

# **Strongly correlated oxide nanosheets: A novel platform for 2D magnetism**

विद्या वाचस्पति की उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

A thesis submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy

द्वारा / By

दीपक कुमार रॉय / **Deepak Kumar Roy**

पंजीकरण सं. / Registration No.

**20152037**

शोध प्रबंध पर्यवेक्षक / Thesis Supervisor:

प्रो. मुकुल कबीर / **Prof. Mukul Kabir**



भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे

Indian Institute of Science Education and Research (IISER) Pune

2025

## CERTIFICATE

This is to certify that the work incorporated in the thesis entitled “*Strongly correlated oxide nanosheets: A novel platform for 2D magnetism*” submitted by **Deepak Kumar Roy** was carried out by the candidate under my supervision. To the best of my knowledge, the work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.



Prof. Mukul Kabir

Thesis Supervisor

Pune

14<sup>th</sup> January, 2025



## DECLARATION

I declare that this written submission represents my idea in my own words and where other's ideas have been included; I have adequately cited and referenced the original sources. I declare that I have acknowledged collaborative work and discussions wherever such work has been included. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

The work reported in this thesis is the original work done by me under the guidance of **Prof. Mukul Kabir**.



Deepak Kumar Roy  
(Reg. No. 20152037)

Pune

14<sup>th</sup> January, 2025



Perhaps happiness is always to be found in the journey uphill, and not in the  
fleeting sense of satisfaction awaiting at the next peak.

*Jordan B. Peterson*



Dedicated to

my grandparents Thakurda, Thakuma, Dadu and Deeda  
and my parents Dad and Maa

## ACKNOWLEDGEMENTS

As I write this thesis, I am filled with gratitude for the support and guidance I have received throughout this journey. This journey would not have been possible without the support of many individuals including my supervisor, staff at IISER Pune, my family, friends and colleagues.

First of all, I would like to thank my supervisor, Prof. Mukul Kabir, who gave me the opportunity to join his research group at a difficult point in my life and without whose support this thesis would simply be impossible. His ideas are brilliant and novel, such that it made me feel proud while presenting our work across India at various conferences. Whenever we would get stuck or be confused, his approach to the problems would be: go back to the basics. He often took the time to share valuable advice, drawing from his experiences in overcoming challenging projects. He helped immensely in writing the final draft of the manuscripts and developed an overall perception of the projects on a fundamental level.

I would like to thank Dr. Changsong Xu and Prof. Hongjun Xiang of Fudan University for addressing my queries regarding the four-state energy method. I acknowledge initial discussions with Dr. Ashna Bajpai following the exfoliation of  $\text{Na}_2\text{IrO}_3$  and  $\text{SrRu}_2\text{O}_6$  in her group which led to the inception of these theoretical investigations. I would also like to thank my RAC members Dr. Sreejith GJ and Prof. Aftab Alam. I thank Prof. Satishchandra B. Ogale and Dr. Shouvik Datta for providing the opportunity to work in their lab and Prof. Sudarshan Ananth and Prof. MS Santhanam for their support and guidance during my initial i-PhD years.

I am grateful for financial support from IISER Pune, CSIR India and I-Hub QTF. I acknowledge the computational support provided by CCMS Tohoku University Japan, SBNCBS Kolkata, Athena under Nano Mission project SR/NM/TP-13/2016 by SERB and Param Brahma at IISER Pune under NSM.

I am thankful to my family especially my mother, father and brothers. My parents always had faith in me irrespective of the situations. My brother's words were always encouraging throughout this journey.

I owe my fundamental concepts to my senior high school teacher, the late Battagani Prabhakar, undergraduate teacher Dr. Sudipto Roy at St. Xavier's College Kolkata and postgraduate teachers Prof. Surjeet Singh, Dr. Suneeta Vardarajan and Prof. Mukul Kabir at IISER Pune.

I thank my friends/relatives for their support and presence: Rohit Babar, Abhisek Maity, Naveen Nishad, Shailendra Chaubey, Ashis Kundu, Udaya H S, Sanjit Dey, Basavaraja G, Bhumika Kansal, Swagatha Ghosh, Shruti Chakravarty, Amit Pratap Singh, Arindam Bhattacharya, Shatruhan Singh Rajput, Surya Pratap Deopa, Kalpana Chaudhary, Bhagyashri Bhat, Mohit Singh, Anweshi Dewan, Rajeev Ranjan, Ganesh Shinde, Mangal & Anurupa Sarkar, Madhu & Paapiya Sarkar, Mitali Tarafdar, Sujit & Moumita Sikdar, Debi Sarkar and Gour & Gauri Singha. I will cherish the time spent with all of them. Maity often encouraged me to keep moving forward. UNO nights at IISER and trekkings around Pune with Nishad, Chaubey and Arindam remain some of my fondest memories. I would never forget the late night returns from work to hostel with Babar, Sanjit and Udaya. The construction of the tennis court fulfilled my long-standing desire to play lawn tennis. The scenic roads of IISER and NCL made every jogging session a delight.

I also thank the past and present colleagues of my research group.

My stay at IISER was made comfortable by my friends, the housekeeping staff, the workers at all the canteens ( $V^2$ , Shiv Sagar and MDP) and the engineering staff. I was supported with official formalities by the physics department staff, and the academic section staff of IISER Pune.





## TABLE OF CONTENTS

|                                                                                    |      |
|------------------------------------------------------------------------------------|------|
| <b>Acknowledgments</b> . . . . .                                                   | ii   |
| <b>Synopsis</b> . . . . .                                                          | viii |
| <b>List of Publications</b> . . . . .                                              | xi   |
| <b>Chapter 1: Introduction</b> . . . . .                                           | 9    |
| 1.1 Two-Dimensional Magnets . . . . .                                              | 9    |
| 1.1.1 Bulk to Monolayer: Evolution of Magnetic and Electronic Properties . . . . . | 11   |
| 1.1.2 Significance of 2D Magnets in Modern Technologies . . . . .                  | 12   |
| 1.1.3 Characterization . . . . .                                                   | 13   |
| 1.1.4 Challenges in 2D Magnetism . . . . .                                         | 15   |
| 1.2 Generic Phase Diagram . . . . .                                                | 18   |
| 1.3 Kitaev Quantum Spin Liquid . . . . .                                           | 20   |
| 1.4 Non-van der Waals oxides: A new platform . . . . .                             | 23   |
| <b>Chapter 2: Computational Methods</b> . . . . .                                  | 27   |
| 2.1 The quantum many-body problem . . . . .                                        | 28   |
| 2.2 Density Functional Theory (DFT) . . . . .                                      | 30   |
| 2.3 Exchange-Correlation Functional . . . . .                                      | 32   |

