imperfections, owing to the delocalization of surface electrons[259].

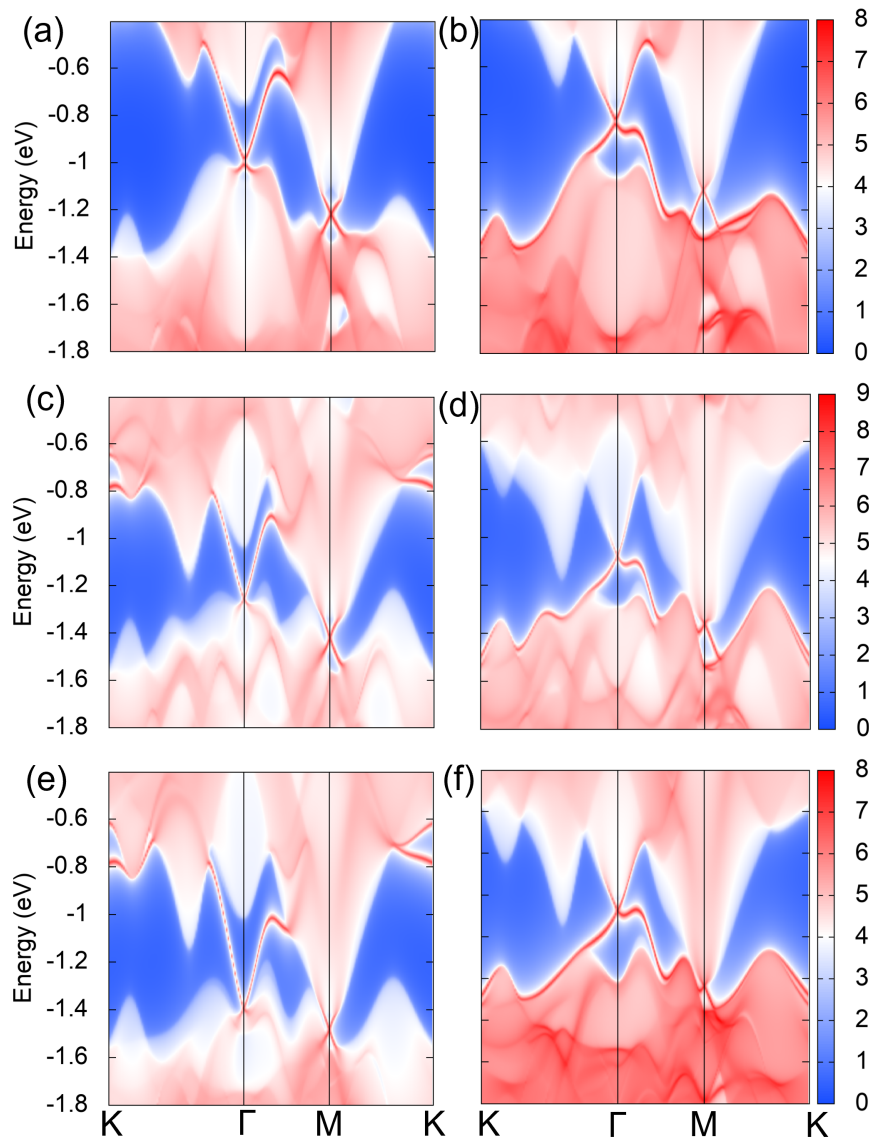


Figure 6.9: Surface states for the left surface of  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$  and  $\text{Bi}_2\text{Se}_2$  are shown in (a), (c), (e) and for the right surface are shown in (b), (d), (f), respectively.

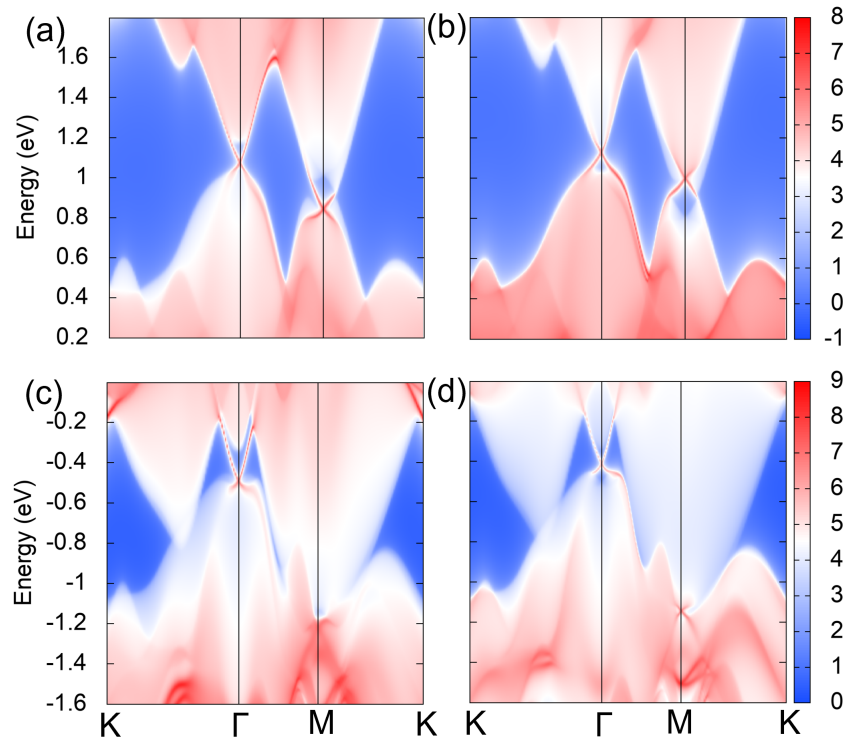


Figure 6.10: Surface states for the left surface of  $\text{TlSnSe}_2$  and  $\text{PbSbSe}_2$  are shown in (a), (c) and for the right surface are shown in (b), (d), respectively.

Table 6.4: Calculated  $Z_2$  invariants for different materials.

| Material                 | $Z_2: (\nu_0; \nu_1 \nu_2 \nu_3)$ | Number of surface states | Type |
|--------------------------|-----------------------------------|--------------------------|------|
| $\text{GaBiSe}_2$        | (1;000)                           | 1                        | STI  |
| $\text{PbBiSe}_2$        | (0;001)                           | 2                        | WTI  |
| $\text{SnBiSe}_2$        | (0;001)                           | 2                        | WTI  |
| $\text{SbBiSe}_2$        | (0;001)                           | 2                        | WTI  |
| $\text{Bi}_2\text{Se}_2$ | (0;001)                           | 2                        | WTI  |
| $\text{TlSnSe}_2$        | (0;001)                           | 2                        | WTI  |
| $\text{PbSbSe}_2$        | (0;111)                           | 2                        | WTI  |

## 6.4 Conclusion

In summary, we have performed isostructural substitutions of materials based on SOC-induced parity inversion in the band structure. Using first-principles based methodologies, viz., PBE,

HSE06, and many-body perturbation theory ( $G_0W_0$ ), we have systematically studied the electronic structure of topological materials belonging to  $R\bar{3}m$  space group. The band gap calculated using  $G_0W_0$ @PBE+SOC is in close agreement with the experimental value. We have confirmed that GaBiSe<sub>2</sub> is an STI as its surface accommodates a single crossing at the  $\Gamma$  point. PbBiSe<sub>2</sub>, SnBiSe<sub>2</sub>, SbBiSe<sub>2</sub>, Bi<sub>2</sub>Se<sub>2</sub>, TlSnSe<sub>2</sub> and PbSbSe<sub>2</sub> are WTI catering even number of surface states within the bulk band gap. The absence of negative frequencies in the phonon band structures indicates dynamical stability. The calculated  $Z_2$  invariants are in accordance with the surface state plots confirming their topological nature. We believe, exploring these materials both theoretically and experimentally will offer a great platform for studying intriguing quantum effects.

# Strain-driven topological quantum phase transition in (pseudo) cubic (mixed)-Cs/MA/FA halide perovskites

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## 7.1 Introduction

Topological phases of matter such as topological insulators [260, 11], Dirac semimetals [261, 262], Weyl semimetals [263, 218, 264], topological semimetals [265], and topological crystalline insulators [266] have occupied ample space in the research areas in the last two decades. Among these phases, topological insulators are one of the most promising materials for application in spintronics due to their conducting surface states within the bulk band gap [267, 268, 269, 270, 271, 272]. Numerous materials like Bi-based selenides and tellurides [53, 273], skutterudites [274], Heusler compounds [245, 244], and Bi-based oxide perovskites ( $\text{ABiO}_3$ ) [275, 276, 277] have been extensively explored for non-trivial topology. More recently, halide perovskites have also attracted attention for research in the area of band topology [278]. These are the compounds with the formula  $\text{ABX}_3$ , where A is an inorganic or organic cation, B is a heavy element, and X is a halogen. These materials are well known for their high performance in the field of optoelectronics, photovoltaics, photocatalysts, and thermoelectrics [279, 280, 281, 282]. Their endeavors can be attributed to the compositional and structural diversity that enables a wide array of functional properties. They possess a suitable orbital symmetry and are structurally flexible to external stimuli such as pressure, temperature, and chemical doping, which make them useful in the field of topology [283, 277]. Furthermore, the molecular orbital picture of topologically non-trivial cubic  $\text{ABiO}_3$ , matches that of cubic halide perovskites ( $\text{CsSnX}_3$ ) [284]. However, unlike oxide perovskites, the  $s$ - $p$  inversion on inclusion of spin-orbit coupling (SOC) is not shown by the halide perovskites. Therefore, the family of halide perovskites is not known to show topologically non-trivial phases at ambient conditions.

