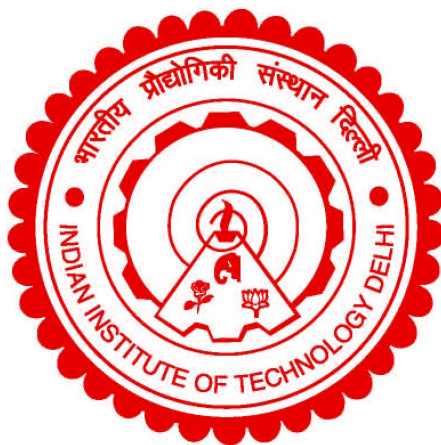


UNVEILING VALLEY AND TOPOLOGICAL PROPERTIES OF QUANTUM MATERIALS USING FIRST-PRINCIPLES SIMULATIONS

ANKITA



DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2026

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

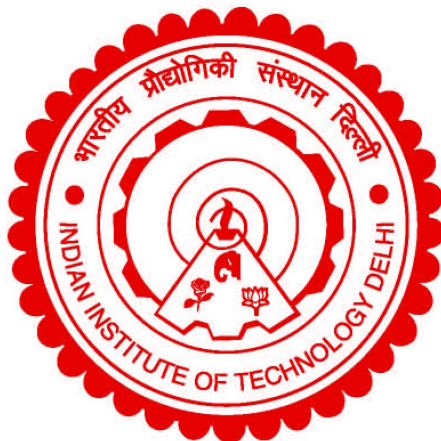
by

ANKITA

Department of Physics

Submitted

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



INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2026

Dedicated to my beloved family

Certificate

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.

Prof. Saswata Bhattacharya

Thesis Supervisor

Department of Physics,

Indian Institute of Technology Delhi,

Hauz Khas, New Delhi 110016, India.

Date:.....

Place: New Delhi

Acknowledgments

First of all, I would like to express my sincere gratitude to my supervisor, Professor Saswata Bhattacharya, for his steady guidance and academic mentorship throughout my research journey. His critical approach, high academic standards, and uncompromising emphasis on scientific rigor consistently challenged me to improve the quality of my work. He provided me the freedom to explore ideas independently while offering timely and precise feedback whenever needed. I am especially thankful for his analytical insights, which helped me refine my research direction, shape my presentation skills, and develop a disciplined approach to academic writing. Beyond academics, I sincerely appreciate his understanding and support during periods of personal difficulty, which enabled me to continue my research with resilience and determination. His mentorship has been instrumental in shaping my professional growth and in bringing this thesis to completion.

I extend my thanks to my collaborators and colleagues in the DISCERE (DISCovering Electronic CorRElation) research group: Dr. Manish Kumar, Dr. Arunima Singh, Dr. Deepika Gill, Dr. Preeti Bhumla, Dr. Manjari Jain, Dr. Sajjan Sheoran, Sanchi Monga, Shantanu Pathak, Divyanshi Tyagi, Udit Kumar, Dhriti Mandal, and Subhodip Paul. I am thankful for their academic help, useful discussions, and cooperation, which created a supportive research environment. I also appreciate the friendly and respectful atmosphere within the group, which provided encouragement beyond academic work and made the research experience more positive.

I would also like to express gratitude to my other collaborators: Professor J.P Singh, Professor Santanu Ghosh, Dr. Arindam Modak, Dr. Jyoti Yadav, and Dr. Sharmishtha Dey, for their fruitful discussions and collaborations.

I am thankful to the Indian Institute of Technology Delhi (IIT Delhi) for providing me the opportunity to pursue my doctoral research at an institution of such high academic standing. Being part of IIT Delhi has been a matter of great pride for me. The institute offered a stimulating

academic environment, excellent research facilities, and essential financial support, including travel grants that allowed me to present my work at conferences and interact with the wider scientific community. These experiences have played an important role in shaping my academic growth.

My sincere thanks go to my student research committee (SRC) members: Professor Sankalpa Ghosh, Professor Kaustuv Manna and Professor Hemant K. Kashyap for their thoughtful evaluation of my research. Their insightful questions and comments were invaluable in guiding my investigation.