|                                                                                                                                           |                                            |    |
|-------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|----|
| 2.3.1                                                                                                                                     | Local Density Approximation (LDA)          | 32 |
| 2.3.2                                                                                                                                     | Generalized Gradient Approximation (GGA)   | 33 |
| 2.3.3                                                                                                                                     | DFT+ $U$                                   | 33 |
| 2.3.4                                                                                                                                     | Hybrid Functional                          | 34 |
| 2.3.5                                                                                                                                     | $r^2$ SCAN meta-GGA                        | 35 |
| 2.4                                                                                                                                       | Energy-Mapping analysis                    | 36 |
| 2.5                                                                                                                                       | Four-State Energy method                   | 38 |
| 2.6                                                                                                                                       | Monte Carlo simulation                     | 41 |
| <br><b>Chapter 3: Robust Magnetism and Phase Transitions in Ultrathin Quantum Spin Liquid <math>\text{Na}_2\text{IrO}_3</math> Flakes</b> |                                            |    |
|                                                                                                                                           |                                            | 45 |
| 3.1                                                                                                                                       | Introduction                               | 45 |
| 3.2                                                                                                                                       | Computational Details                      | 48 |
| 3.3                                                                                                                                       | Relativistic Mott insulating bulk          | 50 |
| 3.4                                                                                                                                       | Ultrathin $\text{Na}_2\text{IrO}_3$ flakes | 55 |
| 3.4.1                                                                                                                                     | Charge-neutral flakes                      | 56 |
| 3.4.2                                                                                                                                     | Charge-doped flakes                        | 59 |
| 3.5                                                                                                                                       | Extended Heisenberg-Kitaev model           | 68 |
| 3.6                                                                                                                                       | Summary                                    | 71 |
| <br><b>Chapter 4: High temperature antiferromagnetism in ultrathin <math>\text{SrRu}_2\text{O}_6</math> nano-sheets</b>                   |                                            |    |
|                                                                                                                                           |                                            | 73 |
| 4.1                                                                                                                                       | Introduction                               | 74 |
| 4.2                                                                                                                                       | Methodology                                | 76 |
| 4.3                                                                                                                                       | Results and Discussion                     | 78 |

|                                                                                                 |                                                                            |            |
|-------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|------------|
| 4.3.1                                                                                           | Insulating AFM bulk . . . . .                                              | 78         |
| 4.3.2                                                                                           | Two-dimensional $\text{SrRu}_2\text{O}_6$ sheets . . . . .                 | 85         |
| 4.3.3                                                                                           | Charge-neutral nanosheets . . . . .                                        | 88         |
| 4.3.4                                                                                           | Charge-carrier doped nanosheets . . . . .                                  | 93         |
| 4.4                                                                                             | Summary . . . . .                                                          | 102        |
| <b>Chapter 5: Understanding Spin-Flip Transitions in <math>d^3</math> layered magnets . . .</b> |                                                                            | <b>105</b> |
| 5.1                                                                                             | Introduction . . . . .                                                     | 105        |
| 5.2                                                                                             | Computational Details . . . . .                                            | 109        |
| 5.2.1                                                                                           | $\text{CrI}_3$ monolayer . . . . .                                         | 111        |
| 5.2.2                                                                                           | $\text{CrBr}_3$ monolayer . . . . .                                        | 112        |
| 5.2.3                                                                                           | $\text{CrTe}_2$ : Bulk and monolayers . . . . .                            | 116        |
| 5.2.4                                                                                           | $\text{SrRu}_2\text{O}_6$ : Passivated and self-doped monolayers . . . . . | 117        |
| 5.3                                                                                             | Summary . . . . .                                                          | 120        |
| <b>Chapter 6: Summary and Future Outlook . . . . .</b>                                          |                                                                            | <b>121</b> |
| <b>Bibliography . . . . .</b>                                                                   |                                                                            | <b>128</b> |

## SYNOPSIS

The discovery of intrinsic two-dimensional (2D) magnetism in materials like  $\text{CrI}_3$  and  $\text{Cr}_2\text{Ge}_2\text{Te}_6$  in 2017 revealed that the magnetic order can persist in atomically thin layers, defying the Hohenberg-Mermin-Wagner theorem for isotropic spins systems. This breakthrough has paved the way for advances in spintronics, quantum information, and next-generation flexible devices. While most 2D magnets studied so far are van der Waals materials, this thesis explores a novel platform in oxide nanosheets, which are unique in several respects. The intricate interplay between competing electronic correlations, spin-orbit coupling, and electron kinetic energy underpins the exotic physics in layered  $4d$  and  $5d$  transition metal oxides. Exploring their 2D counterparts offers a promising avenue to uncover novel magnetic and electronic phenomena influenced by reduced dimensionality. The thesis specifically investigates Kitaev spin-liquid physics in 2D  $\text{Na}_2\text{IrO}_3$  nanosheets and the potential for room-temperature antiferromagnetism in  $\text{SrRu}_2\text{O}_6$  flakes.

$\text{Na}_2\text{IrO}_3$ , a non-layered iridate, serves as an exemplary candidate to explore the interplay between Heisenberg and Kitaev interactions in the 2D limit. While the bulk form of  $\text{Na}_2\text{IrO}_3$  exhibits characteristics of a proximate quantum spin liquid, its ultrathin counterpart reveals enhanced magnetic behavior. Contrary to the expected weakening of magnetism in reduced dimensions, first-principles calculations demonstrate that ultrathin  $\text{Na}_2\text{IrO}_3$  stabilizes a zigzag antiferromagnetic state. This stabilization is attributed to the amplification of Heisenberg and off-diagonal exchange interactions, which drive the system further from the Kitaev spin-liquid state. Self-doping in unpassivated flakes induces simultaneous transitions from Mott insulator to metal and antiferromagnetic to ferromagnetic phases. These findings underscore the potential of non-van der Waals correlated oxides as

a platform to investigate and control unconventional magnetic states in 2D.

$\text{SrRu}_2\text{O}_6$ , a  $4d$  transition metal oxide, represents a significant step in the quest for room-temperature nanoscale magnets. Using a combination of first-principles calculations and classical Heisenberg Monte Carlo simulations, this thesis demonstrates that  $\text{SrRu}_2\text{O}_6$  nanosheets retain robust antiferromagnetic ordering with Néel temperatures exceeding 430 K, despite the enhanced spin fluctuations intrinsic to 2D systems. Surface termination plays a crucial role, introducing intrinsic charge doping that influences magnetic behavior. This doping drives insulator-to-metal transitions and modifies Néel temperatures, with microscopic analysis uncovering distinct pathways for electron- and hole-doped systems. This study highlights the potential for room-temperature 2D antiferromagnetism, advancing the progress of both theoretical and experimental materials design.