Nevertheless, if we tune certain aforementioned external parameters, a topological phase can be realized in halide perovskites [285]. It is consistent with the recent theoretical calculations that compressive strain can drive these materials into the topological insulator region [284]. At a critical value of strain, a phase transition takes place, transforming a normal insulator to a topological insulator (NI-TI). In materials preserving inversion symmetry, a continuous topological phase transition (TPT) takes place [286]. However, another type of phase transition, which is discontinuous in nature, has been observed in  $\text{MAPbI}_3$  (MA=methylammonium) via application of pressure. It has been shown that in pseudocubic perovskites like  $\text{MAPbI}_3$ , the inversion symmetry breaking has a profound effect on the nature of phase transition [278] (see Fig. 7.1). The discontinuous phase transition has also been observed in  $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$  and  $\text{TlBiS}_{1-x}\text{Se}_x$  [287, 288, 289, 290]. This is of key importance for device applications based

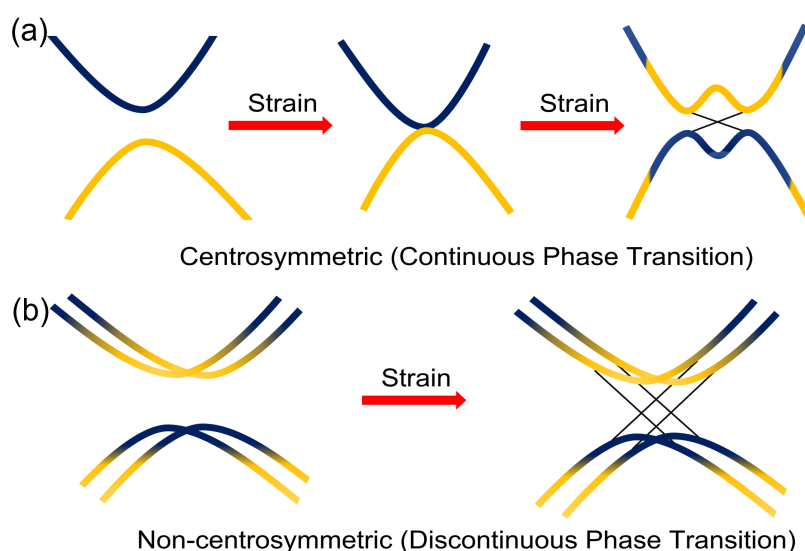


Figure 7.1: Schematic showing (a) continuous and (b) discontinuous topological phase transition.

on tuning the topological properties of the system by external means. Therefore, the realization of non-trivial phases under the effect of strain in pseudocubic perovskite will bring several families of compounds, beyond the intermetallic alloys, into the domain of research on band topology. This could be important in providing various heterostructure interfaces with multifunctional properties.

Motivated by this idea, we have first explored the NI-TI phase transition in  $\text{FAPbI}_3$  (FA = formamidinium) under the effect of compressive strain. It has been found that the nature of TPT is continuous for cubic  $\text{FAPbI}_3$ . But, when the centrosymmetry is broken in  $\text{FAPbI}_3$ , an inverted band gap opens without closing to zero. The absence of inversion symmetry brings a first-order

quantum phase transition on application of strain. We have applied volumetric strain to trigger this non-trivial topology, by inducing a band inversion in the bulk band structure. After that, the surface band structure is obtained to see the origin of surface states with increasing strain. To explore the underlying quantum mechanical process, which occurs due to structural deformation caused by the application of strain, Slater-Koster tight-binding (TB) model has been employed to explore the electronic structure. Further, we have also designed the thermodynamically stable mixed cation halide perovskites with the formula  $\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$  ( $x = 0.25, 0.50, \text{ and } 0.75$ ). The bulk and surface band structures are plotted at different values of strain to observe the TPT. Afterward, the structural stability of all the unstrained and strained configurations at an operational temperature of 300K has been confirmed to signify their practical usage.

## 7.2 Methodology

The calculations are performed using DFT [63, 64] with the Projected Augmented Wave (PAW) [85, 86] method implemented in Vienna *Ab initio* Simulation Package (VASP) [136] code. The electronic structure calculations are performed using the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [80]. The structural parameters are fully optimized until the Hellmann-Feynman forces are smaller than 1 meV/Å. The cutoff energy of 520 eV is used for the plane wave basis set such that the total energy calculations are converged within  $10^{-5}$  eV. A  $\Gamma$ -centered  $4 \times 4 \times 4$   $k$ -grid is used to sample the irreducible Brillouin zone (BZ) of cubic phase with the  $Pm\bar{3}m$  space group. Throughout the calculations, we have included SOC in order to consider the relativistic effects due to the presence of heavy element in the systems. To confirm the accuracy of electronic band inversion, hybrid functional HSE06+SOC calculations have been performed [141]. In HSE06 functional the exchange potential is divided into short range and long range part. A fraction of non-local Hartree-Fock exchange potential mixed with the GGA exchange potential of PBE is described as the short range part [SR]. The long range part [LR] and the correlation potential are described by the PBE (DFT) functional:

$$E_{x_c}^{\text{HSE06}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}} \quad (7.1)$$

here,  $\alpha$  is the mixing coefficient and  $\omega$  is the screening length. We have used many-body perturbation method  $G_0W_0$ @HSE06+SOC for the better estimation of the band gap [253]. We have tuned the  $\alpha$  parameter from 25% to 53% in HSE06+SOC to have a reliable prediction

of the starting point, for the single shot GW calculations. For our GW calculations, we have considered 320 NBANDS (six times the number of occupied bands) and energy cutoff is set to 500 eV. After this, to investigate the topological phases, the first-principles calculations are first performed using fully relativistic norm-conserving pseudopotentials as implemented in the QUANTUM ESPRESSO code [87]. The results of these DFT calculations are then fed as input to WANNIER90 [101] for constructing a TB model based on Maximally Localized Wannier Functions (MLWFs) with  $p$  orbitals of I and  $s$  and  $p$  orbitals Pb. The surface states are then calculated using the Green's function through an interactive method implemented in the Wannier-TOOLS package [256]. A TB model using Slater and Koster approach [291] is constructed in the two-center approximation using the package Tight Binding Studio [292]. A nonlinear fitting algorithm as implemented in Tight Binding Studio is used to find the best fit entries for both Hamiltonian and overlap matrices to reproduce the first-principles data. Finally, the structural stability of different configurations is checked at higher temperature using *ab initio* molecular dynamics (AIMD) by running a 5 ps long simulation with NVT ensemble (Nose-Hoover thermostat) and NPT ensemble (Langevin thermostat).

## 7.3 Results and Discussions

### 7.3.1 Electronic Structure of FAPbI<sub>3</sub>

FAPbI<sub>3</sub> exists in cubic phase with  $Pm\bar{3}m$  space group at 298 K with planar [H<sub>2</sub>N-CH-NH<sub>2</sub>]<sup>+</sup> cation surrounded by [PbI<sub>3</sub>]<sup>−</sup> octahedra as shown in Fig. 7.2(a). The lattice constant is taken as 6.36 Å, which is in close agreement with the previous report [293]. The structural relaxation of FAPbI<sub>3</sub> carried out using DFT methods leads to a distortion in the octahedral cage, causing an asymmetry in the structure [294]. The crystal structure becomes pseudocubic with Pb-I-Pb angle 171.6° as shown in Fig. 7.2(b), which is similar to that of MAPbI<sub>3</sub> [278]. The bulk BZ showing the high symmetry  $k$ -points and the projected surface BZ is shown in Fig. 7.2(c). The conduction bands near the Fermi surface are mainly contributed by the Pb-6 $p$  orbitals, whereas the valence bands are mainly contributed by Pb-6 $s$  and I-5 $p$  orbitals [295] (for partial density of states plot see Fig. 7.3). The energy states of other elements in FA are mainly distributed in the deep energy levels, and are not involved in bonding. The Pb- $\{s,p\}$ -X- $p$  covalent interaction in the octahedron gives rise to four bonding and antibonding bands along with five nonbonding bands [296]. As seen in Fig. 7.2(d), the orbitals denoted by  $\sigma_{s-p}$ ,  $\pi_{p-p}$  and  $\sigma_{p-p}$  are the bonding



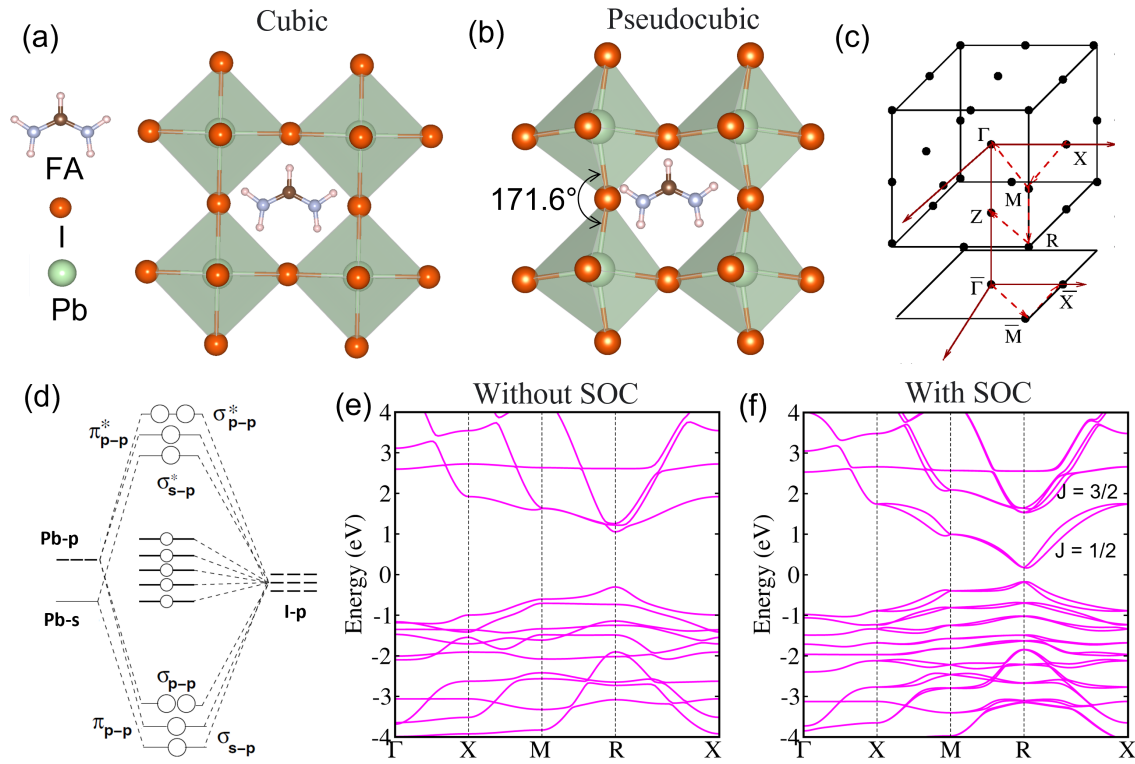


Figure 7.2: Crystal structure of (a) cubic and (b) pseudocubic  $\text{FAPbI}_3$ . (c) 3D BZ along with the projected 2D BZ. (d) The molecular orbital picture for  $\text{FAPbI}_3$ . Bulk band structure of  $\text{FAPbI}_3$  in the (e) absence of SOC and (f) presence of SOC.