I am deeply grateful to my parents for their unconditional love, support, and encouragement. This thesis would not have been possible without their sacrifices and hardships. I want to specially thank Bhupinder and Kanishka. Words cannot express the depth of my gratitude for everything they have done.

Finally, and importantly, I acknowledge my own journey through the many challenges and uncertainties of the Ph.D. process. This work demanded patience, discipline, and perseverance, especially during periods of self-doubt and difficulty. Over the years, I have learned to face criticism, adapt to setbacks, and continue moving forward with determination. Completing this thesis is not only an academic achievement for me but also a sign of personal growth. I am proud of the dedication and determination that helped me reach the end of my doctoral studies. I conclude by expressing my deepest gratitude to the Almighty for His constant blessings, and protection throughout this journey. In moments of uncertainty and difficulty, my faith provided strength, patience, and clarity, enabling me to persevere and remain focused on my goals. I humbly seek forgiveness for any shortcomings in this work and pray for continued wisdom, strength, and purpose in the path ahead.

Ankita

Abstract

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 Cr_2CSF . Cr_2CSF , 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 Cr_2CSF 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 Al_2S_3 . Our findings indicate that the reversible switching of the AVH effect can be precisely manipulated by reversing the ferroelectric polarization of Al_2S_3 via an applied electric field. Crucially, the regulated AVH state of VSSe remains stably preserved due to the intrinsic ferroelectric nonvolatility of Al_2S_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, 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 GaBiSe_2 emerges as a strong TI. Additionally,

we identify six weak TIs: PbBiSe_2 , SnBiSe_2 , SbBiSe_2 , Bi_2Se_2 , TlSnSe_2 , and 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 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 Cr_2CSF में आंतरिक वैली संबंधित स्विच करने योग्य हॉल प्रभावों की पहचान प्रस्तुत करते हैं। उच्च आउट-ऑफ-प्लेन मैग्नेटिक अनिसोट्रॉपी वाला Cr_2CSF , 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 Cr_2CSF 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 पोटेन्शियल 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 Al_2S_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 Al_2S_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 Al_2S_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, 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 GaBiSe_2 एक स्ट्रांग TI के रूप में उभरता है। इसके अलावा, हम छह वीक TIs की पहचान करते हैं: -PbBiSe_2 , SnBiSe_2 , SbBiSe_2 , Bi_2Se_2 , TlSnSe_2 तथा 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 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।

Contents

Certificate	i
Acknowledgements	ii
Abstract	iv
List of Figures	xiv
List of Tables	xxii
1 Introduction	1
1.1 The dawn of quantum materials: beyond conventional electronics	1
1.2 Valleytronics	2
1.3 Hall effect and its analogues	7
1.3.1 Anomalous Hall effect	8
1.3.2 Valley Hall Effect	8
1.4 The Berry curvature	9
1.5 The quantum Hall effect	11
1.6 The quantum spin Hall effect	13
1.7 Topology	15
1.8 Bulk boundary correspondance	16
1.9 Topological Insulators	18
1.9.1 2D Topological Insulators	20
1.9.2 $\mathbb{Z}_2$ classification of topological insulator	21
1.9.3 3D Topological insulators	23
1.10 A short overview	26

2	Theoretical methodology	29
2.1	Computer simulation	29
2.2	First-principles calculation	31
2.3	Introduction to theoretical framework	32
2.4	Wavefunction	34
2.5	Time-independent many-body Schrödinger equation	35
2.6	Born-Oppenheimer approximation	36
2.7	The Hartree approximation	38
2.8	The Hartree-Fock approximation	41
2.9	Functional	44
2.10	Density Functional Theory	45
2.10.1	The Thomas-Fermi Model	45
2.10.2	Hohenberg and Kohn Theorem	46
2.10.2.1	Kohn-Sham equations	48
2.10.3	Exchange and correlation energy	51
2.11	DFT+U	56
2.11.1	Mott Insulators and the Hubbard Model	57
2.12	Basis set	59
2.12.1	The Plane wave basis set	59
2.12.2	Plane wave pseudopotential method	62
2.12.3	Norm-conserving pseudopotential	63
2.12.4	Ultrasoft pseudopotential	64
2.12.5	Projector augmented-wave method (PAW)	65
2.13	Tight-Binding Method and the Linear Combination of Atomic Orbitals (LCAO)	67
2.14	Wannier Functions and Maximally Localized Wannier Functions	69
2.14.1	Maximally Localized Wannier Functions	70
2.14.1.1	Reciprocal-Space Formulation	71
3	Reversible switching of anomalous valley Hall effect to quasi-half-valley metal state in 2D magnetic MXenes: A case study of Cr₂CSF	73
3.1	Introduction	73
3.2	Methodology	75
3.3	Results and Discussions	75