Magnetic anisotropy is critical for the functionality of 2D magnets, strongly influencing their application in spintronics and quantum computing. This thesis investigates the origins of magnetic anisotropy in  $d^3$  compounds, focusing on honeycomb and triangular lattice geometries in ferromagnetic (FM) and antiferromagnetic (AFM) phases. First-principles calculations reveal that spin-orbit coupling (SOC) and orbital geometry near the Fermi level are key determinants of spin alignment. Electron doping beyond a critical level induces an easy-plane spin alignment, a behavior similarly observed under strain and dimensional confinement. In materials such as  $\text{CrI}_3$ ,  $\text{CrTe}_2$ , and  $\text{SrRu}_2\text{O}_6$ , the presence or absence of  $p_z$  and  $d_{z^2}$  orbitals near the Fermi-energy impacts its spin orientation. These findings offer a pathway for engineering materials with tunable magnetic anisotropy, essential for next-generation quantum devices.

This thesis makes a significant contribution to the field of correlated oxide magnetism by systematically investigating the magnetic properties of  $\text{Na}_2\text{IrO}_3$  and  $\text{SrRu}_2\text{O}_6$  in their ultrathin forms, while unraveling the mechanisms driving

magnetic anisotropy in strongly correlated systems. The interplay between spin-orbit coupling, electron correlations, and structural distortions in these materials provides a robust platform for uncovering and controlling novel quantum states, paving the way for designing next-generation materials for quantum computing and spintronic applications.

## LIST OF PUBLICATIONS

### Publications included in this thesis

1. *Robust magnetism and phase transitions in ultrathin  $\text{Na}_2\text{IrO}_3$  flakes*

**Deepak K. Roy** and Mukul Kabir

[Physical Review B 110, L020403 \(2024\)](#)

2. *High temperature antiferromagnetism in ultrathin  $\text{SrRu}_2\text{O}_6$  nanosheets*

**Deepak K. Roy** and Mukul Kabir

[Physical Review B 111, 134409 \(2025\)](#)

3. *Understanding Spin-Flip Transitions in  $d^3$  layered magnets*

**Deepak K. Roy** and Mukul Kabir

Manuscript under preparation

### Publications not included in this thesis

1. *Temperature dependent transport spin-polarization in the low Curie temperature complex itinerant ferromagnet  $\text{EuTi}_{1-x}\text{Nb}_x\text{O}_3$*

Suman Kamboj, **Deepak K Roy**, Susmita Roy, Rajeswari Roy Chowdhury, Prabhat Mandal, Mukul Kabir and Goutam Sheet

[Journal of Physics: Condensed Matter, 31 415601 \(2019\)](#)

2. *Evolution of the structural, magnetic, and electronic properties of the triple perovskite  $\text{Ba}_3\text{CoIr}_2\text{O}_9$*

Charu Garg, **Deepak Roy**, Martin Lonsky, Pascal Manuel, Antonio Cervellino, Jens Müller, Mukul Kabir and Sunil Nair

[Physical Review B 103, 014437 \(2021\)](#)

3. *Chemically Induced Surface Potential Modulation at  $\text{Pd}|\text{Al}_2\text{O}_3|\text{Graphene}$  Field Effect Transistors: Implications for Enhanced  $\text{H}_2$  Sensing*

Pooja Agarwal, Tanmay Maiti, Suvankar Purkait, **Deepak Roy**, Mukul Kabir,

Arti Garg, Dulal Senapati and Biswajit Karmakar

[ACS Applied Nano Materials 5, 8, 10941–10950 \(2022\)](#)

4. *Strong spin-lattice coupling in monolayer CrTe<sub>2</sub>*

Anupama S, **Deepak Roy** and Mukul Kabir

Manuscript under preparation





# CHAPTER 1

## INTRODUCTION

*“A mind that is stretched by a new experience can never go back to its old dimensions.”*

– Oliver Wendell Homes, Jr.

Two-dimensional materials have garnered significant research interest over the past few decades due to their remarkable and versatile properties, such as quantum confinement effects, mechanical flexibility, tunability under various physical fields (e.g., electrical, magnetic, or electromagnetic), seamless integration into arbitrary heterostructures and their response to defect and strain engineering [1, 2]. As a result, inducing magnetism in nonmagnetic 2D systems or discovering materials with intrinsic 2D magnetic properties has been a highly pursued objective. Solids with van der Waals inter-layer interactions have been among the most extensively studied 2D materials. However, in this thesis we will delve into the physics of atomically-thin strongly correlated non-layered materials.

### 1.1 Two-Dimensional Magnets

Magnetic ordering, characterized by the uniform arrangement of spins, occurs only when continuous symmetries - time-reversal, rotational and translational symmetry, are spontaneously broken. In 3D systems with isotropic spins, which have all three degrees of freedom, magnetic interactions can lead to ordering below a finite critical temperature. Whereas, thermal fluctuations destroy any possibility

of a long range order at  $T_C > 0$  K in 1D and 2D lattices. This phenomenon was explained in the seminal works of Hohenberg, and Mermin and Wagner [3, 4]. The magnon energy spectrum is gapless which prevents any magnetic ordering. However, for 2D systems with rather two degrees of freedom (XY-model), a quasi-long range magnetic ordering was shown to exist along with the formation of bound vortex and anti-vortex spin clusters below  $T_{KT} > 0$  K [5, 6]. And when spins possess only one degree of freedom, commonly referred to as Ising spins, Onsager demonstrated long ago that a magnetic phase transition is possible at temperatures below  $T_C > 0$  K in 2D lattices [7]. Several ultrathin films of magnetic layers have displayed a phase transition below a finite temperature [8], suggesting that a single 2D-layer may have the potential for magnetic ordering. Magnetic anisotropy is thought to be the key property that enables such ordering in 2D systems. The anisotropic Heisenberg model provides a theoretical framework to describe this phenomenon :

$$H = \sum_{\langle ij \rangle} (J \mathbf{S}_i \cdot \mathbf{S}_j + \Lambda S_i^z S_j^z) + \sum_i A_z (S_i^z)^2 \quad (1.1)$$

Where  $\mathbf{S}_i$ 's are the three component spins on site  $i$ ,  $J$  is the Heisenberg-coupling,  $\Lambda$  is the anisotropic exchange and  $A_z$  is the single-ion-anisotropy with respect to the out-of-plane direction. In Ising-model,  $A_z \rightarrow -\infty$ . A finite magnetic anisotropy, whether along the out-of-plane or in-plane direction, is instrumental in triggering a magnetic phase transition by creating a gap in the spin-wave excitation spectrum. Thus, after overcoming the challenges in synthesis and characterization, the first monolayer and bilayer magnets -  $\text{CrI}_3$  and  $\text{Cr}_2\text{Ge}_2\text{Te}_6$ , were successfully discovered [9, 10]. Since then, many other 2D magnets derived from van der Waals compounds have been discovered [11].