molecular orbitals, whereas the orbitals denoted by  $\sigma^*_{s-p}$ ,  $\pi^*_{p-p}$  and  $\sigma^*_{p-p}$  are the antibonding molecular orbitals. FA contributes one electron, Pb contributes four and I contributes five electrons per formula unit, hence, the valence electron count becomes 20. Therefore, the states up to  $\sigma^*_{s-p}$  are filled and the Fermi level exists in between the lower-lying Pb-s and upper-lying Pb-p antibonding bands. The SOC arising due to the presence of heavy element affects the band structure near the Fermi level. Fig. 7.2(e) shows the electronic band structure of  $\text{FAPbI}_3$  in the absence of SOC. On inclusion of SOC, the  $\mathbf{L} \cdot \mathbf{S}$  coupling lifts the degeneracy between the states  $\mathbf{J} = \frac{1}{2}$  and  $\mathbf{J} = \frac{3}{2}$  as shown in Fig. 7.2(f). The strength of atomic SOC is the deterministic factor towards tailoring the non-trivial topological phases in  $\text{ABX}_3$ . However, the breaking down of the inversion symmetry causes both the atomic SOC and Rashba SOC to become deterministic in tailoring the electronic behavior of these noncentrosymmetric quantum materials [297].

The experimentally reported band gap of  $\text{FAPbI}_3$  is 1.48 eV [298]. The closest band gap of 1.56 eV is reproduced by  $\text{G}_0\text{W}_0\text{@HSE06+SOC}$  with  $\alpha$  (HF exchange) = 53%, which is in agreement with the previous report [299].  $\alpha$  parameter determines the proportion of Hartree-

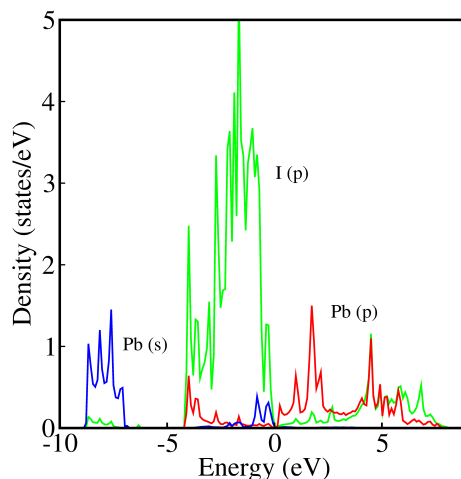


Figure 7.3: Partial density of states for FAPbI<sub>3</sub> showing I-p, Pb-s and Pb-p states in green, blue and red colours, respectively.

Fock (HF) exchange included in the exchange-correlation energy. We have observed that except for the band gaps, other band features are similar irrespective of the choice of functional (see Fig. 7.4). Therefore, we have used PBE functional for further calculations in view of its low computational cost. The compressional strain is a natural external stimulus to vary the bond length while maintaining the symmetry of the lattice [300, 301, 302, 303]. Therefore, we have investigated the effect of strain on the evolution of band structure. The primary objective of this study is to examine the influence of centrosymmetry on the nature of topological phase transitions. Therefore, we have investigated this effect by conducting parallel calculations on both cubic and pseudocubic halide perovskite structures. By analyzing these two systems, we aim to gain insights into how the presence or absence of centrosymmetry impacts the characteristics of topological phase transitions.

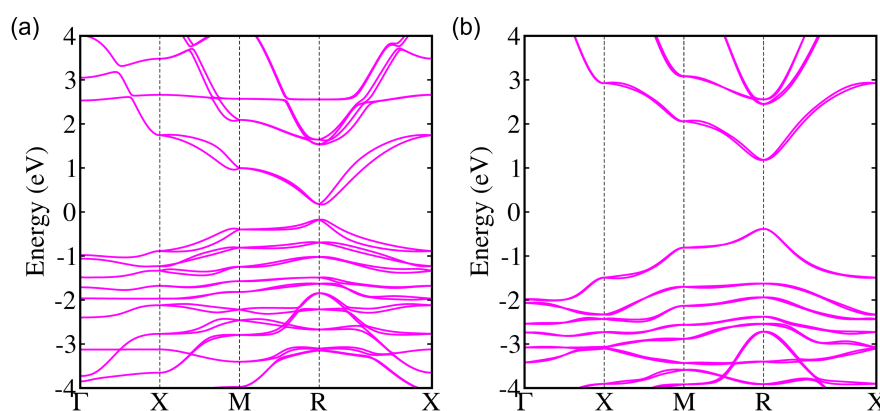


Figure 7.4: Band structure of FAPbI<sub>3</sub> calculated using (a) PBE+SOC and (b) G<sub>0</sub>W<sub>0</sub>@HSE06+SOC.

In the case of cubic FAPbI<sub>3</sub>, at a critical compression  $\gamma$  ( $V/V_0$ ) = 0.76, the inversion between

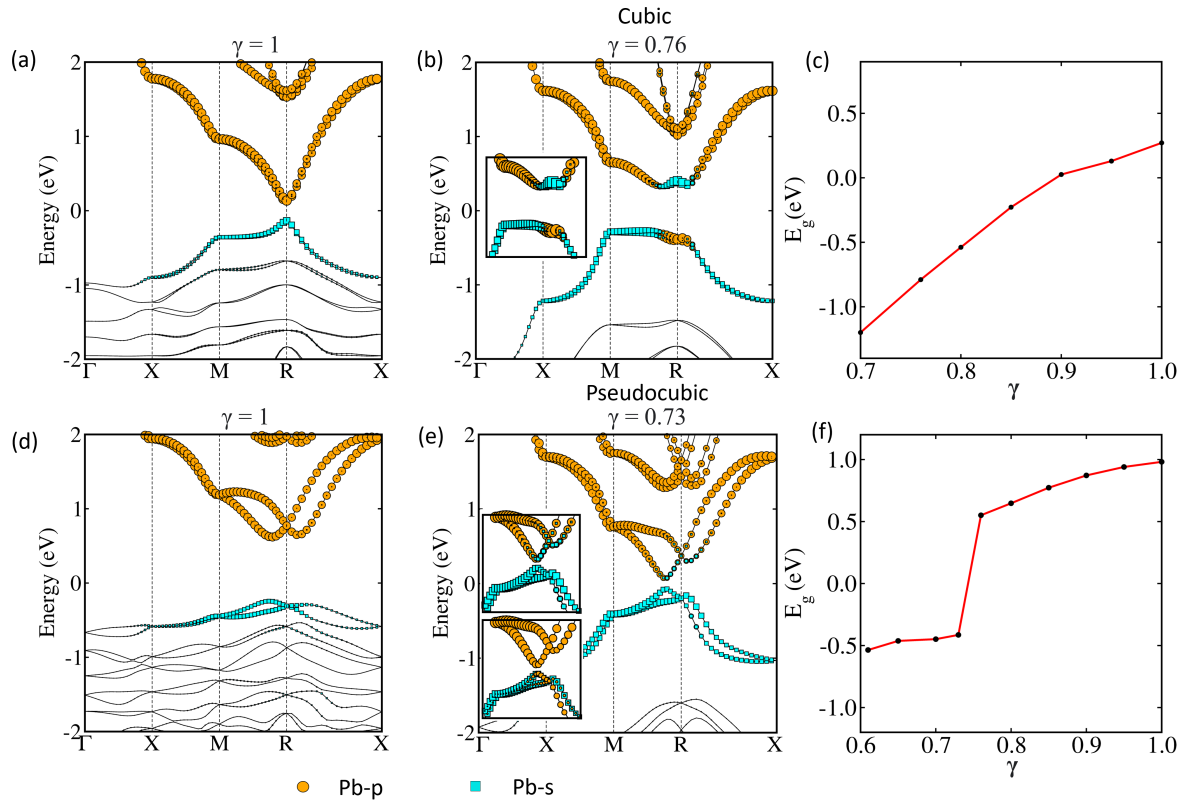


Figure 7.5: Orbital resolved band structure in presence of SOC for cubic and pseudocubic FAPbI<sub>3</sub> (a), (d) without compression, and (b), (e) at critical compression  $\gamma = 0.76$ , and  $\gamma = 0.73$ , respectively. The insets in (b) and (e) show zoomed image of band inversion. Band gap at different values of strain in (c) cubic FAPbI<sub>3</sub> showing its continuous nature, and (f) pseudocubic FAPbI<sub>3</sub> showing a discontinuity at the critical value of strain.

the Pb-s and Pb-p orbital takes place. This *s-p* inversion takes place at R point and gives the initial indication of the existence of non-trivial topology under the effect of strain. The orbital projected band structure with the orbital contribution proportional to the thickness of the symbols is shown in Fig. 7.5(a) and (b). The continuous TPT takes place in three steps, i) shrinking ii) closing iii) reemergence of the inverted band gap, and is shown in the Fig. 7.5(c). However, if the inversion symmetry is not preserved in a material then the nature of phase transition changes. In the case of noncentrosymmetric FAPbI<sub>3</sub>, as we keep on increasing the strain the band gap decreases initially. But, after reaching a certain minimum value, a new negative band gap emerges with valence band maxima (VBM) and conduction band minima (CBM) inverting their orbital character. In this case, the value of this critical strain  $\gamma$  is 0.73 (see Fig. 7.5(d) and (e)). This flip in the character of band structure at the critical value indicates the change in

the topological nature of the material. This type of phase transition in which the gapless state is not stabilized, resulting in discontinuity in the band gap as shown in Fig. 7.5(f), is termed a discontinuous TPT. It is also called a first-order phase transition. The distortion caused in the octahedral cage of PbI due to structural optimization is responsible for the discontinuous phase transition. In order to rule out that the inversion could be an artifact of the use of inaccurate  $\epsilon_{xc}$ , we have shown that the s-p inversion takes place even with HSE06 + SOC (see Fig. 7.6). Subsequently, the structural stability of cubic and pseudocubic FAPbI<sub>3</sub> along with the strained configurations is confirmed using AIMD. The radial distribution function ( $g(r)$ ) plots at  $T = 0$  K and  $T = 300$  K are shown in Fig. 7.7 .