3.3.1	Structure and magnetism	75
3.3.2	Electronic properties	81
3.3.3	SOC Hamiltonian model	83
3.3.4	Effect of strain	87
3.4	Conclusion	88
4	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	89
4.1	Introduction	89
4.2	Methodology	90
4.3	Results and Discussions	91
4.3.1	Crystal structure and magnetic ground state	91
4.3.2	Valley spitting and Berry curvature	92
4.3.3	Spin spitting caused by electric field	98
4.3.4	Spin spitting caused by Janus structure	101
4.4	Conclusion	104
5	Unlocking reversible and nonvolatile anomalous valley Hall control through multiferroic van der Waals heterostructures	105
5.1	Introduction	105
5.2	Methodology	106
5.3	Results and Discussions	107
5.3.1	Crystal structure and magnetic ground state	107
5.3.2	Valley spitting and Berry curvature	111
5.3.3	Valleytronic memory device	114
5.4	Conclusion	115
6	Exploring strong and weak topological states on isostructural substitutions in TlBiSe_2	117
6.1	Introduction	117
6.2	Methodology	119
6.3	Results and Discussions	120
6.3.1	Bulk electronic structure and band inversion	120
6.3.2	Topological surface states and Z_2 invariant	127
6.4	Conclusion	130

7	Strain-driven topological quantum phase transition in (pseudo) cubic (mixed)-Cs/MA/FA halide perovskites	132
7.1	Introduction	132
7.2	Methodology	134
7.3	Results and Discussions	135
7.3.1	Electronic Structure of FAPbI ₃	135
7.3.2	Tight-Binding Model	139
7.3.3	Surface Electronic Structure	143
7.3.4	TPT in Mixed Cation Perovskites	146
7.4	Conclusion	149
8	Epilogue and outlook	151
	List of Publications	186
	Author's Biodata	187

List of Figures

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].	4
1.2	Methods for the control of the valley state are, (a) optical, (b) magnetic [2, 3], (c) electrostatic.	7
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].	12
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 " $4 = 2 + 2$ ".	14
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.	16

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.	17
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].	20
1.8	First-principles derived surface electronic dispersions along the (111) surface for (a) Sb_2Se_3 , (b) Sb_2Te_3 , (c) Bi_2Se_3 , and (d) Bi_2Te_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].	24
2.1	Steps involved in creating a computer model and interaction between theory, simulation, and experiment.	30
2.2	Multi-scale simulation in various length and time scales.	31
2.3	Flowchart of the Hartree method for many electron framework.	40
2.4	Schematic flowchart Hartree-Fock method for the solution of many electron system.	43
2.5	Hohenberg-Kohn approach in DFT.	47
2.6	Schematic representation of interacting and non-interacting many-electron system having the same ground-state electron density.	49
2.7	Schematic diagram of Jacob's ladder of density functional theory with different approximations for exchange-correlation energy.	54