### 1.1.1 Bulk to Monolayer: Evolution of Magnetic and Electronic Properties

As highlighted in the previous section, dimensionality significantly shapes magnetism. In the transition from bulk to two-dimensional systems, spins become quantum confined, coordination among magnetic atoms and surrounding ligands is reduced and surface effects become more pronounced. Symmetry is lowered owing to broken translational invariance in the out-of-plane direction.

In 3D systems, spin–orbit coupling (SOC) typically plays a secondary role, fine-tuning spin alignment particularly in materials with heavier elements. . In contrast, in 2D systems, SOC becomes central to stabilizing long-range magnetic order by inducing magnetic anisotropy. The reduced symmetry and pronounced surface effects in 2D amplify SOC’s impact, leading to an increase in magnetic anisotropy energy. For example, in  $\text{Fe}_3\text{GeTe}_2$  [12, 13] and similar observations are noted later in Chapter 4. The SOC and inversion-asymmetric nature of 2D materials make it a viable platform for observing the Rashba effect [14, 15]. A more detailed discussion of spin–orbit coupling (SOC) is presented in Section 1.2 and Chapter 5.

Collinear spin order is typically favored in three-dimensional lattices due to strong exchange interactions and crystal field stabilization. Non-collinear spin textures, such as canted or spiral configurations, are uncommon and usually arise from magnetic frustration or competing interactions. In contrast, 2D magnets experience weakened interlayer coupling and reduced geometric constraints, enhancing their propensity for non-collinear arrangements. This tendency is further reinforced by SOC-driven Dzyaloshinskii–Moriya interactions.

Electron correlation also evolves with dimensionality. In three-dimensions, extensive orbital overlap promotes electron delocalization, strengthening exchange interactions and stabilizing high critical temperatures and large magnetic domains.

In contrast, 2D confinement enhances electron correlation by narrowing bandwidth and increasing Coulomb interactions, leading to lower critical temperatures. However, this localization also enables tunability through external factors such as gating or strain, a feature less pronounced in systems with delocalized states.

Dimensionality strongly influences magnetism, with 2D systems showing enhanced spin-orbit effects, increased anisotropy, localized spin densities and a greater tendency for non-collinear spins, in contrast to the more stable, collinear order found in its 3D counterparts.

### **1.1.2 Significance of 2D Magnets in Modern Technologies**

The silicon-CMOS technology has been facing the difficulty of exponential rise in leakage current as physical dimensions are reduced for reaching higher speed and efficiency. Spintronics has emerged as a highly promising technology, offering the potential to partially replace traditional electronics and bypass the issue of leakage currents. Spintronics uses the quantum mechanical property of electrons - the spin or spin angular momentum which are essentially picoscopic bar magnets. 2D magnets have been instrumental in driving significant advancements in the performance of spintronics devices. Spin-valves were first developed in Stuart Parkin's lab and have found applications in magnetic sensors, hard disk read heads, and Magnetic Random Access Memory (MRAM) [16]. They operate based on the following principle: thin-film ferromagnets (FM) separated by a nonmagnetic metallic layer, where parallel magnetic moments offer lower resistance, while anti-parallel moments lead to a higher resistive path. The orientation of one of the films is fixed by another FM or an antiferromagnet (AFM) while the other film is a free layer. On replacing the nonmagnetic metallic layer with a very thin insulating layer, a greater read-out signal is achieved through the quantum mechanical phenomena of tunneling magnetoresistance (TMR) [17].

Furthermore, spin-orbit torque effect, spin field-effect transistor based on non-volatile all-spin logic, spin-filter magnetic tunnel junctions and layer-stacking dependent magnetism (twistronics) are the other mechanisms/configurations that are poised to drive the advances in spintronics [2, 18]. For the next generation of hard-disk storage technology, a very high easy-axis magnetic anisotropy is essential. Researchers have identified transition metal/oxide interfaces that demonstrate such elevated levels of anisotropy [19]. However, 2D Ising-type magnets are virtually non-existent which provides the impetus for further research.

### 1.1.3 Characterization

Atomically thin ferromagnetic films would naturally have an extremely low total magnetisation. The lateral dimensions of flakes produced through mechanical or liquid exfoliation are typically limited to a few micrometers. Conventional methods for magnetic characterization, including superconducting quantum interference device (SQUID) magnetometry, vibrating sample magnetometry (VSM) and neutron diffraction, proved ineffective in detecting magnetism in 2D materials. The limited sensitivity of these techniques and the miniscule size of the 2D samples posed significant challenges. Consequently, specialized approaches were developed to probe the magnetic properties of 2D systems.

#### Magneto-optical Kerr effect (MOKE)

The most popular technique for measuring magnetisation in 2D magnets is the Magneto-optical Kerr Effect (MOKE) [20]. The first 2D magnets were characterised using this experimental setup [9, 10]. MOKE works on the principle of circular birefringence. When a linearly polarized light, composed of two circularly polarized light of opposite polarities, falls over a magnetic media, the reflected light develops a phase difference between the two components. This phase shift alters

the polarization direction of the incident light, and the resulting angular change is referred to as the Kerr rotation. Hysteresis loops can be scanned by changing the external magnetic field strengths. For antiferromagnets, where the net magnetization is zero, AC-MOKE measurements offer an effective means of probing their magnetic behavior.

### **Optical Detection of Magnetic Resonance (ODMR)**

The advancement of ultra-high-precision techniques, such as Atomic Force Microscopy, and the capability to create single nitrogen-vacancy (NV) defects in diamond, have paved the way for the development of Optical Detection of Magnetic Resonance (ODMR) [21]. By employing confocal microscopy, the nitrogen-vacancy (NV) color center within a diamond crystal is positioned in close proximity to the magnetic sample. The defect center is then excited using a resonant microwave frequency. The sample magnetic field causes the energy levels of the color center to undergo Zeeman splitting. The resulting fluorescence intensity from the defect center provides detailed spatial and magnetization information of the 2D material.