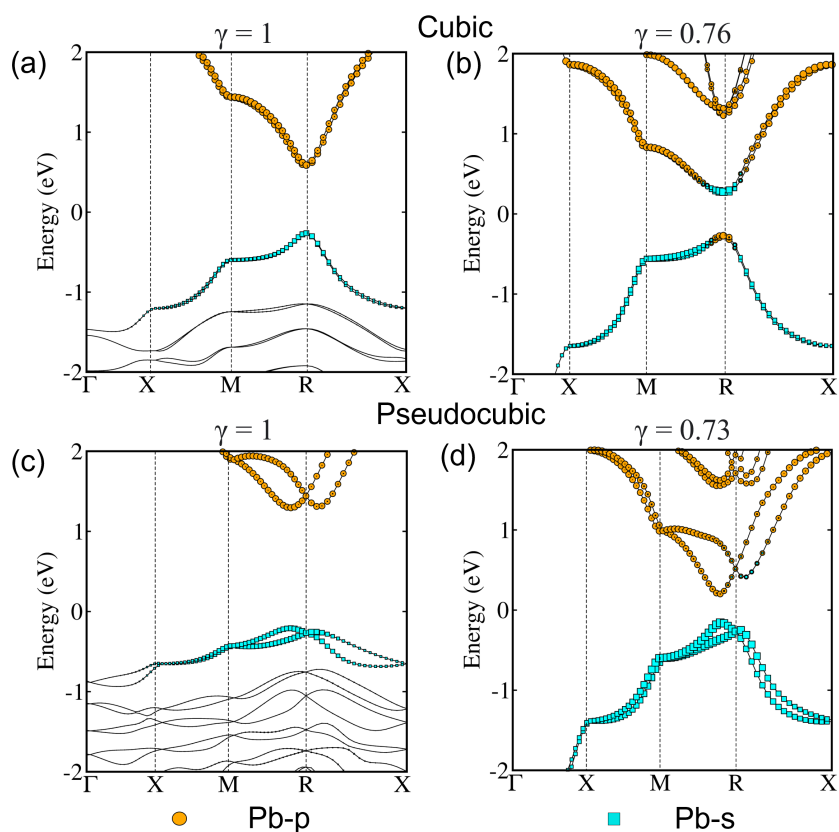


Figure 7.6: Orbital resolved HSE06+SOC band structure for cubic and pseudocubic FAPbI<sub>3</sub> (a), (d) without compression, and (b), (e) at critical compression  $\gamma = 0.76$ , and  $\gamma = 0.73$ , respectively.

### 7.3.2 Tight-Binding Model

Slater-Koster TB Hamiltonian studies are useful in providing information regarding the underlying quantum mechanical process responsible for phase transition due to structural defor-

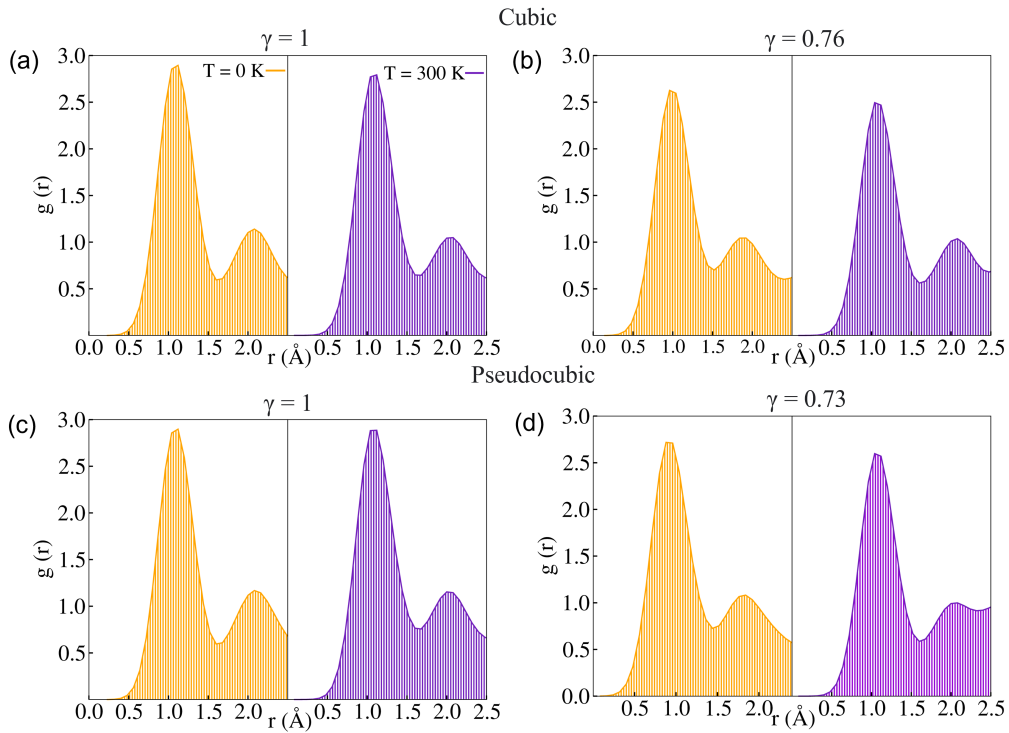


Figure 7.7: Radial distribution function using NVT ensemble for different phases of FAPbI<sub>3</sub> namely (a) cubic, (b) strained cubic ( $\gamma = 0.76$ ), (c) pseudocubic and (d) strained pseudocubic ( $\gamma = 0.73$ ) at T = 0 K and T = 300 K.

mation [304, 291]. The TB model Hamiltonian in the second quantized notation is written as [305, 296]

$$H = \sum_{i,\alpha} \epsilon_{i\alpha} c_{i\alpha}^\dagger c_{i\alpha} + \sum_{ij:\alpha\beta} t_{i\alpha j\beta} (c_{i\alpha}^\dagger c_{j\beta} + h.c.) + \lambda \mathbf{L} \cdot \mathbf{S} + H_R. \quad (7.2)$$

$$H = \begin{pmatrix} M_{4 \times 4}^{Pb-Pb} & M_{4 \times 9}^{Pb-I} \\ (M_{4 \times 9}^{Pb-I})^\dagger & M_{9 \times 9}^{I-I} \end{pmatrix}. \quad (7.3)$$

The individual blocks of this matrix are given as:

$$M_{4 \times 4}^{Pb-Pb} = \begin{pmatrix} \epsilon_s + g_1 & 2it_{sp\sigma}^{Pb-Pb} \sin(k_x a) & 2it_{sp\sigma}^{Pb-Pb} \sin(k_y a) & 2it_{sp\sigma}^{Pb-Pb} \sin(k_z a) \\ -2it_{sp\sigma}^{Pb-Pb} \sin(k_y a) & \epsilon_{p1} + g_2 & 0 & 0 \\ -2it_{sp\sigma}^{Pb-Pb} \sin(k_x a) & 0 & \epsilon_{p1} + g_3 & 0 \\ -2it_{sp\sigma}^{Pb-Pb} \sin(k_z a) & 0 & 0 & \epsilon_{p1} + g_4 \end{pmatrix} \quad (7.4)$$

$$M_{4 \times 9}^{Pb-I} = \begin{pmatrix} t_{sp\sigma}^{Pb-I} S_x & 0 & 0 & 0 & t_{sp\sigma}^{Pb-I} S_y & 0 & 0 & 0 & t_{sp\sigma}^{Pb-I} S_z \\ t_{pp\sigma}^{Pb-I} C_x & 0 & 0 & t_{pp\pi}^{Pb-I} C_y & 0 & 0 & t_{pp\pi}^{Pb-I} C_z & 0 & 0 \\ 0 & t_{pp\pi}^{Pb-I} C_x & 0 & 0 & t_{pp\pi}^{Pb-I} C_y & 0 & 0 & t_{pp\pi}^{Pb-I} C_z & 0 \\ 0 & 0 & t_{pp\pi}^{Pb-I} C_x & 0 & 0 & t_{pp\pi}^{Pb-I} C_y & 0 & 0 & t_{pp\sigma}^{Pb-I} C_z \end{pmatrix} \quad (7.5)$$

$$M_{9 \times 9}^{I-I} = \begin{pmatrix} \epsilon_{p2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \epsilon_{p2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \epsilon_{p2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \epsilon_{p2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \epsilon_{p2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \epsilon_{p2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \epsilon_{p2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \epsilon_{p2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \epsilon_{p2} \end{pmatrix}. \quad (7.6)$$

Here  $\epsilon_s$ ,  $\epsilon_{p1}$ , and  $\epsilon_{p2}$  are the onsite energies of Pb- $s$ , Pb- $p$  and I- $p$  orbitals, respectively. The terms  $C_z$  and  $S_z$  are the representations for  $2\cos(k_z a/2)$  and  $2i\sin(k_z a/2)$ , and  $g_i$  ( $i = 1, 2, 3, 4$ ) are the  $k$ -dependent hopping integrals arising from the Pb-Pb second neighbor interactions given by

$$\begin{aligned} g_1 &= 2t_{ss}^{Pb-Pb} [\cos(k_x a) + \cos(k_y a) + \cos(k_z a)], \\ g_2 &= 2t_{pp\sigma}^{Pb-Pb} \cos(k_x a) + 2t_{pp\pi}^{Pb-Pb} [\cos(k_y a) + \cos(k_z a)], \\ g_3 &= 2t_{pp\sigma}^{Pb-Pb} \cos(k_y a) + 2t_{pp\pi}^{Pb-Pb} [\cos(k_x a) + \cos(k_z a)], \\ g_4 &= 2t_{pp\sigma}^{Pb-Pb} \cos(k_z a) + 2t_{pp\pi}^{Pb-Pb} [\cos(k_x a) + \cos(k_y a)]. \end{aligned} \quad (7.7)$$