2.8	Schematic illustration of self-consistent loop for the solution of the Kohn-Sham equations.	55
2.9	Representation of the pseudopotential approximation. The solid and dashed lines represent the all-electron and pseudo-wavefunctions, respectively [7]. . . .	62
3.1	Crystal structure of (a) Type I, (b) Type II, (c) Type III, and (d) Type IV Cr ₂ CSX (X = F, O, H, Cl, Br, I) MXene.	76
3.2	(a) Side and top views of Cr ₂ 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 ₂ CSF, which is renormalized to values between 0 for charge depletion and 1 for charge accumulation.	78
3.3	(a) Phonon dispersion map of Cr ₂ CSF. (b) Spin-polarized charge densities on Cr ₂ CSF MXene, where spin-up density is shown in yellow. (c) The predicted occupations of <i>d</i> orbitals of Cr _S and Cr _F atoms.	79
3.4	Crystal structure of (a) one FM and (b), (c), (d) three AFM states of Cr ₂ C MXene.	79
3.5	Dependence of specific heat capacity on the temperature.	81
3.6	Band structure of Cr ₂ 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.	82
3.7	Band structure of (a) Cr ₂ CSH, (b) Cr ₂ CSO, (c) Cr ₂ CSCl, (d) Cr ₂ CSBr, (e) Cr ₂ CSI MXene in presence of SOC.	83
3.8	Visual representation of polar angles θ and ϕ	84
3.9	(a) Berry curvature of Cr ₂ CSF along the high symmetry path. (b) Contour diagram of Berry curvature. (c) Schematic of AVH in Cr ₂ CSF under the in-plane electric field and electron doping showing the movement of electrons towards right edge of the sample.	85
3.10	The anomalous Hall conductivity as a function of E_F	86
3.11	(a) Band structure of Cr ₂ CSF under uniaxial strain of 3.5% showing QHVM phase. (b) Berry curvature of Cr ₂ CSF along the high symmetry path. (c) Schematic of hole-electron charge carriers separation on application of in-plane electric field.	87

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.	92
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.	93
4.3	The electronic band structure of (a) Fe_2CF_2 showing well defined valleys at $+\text{K}$ and $-\text{K}$ points in the conduction band, (b) Fe_2CCl_2 , (c) Fe_2CO_2 , and (d) Fe_2CS_2 showing that there are no well defined valleys at high symmetry points.	94
4.4	The electronic band structure of Fe_2CF_2 MXene with SOC showing valley polarization of magnitude 100 meV.	94
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.	95
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.	96
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.	97
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.	98
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 ($S_{+\text{K}}$ and $S_{-\text{K}}$ at $+\text{K}$ and $-\text{K}$ valleys, respectively) in the conduction band as a function of electric field.	99

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) (e), and (h) at corresponding electric fields in the presence of SOC.	100
4.11	Reversal of the spin order of spin splitting on reversing the direction of electric field.	100
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.	102
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.	103
4.14	The distribution of (a) spin-up, and (b) spin-down Berry curvatures for $\text{Fe}_2\text{C}(\text{OH})\text{F}$. 103	
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.	108
5.2	(a), (b) Crystal structures of monolayer Al_2S_3 from side views with different ferroelectric polarization. (c) Band structures of monolayer Al_2S_3 without SOC. (d) Band structures of monolayer Al_2S_3 with SOC. The Fermi level is set to zero.	109
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.	110
5.4	Crystal structures of different stacking configurations of the VSSe/ Al_2S_3 heterostructures with (a), (c), (e), (g), (i), (k) P_{up} and (b), (d), (f), (h), (j), (l) P_{dn} polarization.	110
5.5	Structure of (a-d) type-I P_{up} and (e-h) type-I P_{dn} with FM and AFM configurations.	111
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. 112	

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.	113
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.	115
6.1	(a) Primitive crystal structure of $TlBiSe_2$, (b) 3D BZ for primitive unit cell with four time-reversal invariant points Γ , 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.	120
6.2	Band structure of $TlBiSe_2$ calculated using (a) PBE+SOC (b) G_0W_0 @PBE+SOC.	121
6.3	The band structures for $TlBiSe_2$, $GaBiSe_2$ and $PbBiSe_2$ 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.	122
6.4	The band structures for $SnBiSe_2$, $SbBiSe_2$ and Bi_2Se_2 without SOC are shown in (a), (c), (e) and with SOC are shown in (b), (d), (f), respectively.	124
6.5	The band structures for $TlSnSe_2$ and $PbSbSe_2$ without SOC are shown in (a), (c) and with SOC are shown in (b), (d), respectively.	125
6.6	Phonon band structures of (a) $GaBiSe_2$ and (b) $PbBiSe_2$	126
6.7	Phonon band structures of (a) $SnBiSe_2$, (b) $SbBiSe_2$, (c) Bi_2Se_2 , (d) $TlSnSe_2$ and (e) $PbSbSe_2$	126
6.8	Surface states for the left surface of $TlBiSe_2$, $GaBiSe_2$ and $PbBiSe_2$ 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.	128
6.9	Surface states for the left surface of $SnBiSe_2$, $SbBiSe_2$ and Bi_2Se_2 are shown in (a), (c), (e) and for the right surface are shown in (b), (d), (f), respectively.	129
6.10	Surface states for the left surface of $TlSnSe_2$ and $PbSbSe_2$ are shown in (a), (c) and for the right surface are shown in (b), (d), respectively.	130
7.1	Schematic showing (a) continuous and (b) discontinuous topological phase transition.	133