### **Raman Spectroscopy**

Raman spectroscopy is a widely recognized technique for probing the phonon signature of materials and has been extensively employed in the characterization of 2D magnets [22]. Spin ordering can influence a material's vibrational modes through spin-phonon or spin-lattice coupling, leading to shifts in Raman peak positions, intensity changes, or new spectral features. These effects offer valuable insights into the material's spin dynamics and magnetic properties.

## Photoemission Electron Microscopy

X-ray Photoemission Electron Microscopy (X-PEEM) is a high-resolution technique used to examine secondary electrons emitted from a sample's surface upon exposure to X-rays. The added advantage of this method is that it also provides additional information on the sample's topography and chemical composition. For example, it was used in the observation of ferromagnetic domains in 2D  $\text{Fe}_3\text{GeTe}_2$  flakes [23].

The other experimental characterization techniques include Lorentz transmission electron microscopy, photoluminescence, scanning tunneling microscopy, magnetic circular dichroism and secondary harmonic generation measurements [2, 11, 24]. The relevant transport measurement include anomalous Hall effect and tunneling transport.

## Computational Probe

Theoretically, we can calculate the electronic properties of 2D materials using Density Functional Theory [25, 26]. The magnetic energies derived from these calculations are then used to determine the magnetic interaction parameters, employing methods like energy-mapping, four-state method or Wannier localization [27–29]. Subsequently, the magnetic phase transition temperatures can be predicted by running Monte Carlo simulations.

### 1.1.4 Challenges in 2D Magnetism

1. The major limitation of most 2D magnets is that they order only at cryogenic temperatures [Fig.1.1]. For spintronics and data storage applications, 2D magnets must function reliably at room temperature to ensure practical usability.



2. Widely studied 2D magnets, such as  $\text{CrI}_3$ ,  $\text{Fe}_3\text{GeTe}_2$  and  $\text{CrTe}_2$ , are prone to oxidation in air. The unstable structure is also unfavourable for device operations.
3. There is a need for developing more controllable and facile synthesis methods for large-scale production and uniform quality of 2D-films. For example, mechanical and liquid exfoliation are economical methods but the flake sizes are random and good quality flakes are limited. Molecular-Beam Epitaxy on the other hand can yield very high grade films, yet its operation is prohibitively expensive.
4. Research on 2D magnetism has predominantly focused on ferromagnetic materials. AFM magnets on the other hand, are less explored, but have the attractive properties of being unperturbed in stray fields and rapid spin dynamics.
5. Expanding the family of 2D magnetic materials offers promising opportunities for discovering new properties and applications.

| Crystal                                                                                | Side view | Top view | Space group  | Electronic type                                 | Magnetic type                                    | Magnetic transition temperature (K)                                                  |
|----------------------------------------------------------------------------------------|-----------|----------|--------------|-------------------------------------------------|--------------------------------------------------|--------------------------------------------------------------------------------------|
| CrS <sub>2</sub><br>CrSe <sub>2</sub><br>CrTe <sub>2</sub>                             |           |          | $P\bar{3}m1$ | Metallic                                        | AFM<br>AFM<br>FM                                 | —<br>—<br>219 <sup>88</sup>                                                          |
| VTe <sub>2</sub><br>Fe <sub>3</sub> GeTe <sub>2</sub>                                  |           |          | $P6_3/mmc$   | Metallic                                        | FM<br>Ising-FM                                   | —<br>130 <sup>91</sup>                                                               |
| CrCl <sub>3</sub><br>CrI <sub>3</sub><br>CrBr <sub>3</sub>                             |           |          | $C2/m$       | Insulating                                      | XY-FM<br>Ising-FM<br>Ising-FM                    | 17 (f-L) <sup>92</sup><br>45 <sup>51</sup><br>34 <sup>93</sup>                       |
| FePS <sub>3</sub><br>MnPS <sub>3</sub><br>NiPS <sub>3</sub>                            |           |          | $C2/m$       | Insulating                                      | Ising-AFM<br>Heisenberg-AFM<br>XY-AFM            | 110 <sup>78</sup><br>78 (5 L) <sup>94</sup><br><25 (155 bulk) <sup>95</sup>          |
| FePSe <sub>3</sub><br>MnPSe <sub>3</sub><br>CrSiTe <sub>3</sub><br>CrGeTe <sub>3</sub> |           |          | $R\bar{3}$   | Insulating                                      | Ising-AFM<br>XY-AFM<br>Ising-FM<br>Heisenberg-FM | 119 <sup>96</sup><br>74 <sup>96</sup><br>32 (bulk) <sup>97</sup><br>30 <sup>50</sup> |
| MnBi <sub>2</sub> Te <sub>4</sub>                                                      |           |          | $R\bar{3}m$  | Insulating                                      | Heisenberg-AFM                                   | 25 (bulk) <sup>98</sup>                                                              |
| $\alpha$ -RuCl <sub>3</sub>                                                            |           |          | $P312$       | Semiconductive, direct bandgap 1.9 eV (ref. 99) | Kitaev-AFM                                       | 7 (bulk) <sup>100</sup>                                                              |

Figure 1.1: The magnetic and electronic ground state and the magnetic transition temperatures of recently discovered 2D-magnets. Nearly all the flakes have cryogenic transition temperatures. (The table is reproduced from reference [30] under CC BY-NC 3.0 Unported Licence)

## 1.2 Generic Phase Diagram

In order to overcome the challenge of cryogenic transition temperatures, we turn our attention to equation 1.1. The transition temperature depends on magnetic interaction parameter  $J$ , local moment  $S$  and the single-ion-anisotropy  $A_z$ . The magnetic anisotropy depends on the spin-orbit-coupling (SOC) present in a system. SOC is the interaction between an electron's spin moment and its orbital moment due to its motion around the nucleus. In most of the 2D magnets that have been studied, the magnetic atoms belong to the first period of transition elements and host  $3d$  electrons. The SOC scales strongly with the atomic number, it effectively depends on the fourth power of  $Z$ , i.e.  $Z^4$ . Therefore, moving down the periodic table to  $4d$  and  $5d$  elements, we anticipate larger single-ion anisotropy in magnetic compounds due to stronger SOC.