The SOC component of the Hamiltonian is obtained by applying  $\lambda \mathbf{L} \cdot \mathbf{S}$  on the Pb- $p$  states, as Pb being heavy is responsible for the SOC. We have obtained the matrix elements for the SOC Hamiltonian with the basis set in the order:  $|p_x^{Pb} \uparrow\rangle$ ,  $|p_y^{Pb} \uparrow\rangle$ ,  $|p_z^{Pb} \uparrow\rangle$ ,  $|p_x^{Pb} \downarrow\rangle$ ,  $|p_y^{Pb} \downarrow\rangle$ ,

$$\begin{aligned}
& \left| p_z^{Pb} \downarrow \right\rangle \\
& H_{SOC} = \lambda \begin{pmatrix} 0 & -i & 0 & 0 & 0 & 1 \\ i & 0 & 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 1 & -i & 0 \\ 0 & 0 & 1 & 0 & i & 0 \\ 0 & 0 & i & -i & 0 & 0 \\ 1 & i & 0 & 0 & 0 & 0 \end{pmatrix} \quad (7.8)
\end{aligned}$$

Table 7.1: Interaction parameters and SOC strength for FAPbI<sub>3</sub> from thirteen band Hamiltonian at zero and critical compression strength in units of eV.

| Type                            | $E_{Pb-s}$ | $E_{Pb-p}$ | $E_{I-p}$ | $t_{sp\sigma}^{Pb-I}$ | $t_{pp\sigma}^{Pb-I}$ | $t_{pp\pi}^{Pb-I}$ | $t_{ss\sigma}^{Pb-Pb}$ | $t_{sp\sigma}^{Pb-Pb}$ | $t_{pp\sigma}^{Pb-Pb}$ | $t_{pp\pi}^{Pb-Pb}$ | $\lambda$ |
|---------------------------------|------------|------------|-----------|-----------------------|-----------------------|--------------------|------------------------|------------------------|------------------------|---------------------|-----------|
| Cubic ( $\gamma = 1$ )          | -1         | 2.5        | -2        | 0.15                  | 0.4                   | 0.3                | -0.1                   | 0.3                    | 0.4                    | 0.1                 | 0.5       |
| Cubic ( $\gamma = 0.76$ )       | -1         | 2.5        | -2        | 0.1                   | 0.7                   | 0.5                | -0.1                   | 0.3                    | 0.76                   | 0.17                | 0.5       |
| Pseudocubic ( $\gamma = 1$ )    | -0.8       | 3          | -1        | 0.15                  | 0.4                   | 0.3                | -0.07                  | 0.45                   | 0.5                    | 0.4                 | 0.4       |
| Pseudocubic ( $\gamma = 0.73$ ) | -1         | 3          | -2        | 0.1                   | 0.5                   | 0.5                | -0.11                  | 0.5                    | 0.95                   | 0.07                | 0.4       |

Fitting this thirteen band model with the DFT bands, we get the effective onsite and hopping terms. The parameters obtained at no strain and critical strain are provided in Table 7.1. In the case of FAPbI<sub>3</sub>, the bands forming the VBM and CBM are primarily composed of Pb- $\{s,p\}$  orbitals. Also, the band inversion is taking place between Pb- $s$ , and Pb- $p$  orbitals. Therefore, a minimal basis Hamiltonian containing only essential interactions have been developed. The second neighbor Pb-Pb interactions has been considered in formulating the four band model. The SOC incorporated four band Hamiltonian is written as

$$\mathbf{H} = \begin{pmatrix} H_{\uparrow\uparrow} & H_{\uparrow\downarrow} \\ H_{\downarrow\uparrow}^\dagger & H_{\downarrow\downarrow} \end{pmatrix} \quad (7.9)$$

where

$$H_{\uparrow\downarrow} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda \\ 0 & 0 & 0 & -i\lambda \\ 0 & 0 & \lambda & -i\lambda \end{pmatrix} \quad (7.10)$$

$$H_{\uparrow\uparrow} = \begin{pmatrix} \epsilon_s + g_1 & 2it_{sp\sigma}^{Pb-Pb}\sin(k_x a) & 2it_{sp\sigma}^{Pb-Pb}\sin(k_y a) & 2it_{sp\sigma}^{Pb-Pb}\sin(k_z a) \\ -2it_{sp\sigma}^{Pb-Pb}\sin(k_y a) & \epsilon_{p1} + g_2 & 0 & 0 \\ -2it_{sp\sigma}^{Pb-Pb}\sin(k_x a) & 0 & \epsilon_{p1} + g_3 & 0 \\ -2it_{sp\sigma}^{Pb-Pb}\sin(k_z a) & 0 & 0 & \epsilon_{p1} + g_4 \end{pmatrix} \quad (7.11)$$

 Table 7.2: Interaction parameters and SOC strength for FAPbI<sub>3</sub> from four band hamiltonian at zero and critical compression strength in units of eV.

| Type                            | $E_{Pb-s}$ | $E_{Pb-p}$ | $t_{ss\sigma}^{Pb-Pb}$ | $t_{sp\sigma}^{Pb-Pb}$ | $t_{pp\sigma}^{Pb-Pb}$ | $t_{pp\pi}^{Pb-Pb}$ | $\lambda$ |
|---------------------------------|------------|------------|------------------------|------------------------|------------------------|---------------------|-----------|
| Cubic ( $\gamma = 1$ )          | -0.8       | 2.5        | -0.09                  | 0.3                    | 0.4                    | 0.1                 | 0.5       |
| Cubic ( $\gamma = 0.76$ )       | -1.2       | 2.5        | -0.19                  | 0.44                   | 0.75                   | 0.16                | 0.5       |
| Pseudocubic ( $\gamma = 1$ )    | -0.8       | 2.5        | -0.1                   | 0.25                   | 0.2                    | 0.06                | 0.5       |
| Pseudocubic ( $\gamma = 0.73$ ) | -1         | 3          | -0.12                  | 0.4                    | 0.8                    | 0.1                 | 0.5       |

The interaction parameters for both cubic and pseudocubic FAPbI<sub>3</sub>, from the four band model fitting are provided in Table 7.2. Magnitude of all the parameters increase with rise in strain. With the increase in compression, the bond length decreases and hence the strength of interactions increases. In comparison to Pb-Pb  $ss\sigma$ ,  $sp\sigma$  and  $pp\pi$ , the  $pp\sigma$  interactions are most sensitive to the strain. For cubic structure the  $pp\sigma$  interaction rises from 0.4 to 0.75, while for pseudocubic, it rises from 0.2 to 0.7, upon the application of respective critical strain. We have also observed that  $\lambda$  does not change with compression, therefore, SOC is insensitive to the strain. From the electronic band structure calculations, it is evident that the universality of the band structure arises from the nearest-neighbor Pb- $\{s,p\}$ -X- $p$  covalent interactions. However, the TB model elucidates that the second neighbor Pb- $\{s,p\}$ -Pb- $\{s,p\}$  interactions act as a driving force for band gap engineering and non-trivial phases. This type of TB model is universal, as it is independent of the choice of functional adopted [296].

### 7.3.3 Surface Electronic Structure

The study of bulk electronic structure has enabled us to identify the possibility of non-trivial topology and phase transition in halide perovskites. However, the practical observation of



these states comes from the calculation of surface states [306]. The DFT based calculations on the slab structure require a huge amount of computational time and memory to analyze these properties. So, we have used the MLWF based TB approach to construct a semi-infinite slab along (001) direction, minimizing the total spread of MLWF. As expected, there is an absence of the surface states in FAPbI<sub>3</sub> at ambient conditions (see Fig. 7.8(a) and (c)). However,

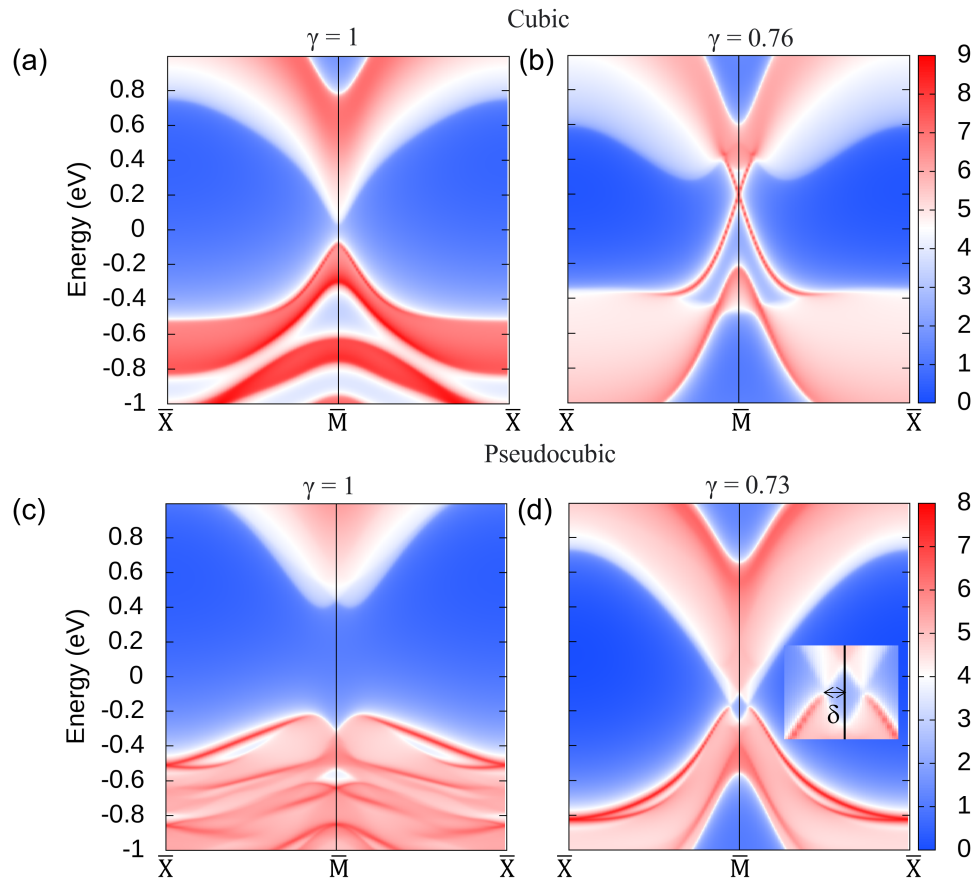


Figure 7.8: Surface band structure in presence of SOC for cubic FAPbI<sub>3</sub> (a) without compression, (b) at critical compression  $\gamma = 0.76$ , and pseudocubic FAPbI<sub>3</sub> (c) without compression, (d) at critical compression  $\gamma = 0.73$ .