- 7.2 Crystal structure of (a) cubic and (b) pseudocubic FAPbI_3 . (c) 3D BZ along with the projected 2D BZ. (d) The molecular orbital picture for FAPbI_3 . Bulk band structure of FAPbI_3 in the (e) absence of SOC and (f) presence of SOC. . 136
- 7.3 Partial density of states for FAPbI_3 showing I-p, Pb-s and Pb-p states in green, blue and red colours, respectively. 137
- 7.4 Band structure of FAPbI_3 calculated using (a) PBE+SOC and (b) G_0W_0 @HSE06+SOC. 137
- 7.5 Orbital resolved band structure in presence of SOC for cubic and pseudocubic FAPbI_3 (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_3 showing its continuous nature, and (f) pseudocubic FAPbI_3 showing a discontinuity at the critical value of strain. 138
- 7.6 Orbital resolved HSE06+SOC band structure for cubic and pseudocubic FAPbI_3 (a), (d) without compression, and (b), (e) at critical compression $\gamma = 0.76$, and $\gamma = 0.73$, respectively. 139
- 7.7 Radial distribution function using NVT ensemble for different phases of FAPbI_3 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. 140
- 7.8 Surface band structure in presence of SOC for cubic FAPbI_3 (a) without compression, (b) at critical compression $\gamma = 0.76$, and pseudocubic FAPbI_3 (c) without compression, (d) at critical compression $\gamma = 0.73$ 144
- 7.9 (a) Crystal structure of FAPbI_3 showing a different orientation of FA cation and (b) topological surface states at critical strain value. 145
- 7.10 Logarithm of probability of occurrence of different configurations at $T = 300$ K. Orientation of FA is different in all the configurations. 146
- 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) $\text{Cs}_{0.25}\text{MA}_{0.75}\text{PbI}_3$. 146
- 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. 148

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 $\gamma = 0.74$	149
--	-----

List of Tables

3.1	Four types of functionalization adsorption sites on Cr_2CSX MXenes. The most stable type has been set up to zero for each MXene (in units of eV).	77
3.2	Energies of different types of configurations of Cr_2CSF MXene using HSE06 functional. The most stable type has been set up to zero (in units of eV).	77
3.3	Energies of different types of magnetic configurations of Cr_2CSF MXene ($1 \times 2 \times 1$ supercell) using HSE06 functional. The most stable type has been set up to zero (in units of eV).	80
3.4	Coupling constants J_1 , J_2 and J_3 (in units of meV) along with the Curie temperature (in K).	81
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).	93
5.1	Energy of different stacking configurations of $\text{VSSe}/\text{Al}_2\text{S}_3$ heterostructure in units of eV.	111
5.2	Energy of different magnetic configurations of $\text{VSSe}/\text{Al}_2\text{S}_3$ heterostructure in units of eV.	111
6.1	Band gap (in meV) of TlBiSe_2 using different ϵ_{xc} functionals.	121
6.2	Band gap (in meV) of different materials using $\text{G}_0\text{W}_0@\text{PBE}+\text{SOC}$	123
6.3	Optimized lattice parameters for SnBiSe_2 , SbBiSe_2 , Bi_2Se_2 , TlSnSe_2 and PbSbSe_2	123
6.4	Calculated Z_2 invariants for different materials.	130
7.1	Interaction parameters and SOC strength for FAPbI_3 from thirteen band Hamiltonian at zero and critical compression strength in units of eV.	142

7.2	Interaction parameters and SOC strength for FAPbI_3 from four band hamiltonian at zero and critical compression strength in units of eV.	143
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.	149