Equation 1.1 is derived from the following Hubbard-model [31]:

$$H = \sum_{i,j;\alpha\beta} t_{ij,\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + \text{h.c.} + \lambda \sum_i \mathbf{L}_i \cdot \mathbf{S}_i + U \sum_{i,\alpha} n_{i\alpha} (n_{i\alpha} - 1) \quad (1.2)$$

where  $c_{i\alpha}$  is the annihilation operator for an electron in orbital  $\alpha$  at site  $i$ ,  $n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}$  is the corresponding occupation number,  $t$  is the hopping amplitude,  $\lambda$  is the atomic SOC entangling spin ( $S_i$ ) and angular momentum ( $L_i$ ), and  $U$  is the Hubbard repulsion. This is a generic Hamiltonian and the Hund's coupling between electrons in different orbitals on the same site has been skipped for clarity. The physics of condensed matter systems is mainly the interplay between electron-electron correlation  $U$ , the kinetic energy or the bandwidth  $t$ , and the SOC  $\lambda$ .

The  $4d$  or  $5d$  compounds have a higher SOC but suffer from a concomitant decrease in Hubbard repulsion due to more diffuse orbitals. This can potentially decrease the strength of magnetic order by reducing local moment formation. How-

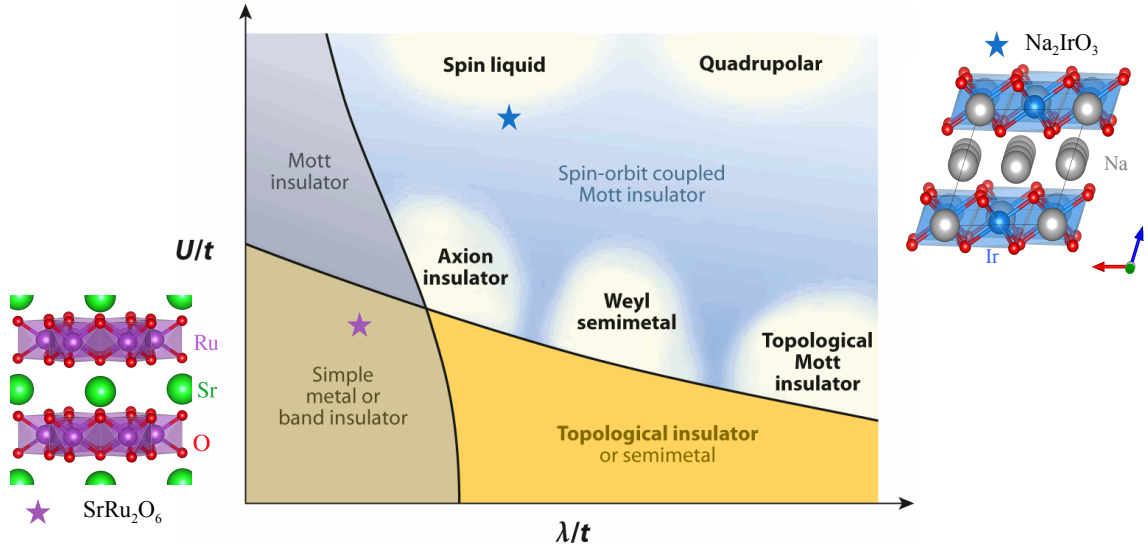


Figure 1.2: The interplay of  $U$ ,  $t$  and SOC,  $\lambda$  can give rise to a variety of exotic physics phenomena. In this thesis we choose  $\text{Na}_2\text{IrO}_3$  (blue star), a Kitaev spin liquid candidate and  $\text{SrRu}_2\text{O}_6$  (purple star), a covalent insulator with a high AFM transition temperature and study its magnetic properties in the 2D regime. (The phase diagram is reproduced from [31] with permission from Annual Reviews, Inc.)

ever, enhanced SOC splits degenerate energy levels and in certain cases, reduces the system's kinetic energy, thereby maintaining a similar  $U/t$  ratio. Moreover, tuning  $U$  and  $\lambda$ , opens avenues to explore diverse physics phenomena, as illustrated in Fig. 1.2

If the ratio  $U/t$  is high, the system becomes a Mott insulator, where strong Coulombic repulsions localize the electrons and the electronic structure is nonconducting despite partially filled orbitals. On the other hand, when  $\lambda/t$  is high, the system enters a topological insulator phase. Intermediate  $U$  and  $\lambda$  can give rise to a richer set of intriguing phases, represented by the light blue region in Fig. 1.2. Usually, SOC and  $U$  synergize to give rise to an insulating state, leading to what is referred to as a spin-orbit coupled Mott insulator in the intermediate regime.

In the following section, we explore the Kitaev spin liquid phase, one of the most fascinating states within the intermediate region (light blue) of Fig. 1.2.

### 1.3 Kitaev Quantum Spin Liquid

$\text{Na}_2\text{IrO}_3$ , a hexagonal iridate studied in this thesis, motivates the discussion of quantum spin liquids (QSL) - an exotic magnetic phase. In typical magnets, lowering the temperature below  $T_C$  breaks continuous symmetry, leading to singularities in order parameters (e.g., susceptibility), entropy release and long-range spin order. However, quantum spin liquids defy this behavior, showing no magnetic order or symmetry breaking even at  $T = 0$  K while still releasing entropy and hosting local spins [32–36]. Anderson was the first to propose that antiferromagnetic Ising spins on a triangular lattice would experience “geometric frustration”, preventing conventional ordering [37].

In  $\text{SU}(2)$  spin models, frustrating interactions among small spins in low dimensions typically inhibit long-range order. The result can be i) a phase with a complex order parameter (e.g., quadrupolar moment or spin current), ii) a valence bond crystal (VBC) that breaks only discrete symmetries (e.g., lattice or point group), or iii) a resonating valence bond (RVB) QSL that avoids symmetry breaking entirely, as proposed by Anderson [37]. A valence bond is a pair of spin-singlet state. In a VBC, an ordered pattern of valence bonds forms, and the resulting excitations are integer-spin and localized. VBCs arise as solutions to models such as the 2D Shastry-Sutherland model and the spin-1/2 Heisenberg model on the 2D pyrochlore lattice [38–40].

In contrast, the QSL has no long range order and exhibits itinerant fractional excitations. Its ground state is a superposition of multiple valence bond configurations, with a hidden non-local order parameter. The paired spins fluctuate dynamically across various configurations, resembling liquid-like behavior. The quantum spins are not magnetically ordered but they are entangled in a complex state.