as the critical value of strain i.e.,  $\gamma = 0.76$  is applied to cubic FAPbI<sub>3</sub>, the conducting states emerge at  $\bar{M}$  point (see Fig. 7.8(b)). The linearly dispersed valence and conduction bands only touch each other at  $\bar{M}$  point, resembling the behavior observed in conventional topological insulators. In the absence of the inversion symmetry breaking field, a pair of doubly degenerate Dirac cones emerges—one from the valence band and one from the conduction band. This degeneracy is a consequence of the formation of Kramer pairs, where the Dirac cones touch each other precisely at the  $\bar{M}$  point and remain protected by the time reversal symmetry. As

a result, the centrosymmetric nature of the system gives rise to a fourfold-degenerate point node at  $\bar{M}$ . However, when the inversion symmetry breaking field is introduced, the Kramer pairing is disrupted, leading to a redistribution of the energy levels. Specifically, one pair of Dirac cones (one from the valence band and one from the conduction band) shifts upward in energy, while the other pair shifts downward. Consequently, the initial fourfold-degenerate point node undergoes a breakdown, resulting in the formation of two twofold degenerate point nodes—one at a higher energy and the other at a lower energy [278]. Therefore, we see two Dirac states at  $\bar{M} \pm \delta$ , along the path  $X-\bar{M}-X$ , as shown in Fig. 7.8(d). The resulting surface states illustrate the presence of discontinuous nature of NI-TI TPT. The discovery of twofold degenerate point nodes remains elusive within the diverse range of topological insulators. On the other hand, the surface band topology convincingly mimics the band structure observed in AA-stacked graphene[307]. Numerous additional studies have also provided evidence for the signature of first-order topological phase transitions by revealing discontinuous changes in various properties[290, 308].

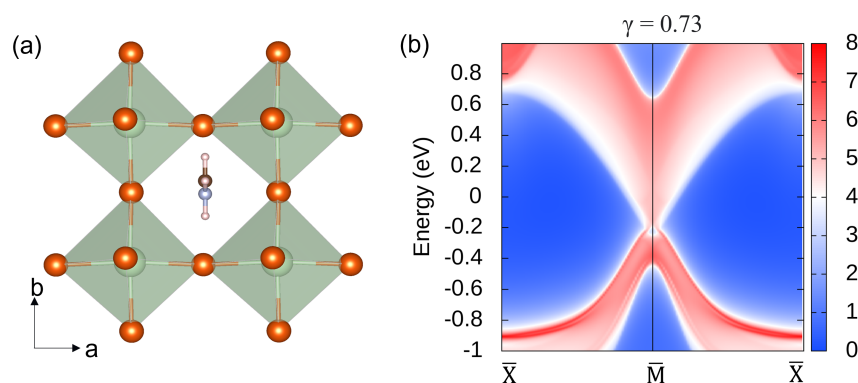


Figure 7.9: (a) Crystal structure of FAPbI<sub>3</sub> showing a different orientation of FA cation and (b) topological surface states at critical strain value.

To strengthen the relevance of our study, we have calculated surface states for two configurations having different orientations of the FA ion. In both the orientations FA is perpendicular to each other and both configurations show topological phase transition at critical value of strain. However, many different orientations of these organic molecules are possible (see Fig. 7.9). Therefore, in order to ensure the experimental relevance of our above analysis, we have estimated the probability of occurrence of different configurations at  $T = 300$  K (see Fig. 7.10).

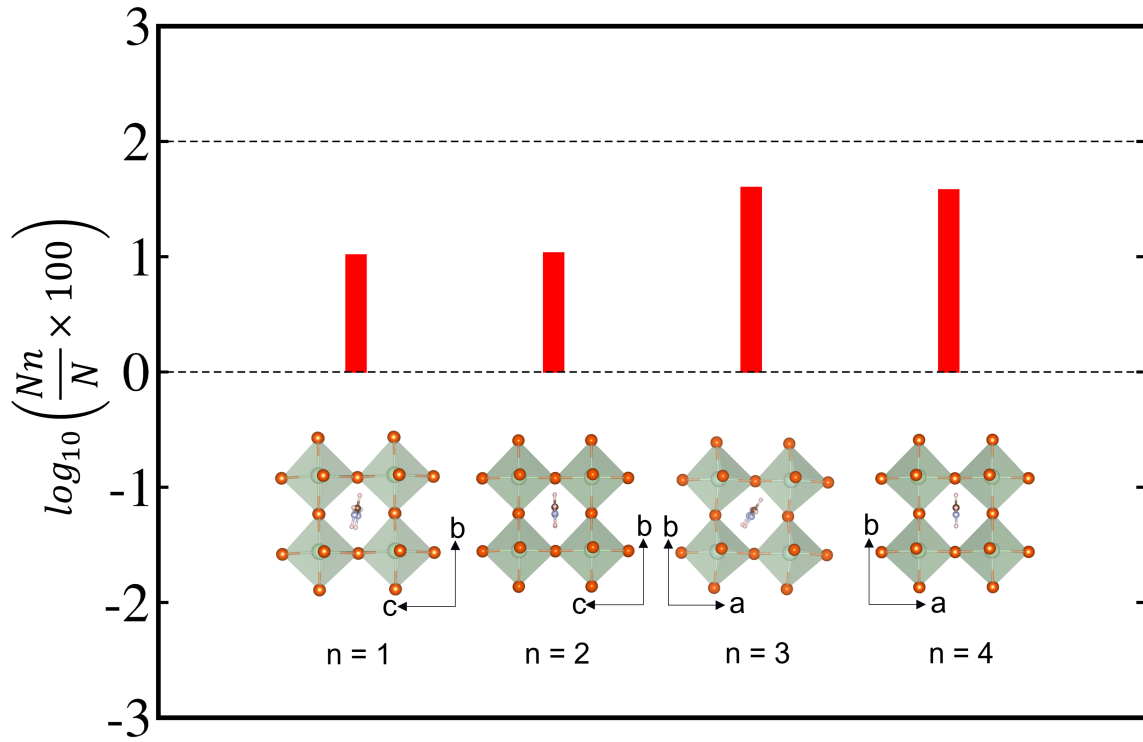


Figure 7.10: Logarithm of probability of occurrence of different configurations at  $T = 300$  K. Orientation of FA is different in all the configurations.

### 7.3.4 TPT in Mixed Cation Perovskites

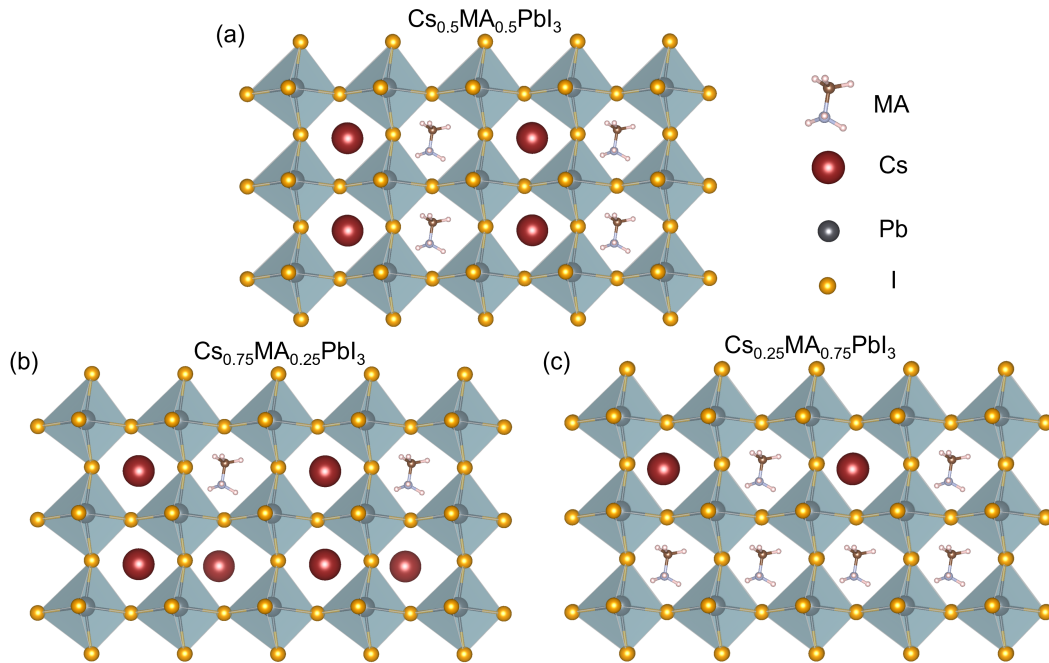


Figure 7.11: Crystal structure of (a)  $\text{Cs}_{0.75}\text{MA}_{0.5}\text{PbI}_3$ , (b)  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  and (c)  $\text{Cs}_{0.25}\text{MA}_{0.75}\text{PbI}_3$ .

We have studied the TPT in both inorganic ( $\text{CsPbI}_3$ ) and organic ( $\text{MAPbI}_3$ ,  $\text{FAPbI}_3$ ) halide

perovskites. CsPbI<sub>3</sub> show continuous TPT at  $\gamma = 0.76$  because of its centrosymmetric nature, whereas MAPbI<sub>3</sub> and FAPbI<sub>3</sub> show similar behaviour. It has been found that by partially replacing MA<sup>+</sup> with Cs<sup>+</sup>, the stability can be enhanced in ambient environment [309]. These mixed cation/anion perovskites have attracted considerable attention due to their higher stability [310]. Thus, we have designed the mixed cation halide perovskites to study the nature of TPT in them. For this, three configurations i.e., Cs<sub>0.75</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, Cs<sub>0.25</sub>MA<sub>0.75</sub>PbI<sub>3</sub>, have been obtained by replacing MA with Cs in the lattice of MAPbI<sub>3</sub> (see Fig. 7.11). Firstly, we have calculated the thermodynamic stability of the mixed cation halide perovskites i.e., Cs<sub>0.75</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, Cs<sub>0.25</sub>MA<sub>0.75</sub>PbI<sub>3</sub>. The precursors considered for the calculation of formation energy ( $E_f$ ) of these perovskites are MAPbI<sub>3</sub>, CsI and PbI<sub>2</sub>. The associated expression is [311]

$$E_f(\text{Cs}_{4-x}\text{MA}_x\text{Pb}_4\text{I}_{12}) = aE(\text{Cs}_{4-x}\text{MA}_x\text{Pb}_4\text{I}_{12}) - bE(\text{MA}_4\text{Pb}_4\text{I}_{12}) - cE(\text{CsI}) - dE(\text{PbI}_2) \quad (7.12)$$

Here,  $x$  corresponds to 1, 2 and 3 for Cs<sub>3</sub>MAPb<sub>4</sub>I<sub>12</sub>, Cs<sub>2</sub>MA<sub>2</sub>Pb<sub>4</sub>I<sub>12</sub> and CsMA<sub>3</sub>Pb<sub>4</sub>I<sub>12</sub> configurations, respectively. The coefficients  $a$ ,  $b$ ,  $c$  and  $d$  of each term on the right hand side are chosen such that they stoichiometrically balance the equation.  $1 \times 2 \times 2$  supercell of MAPbI<sub>3</sub> has been used for the above calculations. After this, the formation energies corresponding to Cs<sub>0.75</sub>MA<sub>0.25</sub>PbI<sub>3</sub>, Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, Cs<sub>0.25</sub>MA<sub>0.75</sub>PbI<sub>3</sub> configurations are calculated and they come out to be -0.78 eV, -0.69 eV and -0.65 eV, respectively. The negative formation energy shows that all the configurations are thermodynamically stable. We have also checked the structural stability of these configurations using AIMD simulations (see Fig. 7.12). After this, we have obtained the band structure for all the configurations with and without SOC. When no strain is applied in Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, the VBM is composed of I- $p$  orbitals, and CBM of Pb- $p$  orbitals (see Fig. 7.13(a)). The inclusion of SOC does not depict any traits of non-trivial topological nature. Subsequently, we have applied the compressional volumetric strain along with the SOC. At the critical strain value of  $\gamma = 0.74$ , the appearance of a negative band gap is observed with the inverted orbital character as seen in Fig. 7.13(b). This suggests the possibility of TPT in Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, whereas, in Cs<sub>0.75</sub>MA<sub>0.25</sub>PbI<sub>3</sub> and Cs<sub>0.25</sub>MA<sub>0.75</sub>PbI<sub>3</sub>, no such parity inversion is observed under the effect of compression. This may be attributed to the difference in the ionic radii of Cs and MA cations, which is 1.88 Å and 2.117 Å, respectively. As the band inversion involves  $p$  orbitals of both I and Pb, therefore, a four band TB model will not

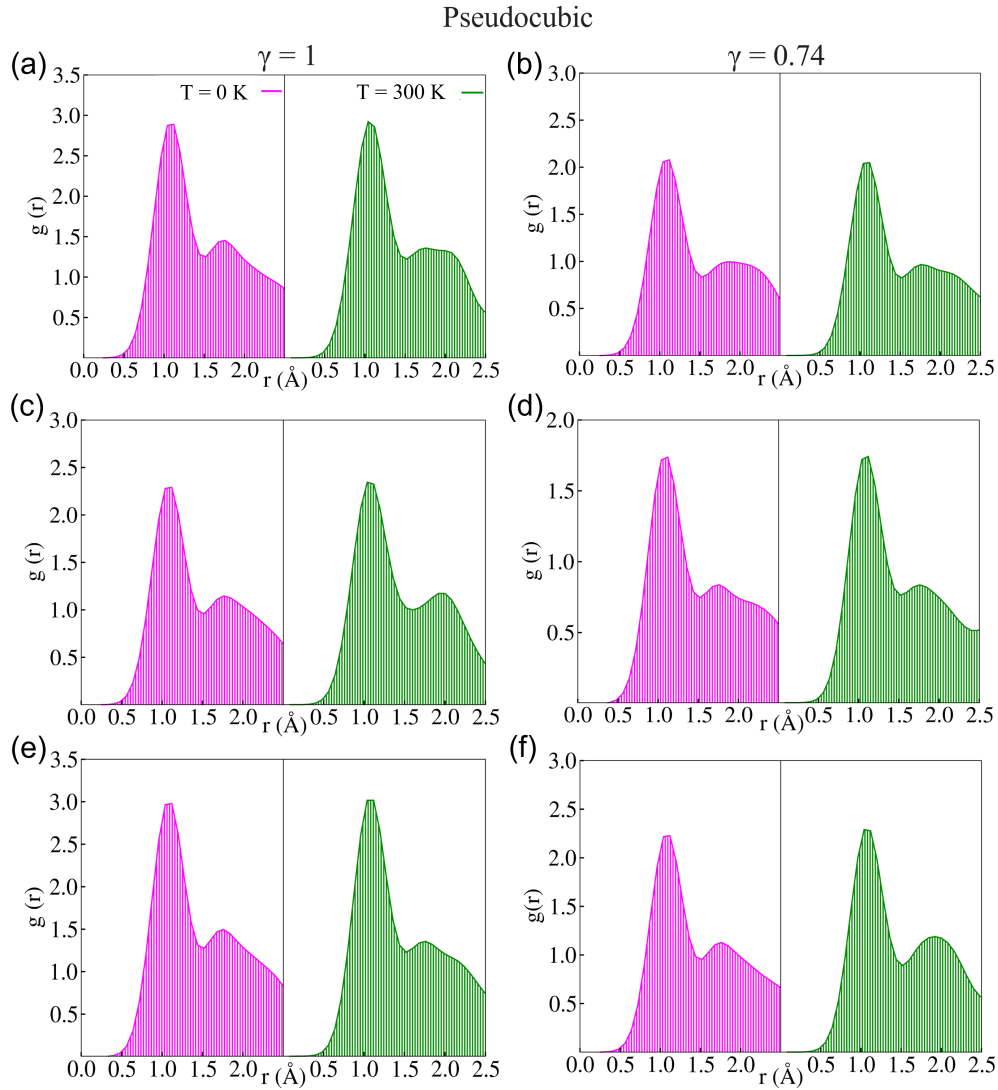


Figure 7.12: Radial distribution function at  $T = 0$  K and  $T = 300$  K for unstrained and strained ( $\gamma = 0.74$ ), (a), (b)  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$ , (c), (d)  $\text{Cs}_{0.75}\text{MA}_{0.25}\text{PbI}_3$ , (e) and (f)  $\text{Cs}_{0.25}\text{MA}_{0.75}\text{PbI}_3$ , respectively.

suffice in predicting the nature of TPT. Thus, using the thirteen band model containing Pb- $\{s,p\}$  and X-p orbitals, we have calculated the onsite energies and hopping integrals (see Table 7.3). All the interaction parameters increase on application of strain, but the Pb-I  $pp\pi$  interactions rising from 1 to 1.5 are most affected by the same. After this, we have plotted the surface state band structure for  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  at  $\gamma = 0$  and  $\gamma = 0.74$ . As seen in the Fig. 7.13(b) and (c), the origin of surface states with strain confirms the TPT at  $\gamma = 0.74$ .

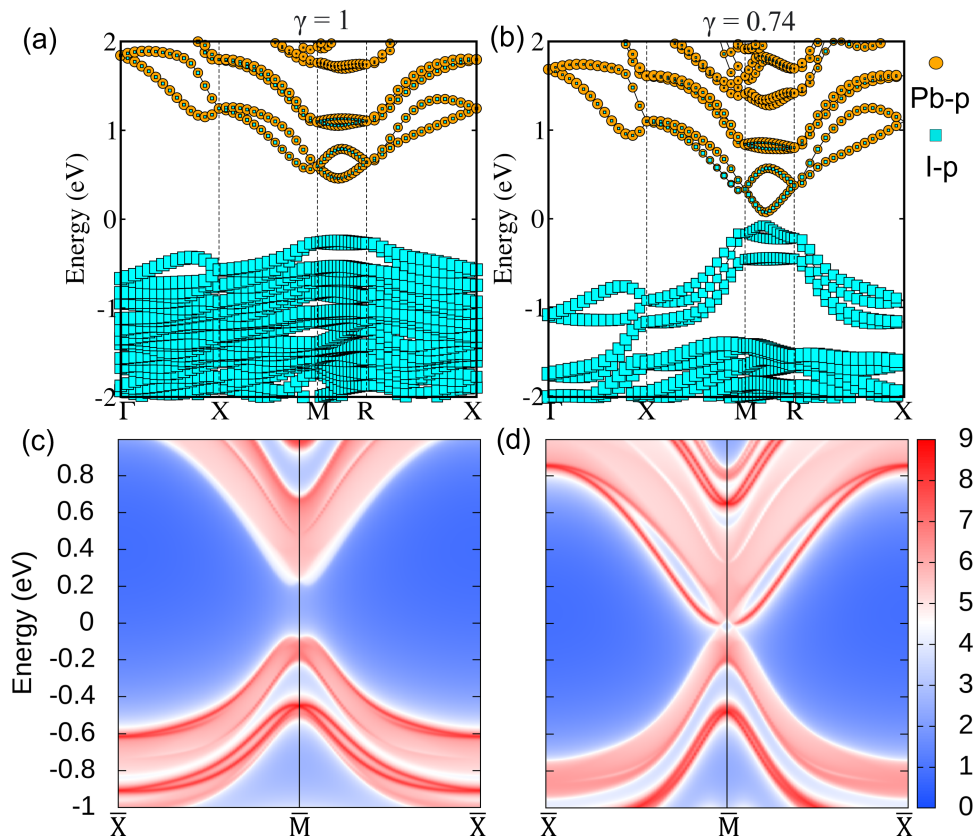


Figure 7.13: Orbital resolved band structure in presence of SOC for  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  (a) without compression, (b) at critical compression  $\gamma = 0.74$ . Surface band structure for  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  (a) without compression, (b) at critical compression  $\gamma = 0.74$ .