Until about two decades ago, all realistic Hamiltonian models provided only

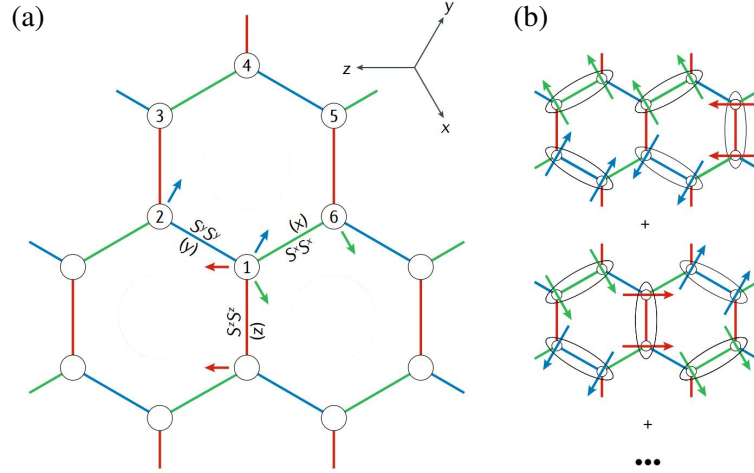


Figure 1.3: a) The Kitaev honeycomb-model is based on bond-dependent exchange, where each neighboring interaction is of Ising-type, with distinct easy-axes along the  $x$  (green),  $y$  (blue), or  $z$  (red) directions. b) The ground state of the Kitaev QSL is a superposition of configurations with various distributions of paired-“happy” (denoted by ellipses) and “unhappy” bonds. (Figure reproduced from [32] with permission from Springer Nature)

approximate solutions for QSLs. Eventually, Alexei Kitaev investigated a spin-1/2 model on a hexagonal lattice and derived an exact QSL solution [41]. In contrast to “geometric frustration,” Kitaev proposed a “bond-dependent exchange frustration,” where each of the three bonds on the honeycomb lattice features an easy-axis aligned along three mutually orthogonal directions ( $x$ ,  $y$  or  $z$ ) [Fig.1.3a]. The interactions are of Ising-type, written as:

$$H = \sum_{\langle ij \rangle_\gamma} K S_i^\gamma S_j^\gamma \quad (1.3)$$

Where  $\langle ij \rangle_\gamma$  represents a  $\gamma$ -type bond ( $\gamma = x, y$  or  $z$ ) and the summation spans all bonds in the honeycomb lattice. In the nearest-neighbor regime, each spin interacts with three adjacent spins and the orthogonal anisotropies associated with these interactions create a conflict for the spin. The ground state of the Kitaev QSL is a superposition of satisfied and unsatisfied bond configurations, with the system tunneling between these states [Fig.1.3b]. In this phase, the spin excitations are

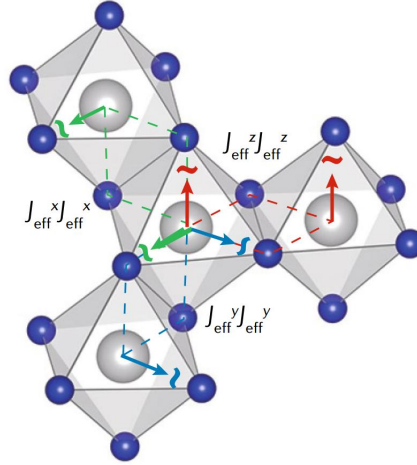


Figure 1.4: Representative crystal structure of  $\text{RuCl}_3$  and  $\text{Na}_2\text{IrO}_3$ . The grey (blue) balls denotes the metal (ligand) atoms. Each spin in the  $\text{MO}_6$  octahedra ( $\text{M} = \text{Ru}, \text{Ir}$ ) is conflicted between  $x$  (green),  $y$  (blue) and  $z$  (red) easy-axes. The easy-axes are perpendicular to the  $\text{M-O-M}$  planes (dashed lines) approximately along the  $\text{M-O}$  bonds (solid lines). (Figure reproduced from [32] with permission from Springer Nature)

fractional quasi-particles called Majorana fermions which are their own particle and anti-particle.

To realize a Kitaev QSL in real materials, the following conditions must be met: a honeycomb lattice, small spin moments ( $S = 1/2$ ), anisotropic interactions driven by SOC, absence of isotropic Heisenberg superexchange and low distortions.  $\text{RuCl}_3$  and  $\text{Na}_2\text{IrO}_3$  are considered proximate Kitaev QSL candidates, whereas  $\text{H}_3\text{LiIr}_2\text{O}_6$  shows all the signatures of a spin liquid [42–45]. In these  $d^5$  hexagonal compounds, SOC breaks the  $t_{2g}$  degeneracy into  $j_{\text{eff}} = 3/2$  quartet and a higher  $j_{\text{eff}} = 1/2$  Kramer's doublet. The superexchange through the two  $\text{M-O-M}$  pathways ( $\text{M} = \text{Ru}, \text{Ir}$ ) of edge sharing  $\text{MO}_6$  octahedra undergo destructive interference, suppressing the conventional Heisenberg term, a phenomena known as the Jackeli-Khalilullin mechanism [46, 47]. The interactions between the  $j_{\text{eff}} = 1/2$  pseudospins are highly anisotropic, with each spin experiencing mutually orthogonal easy-axis anisotropic-exchange simultaneously, as shown in Fig.1.4.

However, a realistic minimal-model for these materials is given by:

$$H = \sum_{\langle ij \rangle \in \alpha\beta(\gamma)} \left[ J_1 \mathbf{S}_i \cdot \mathbf{S}_j + K S_i^\gamma S_j^\gamma + \Gamma \left( S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha \right) \right] + \sum_{\langle\langle ij \rangle\rangle} J_3 \mathbf{S}_i \cdot \mathbf{S}_j \quad (1.4)$$

where  $J_1$  and  $J_3$  are the first and third neighbor Heisenberg interactions and  $\Gamma$  is the symmetric off-diagonal exchange. The other terms are same as in eq.1.1 and 1.3. Real materials are not perfect and naturally possess various distortions. The non-cubic trigonal distortion ( $\Delta_t$ ) of the  $\text{MO}_6$  octahedra weaken the Jackeli-Khaliullin mechanism, giving rise to the Heisenberg superexchange [48]. Moreover, the symmetric off-diagonal exchange also depends on  $\Delta_t$  which introduces non-collinear and incommensurate spiral order to the phase diagram [48, 49]. Further-neighbor interactions can also be significant in these systems. These factors push  $\text{RuCl}_3$  and  $\text{Na}_2\text{IrO}_3$  away from the Kitaev QSL regime, and they magnetically order in a zigzag-AFM state at  $T_N = 7$  K and 15 K, respectively [50, 51]. The ground state can be driven towards the spin-liquid phase by applying external magnetic fields [42–44].