Table 7.3: Interaction parameters and SOC strength for  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  from thirteen band hamiltonian at zero and critical compression strength in units of eV.

| Type            | $E_{Pb-s}$ | $E_{Pb-p}$ | $E_{I-p}$ | $t_{sp\sigma}^{Pb-I}$ | $t_{pp\sigma}^{Pb-I}$ | $t_{pp\pi}^{Pb-I}$ | $t_{ss\sigma}^{Pb-Pb}$ | $t_{sp\sigma}^{Pb-Pb}$ | $t_{pp\sigma}^{Pb-Pb}$ | $t_{pp\pi}^{Pb-Pb}$ | $\lambda$ |
|-----------------|------------|------------|-----------|-----------------------|-----------------------|--------------------|------------------------|------------------------|------------------------|---------------------|-----------|
| $\gamma = 1$    | -7         | 2          | -1.5      | 0.8                   | -1                    | 1                  | -0.25                  | 0.3                    | 0.7                    | 0.01                | 0.5       |
| $\gamma = 0.74$ | -7         | 2.5        | -2        | 1                     | -1.2                  | 1.5                | -0.27                  | 0.4                    | 1.15                   | 0.02                | 0.5       |

## 7.4 Conclusion

The strain free lead halide perovskites are trivial band insulators, however, a TPT can take place via strain engineering. The presence of inversion symmetry plays a vital role in the electronic properties of the halide perovskites. The first-principles calculations suggest that  $\text{FAPbI}_3$  becomes noncentrosymmetric on structural optimization. The centrosymmetric  $\text{FAPbI}_3$  shows

a continuous phase transition on the application of strain. The inversion symmetry breaking changes the nature of this quantum phase transition. At a critical value of  $\gamma = 0.73$ , pseudocubic  $\text{FAPbI}_3$  undergoes a first-order TPT. The discontinuity is evident from the band gaps calculated at various values of strain, and the nature of surface states. This study also shows that although thirteen orbitals participate in the chemical bonding, a four band TB model is sufficient to capture energy dispersion near the Fermi level. The Pb-Pb second neighbor interactions determine the topology of this class of materials. The Pb-Pb  $\text{pp}\sigma$  interactions are the most affected by the application of strain. Hence, these interactions are the driving forces in determining the phase transition. Furthermore, the mixed cation perovskites  $\text{Cs}_{0.75}\text{MA}_{0.25}\text{PbI}_3$ ,  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  and  $\text{Cs}_{0.25}\text{MA}_{0.75}\text{PbI}_3$  are thermodynamically and structurally stable.  $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_3$  shows TPT at a compression of  $\gamma = 0.74$ , which is shown by band inversion and the nature of surface states. The structural stability of these perovskites under strain strengthens that these phase transitions can be realized

## Epilogue and outlook

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This thesis has explored a fascinating realm of valleytronic and spintronic properties in a variety of materials through the lens of first-principles computational methodologies. From valleytronics to topological insulators, we have investigated the intricate interplay between crystal structure, strain engineering, spin-orbit coupling (SOC), and valley degrees of freedom, revealing novel phenomena and potential applications in next-generation spintronic and valleytronic devices.

Our initial investigation focused on valley-dependent properties of two-dimensional materials, specifically MXenes. For  $\text{Cr}_2\text{CSF}$  MXene, our first-principles calculations revealed its nature as an indirect band gap ferromagnetic semiconductor with an intrinsic out-of-plane magnetization. It has a very large magnetocrystalline anisotropy energy (MAE) with a value of 1.16 meV. This out-of-plane magnetization, coupled with time-reversal symmetry breaking, leads to a spontaneous valley polarization in the conduction band. We elucidated the underlying physics of this spontaneous valley polarization using a SOC Hamiltonian model. This inherent valley polarization manifests as an anomalous valley Hall (AVH) effect under an in-plane electric field and electron doping, resulting in the separation of charge carriers with opposite valley indices. Furthermore, we demonstrated the possibility of engineering switchable valley Hall effects through the application of strain. The observation of a quasi-half valley metal state, coupled with the high MAE, positions  $\text{Cr}_2\text{CSF}$  as a promising candidate for valleytronic applications. The ability to manipulate valley polarization and generate valley currents through external stimuli like strain provides a pathway to create novel valley-based devices.

Further, we explored the valley-dependent properties of the antiferromagnetic (AFM) monolayer  $\text{Fe}_2\text{C}(\text{OH})_2$ . This material exhibits a large spontaneous valley polarization in the conduction band. The combined presence of parity and time-reversal ( $PT$ ) symmetry ensures spin degeneracy and suppresses the AVH effect due to zero Berry curvature in momentum space.



However, a layer-locked hidden Berry curvature emerges in real space, leading to a valley layer-spin Hall effect. Intriguingly, the application of an out-of-plane electric field breaks this delicate balance, inducing spin splitting and enabling a layer-locked AVH effect. Furthermore, the direction of the applied electric field can reverse the order of spin splitting. We also investigated the Janus structure  $\text{Fe}_2\text{C}(\text{OH})\text{F}$ , which, due to its built-in electric potential, intrinsically exhibits the AVH effect without the need for an external electric field. These findings highlight the potential of AFM monolayers like  $\text{Fe}_2\text{C}(\text{OH})_2$  and  $\text{Fe}_2\text{C}(\text{OH})\text{F}$  for spintronic and valleytronic applications, particularly for realizing the AVH effect.

Furthermore, we have theoretically developed a robust design principle for achieving reversible, nonvolatile, and energy-efficient control of the AVH effect through a multiferroic heterostructure. Our first-principles calculations demonstrate that stacking a ferrovalley VSSe monolayer on a ferroelectric  $\text{Al}_2\text{S}_3$  substrate enables precise electrical tuning of valley polarization. By simply reversing the ferroelectric substrate's polarization, the valley polarization in VSSe can be switched between the valence band maximum (VBM) and conduction band minimum (CBM), accompanied by a reversal of the Berry curvature sign at the  $+K$  and  $-K$  valleys. This electric-field-driven control provides a highly desirable alternative to conventional magnetic approaches, which are typically energy-intensive and less practical for device applications. Importantly, the sign and magnitude of the transverse Hall voltage are directly modulated by the ferroelectric polarization, enabling a reliable and damage-free mechanism for data readout. The tunable AVH effect realized in this multiferroic heterostructure opens a promising avenue for the design of all-electric, low-power, and nonvolatile valleytronic memory and logic devices.

The thesis then delved into the electronic structure of topological materials belonging to the  $R\bar{3}m$  space group. By employing advanced computational techniques, including PBE, HSE06, and many-body perturbation theory ( $G_0W_0$ ), we systematically studied a series of isostructural substitutions, driven by the intriguing mechanism of SOC-induced parity inversion in the band structure. Specifically, we identified  $\text{GaBiSe}_2$  as a strong topological insulator, characterized by a single Dirac cone at the  $\Gamma$  point on its surface. Furthermore, we demonstrated that  $\text{PbBiSe}_2$ ,  $\text{SnBiSe}_2$ ,  $\text{SbBiSe}_2$ ,  $\text{Bi}_2\text{Se}_2$ ,  $\text{TlSnSe}_2$ , and  $\text{PbSbSe}_2$  exhibit the characteristics of weak topological insulators, hosting an even number of surface states within the bulk band gap. Dynamical stability was confirmed through phonon band structure analysis, and the calculated  $Z_2$  topological invariants corroborated their predicted topological classification. These findings

contribute to the growing library of topological materials and provide a solid foundation for future experimental investigations into quantum phenomena, such as the quantum spin Hall effect and related topological properties. The precise control over the number and type of topological surface states, achieved through isostructural substitution, opens exciting avenues for tailoring material functionalities for specific applications.

Finally, shifting our focus to halide perovskites, we investigated the influence of strain engineering on their electronic properties. While strain-free lead halide perovskites typically behave as trivial band insulators, we demonstrated that a topological phase transition can be induced through the application of strain. Our first-principles calculations revealed that FAPbI<sub>3</sub>, upon structural optimization, adopts a noncentrosymmetric structure, a crucial factor in determining its electronic properties. In centrosymmetric FAPbI<sub>3</sub>, the application of strain leads to a continuous phase transition. However, the breaking of inversion symmetry dramatically alters the nature of this transition. At a critical strain value ( $\gamma = 0.73$ ), pseudocubic FAPbI<sub>3</sub> undergoes a first-order TPT, characterized by a discontinuity in the band gap and a change in the nature of the surface states. A four-band tight-binding model, capturing the essential physics near the Fermi level, highlighted the dominant role of Pb-Pb second-neighbor interactions, particularly the  $pp\sigma$  interactions, in driving the TPT. Furthermore, we demonstrated that mixed cation perovskites, such as Cs<sub>0.75</sub>MA<sub>0.25</sub>PbI<sub>3</sub>, Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub>, and Cs<sub>0.25</sub>MA<sub>0.75</sub>PbI<sub>3</sub>, exhibit structural and thermodynamic stability, and that Cs<sub>0.5</sub>MA<sub>0.5</sub>PbI<sub>3</sub> undergoes a TPT at a compressive strain of  $\gamma = 0.74$ . These findings underscore the potential of strain engineering to manipulate the electronic and topological properties of halide perovskites and pave the way for novel topological devices. The structural stability of these materials under strain further strengthens the possibility of experimentally realizing these predicted phase transitions.

In conclusion, this thesis explore and predict novel valleytronic and spintronic phenomena in a variety of materials. From MXenes with spontaneous valley polarization to AFM monolayers with tunable valley Hall effects, to electric field switchable valley polarization, and from topological insulators with tailored surface states to strain-engineered perovskites exhibiting topological phase transitions, the materials studied in this thesis offer a rich playground for exploring fundamental physics and developing next-generation spintronic and valleytronic devices. The insights gained from these computational studies provide a strong foundation for future experimental investigations and pave the way for realizing the full potential of these materials in advanced technologies.

Overall, these studies contribute to a deeper understanding of fundamental physical phenomena and pave the way for the development of future technologies based on spin and valley degrees of freedom.

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