Kitaev QSLs are fascinating and represent one of the most exotic states of matter. However, much remains to be understood about their properties. The search for new Kitaev QSL candidates offers exciting opportunities for both theoretical and experimental exploration.

## 1.4 Non-van der Waals oxides: A new platform

Transition-metal oxides incorporating  $4d$  or  $5d$  metals represent a compelling class of materials for enhancing anisotropy and uncovering diverse physical phenomena. The strong SOC inherent to these elements fosters anisotropic bond-dependent exchange, providing a conducive environment for realizing the Kitaev QSL phase.

Transition-metal oxides are notoriously difficult to exfoliate due to the pres-



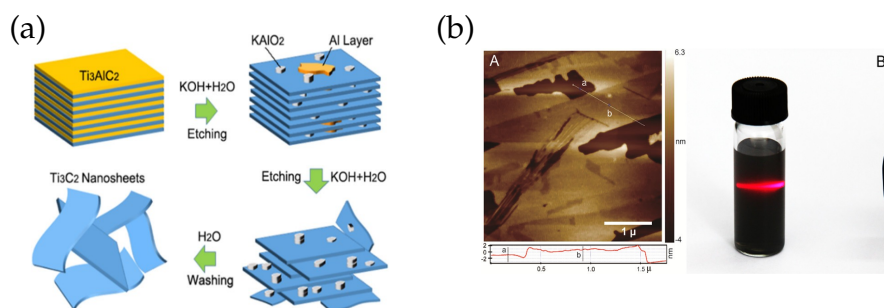


Figure 1.5: MXenes, despite their high exfoliation energies, have been successfully exfoliated using various methods, including wet-chemical synthesis [52, 53]. a) Schematic illustration of the steps involved in the chemical exfoliation of  $\text{Ti}_3\text{C}_2$ . b) Atomic force microscope images of exfoliated  $\text{Ti}_3\text{C}_2(\text{OH})_2$  nanosheets and its solution. (Reprinted (adapted) with permission from [54]. Copyright ©2021, American Chemical Society.)

ence of strong inter-planar chemical bonds. Technically, oxide compounds can be classified as layered or non-layered. In layered oxides, stacked layers are typically bonded through van der Waals forces, whereas in non-layered oxides, the layers are chemically bonded. The non-layered family is harder to cleave and would contain many unsaturated dangling bonds on the surface.

MXenes ( $\text{M}_{n+1}\text{X}_n\text{T}_x$ :  $\text{M}$  = an early transition metal,  $\text{X} = \text{C}$  or  $\text{N}$ ,  $\text{T}_x$  = an element in group 13-15 and  $n = 1-4$ ), a van der Waals layered class of materials, have been successfully exfoliated for many applications such as catalysis, supercapacitor and batteries [Fig.1.5] [52]. Interestingly, some MXenes, despite their layered structure, exhibit exfoliation energies comparable to those of non-van der Waals oxides, yet have still been successfully exfoliated experimentally [53].

Researchers employ both top-down and bottom-up strategies to cleave these challenging compounds. The top-down methods include: mechanical force-assisted method, ultrasonic liquid-phase exfoliation, supercritical  $\text{CO}_2$ -assisted exfoliation and electrochemical exfoliation [55, 56]. The bottom-up approaches involve: solvothermal synthesis, template-assisted method and vapour-deposition methods like chemical vapour deposition, pulsed-laser deposition and atomic-layer deposition.

The liquid-phase exfoliation is a highly economical method, though it lacks pre-

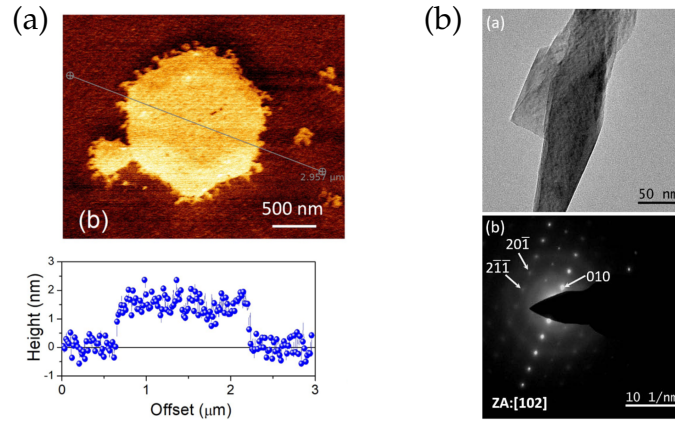


Figure 1.6: SrRu<sub>2</sub>O<sub>6</sub> ultrathin flakes were synthesized through ultrasonic liquid exfoliation. a) Atomic force microscopy (AFM) image of a hexagonal nanoflake. The corresponding height profile below reveals a thickness of approximately 1.5 nm, equivalent to roughly three layers. b) The TEM image and the corresponding SAED pattern of an ultrathin flake. (Reprinted (adapted) with permission from [60]. Copyright ©2021, American Chemical Society.)

cise controllability. In this method, bulk crystals are immersed in a solvent, with or without salts containing ions like Li<sup>+</sup>, K<sup>+</sup> etc. Ultrasound waves are applied, breaking weaker inter-layer bonds, while the ions assist in chemically-cleaving the bonds. This approach has been successfully employed to synthesize 2D counterparts of transition metal-oxide bulk materials, such as hematene ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), chromitene (FeCr<sub>2</sub>O<sub>4</sub>), and ilmenene (FeTiO<sub>3</sub>) [57–59].

In this thesis, we investigate two non-van der Waals transition metal oxides: Na<sub>2</sub>IrO<sub>3</sub> and SrRu<sub>2</sub>O<sub>6</sub>. Ultrathin flakes of SrRu<sub>2</sub>O<sub>6</sub> and Na<sub>2</sub>IrO<sub>3</sub> have been successfully synthesized using the liquid exfoliation method [Fig. 1.6] [60]. Na<sub>2</sub>IrO<sub>3</sub> is a 5d Kitaev spin liquid candidate and categorized as a spin-orbit-assisted Mott insulator [Fig. 1.2] [51]. Since lower-dimensional systems are more prone to QSL behavior, investigating ultrathin flakes of Na<sub>2</sub>IrO<sub>3</sub> as a 2D Kitaev QSL presents a promising avenue. SrRu<sub>2</sub>O<sub>6</sub> is a 4d high-temperature antiferromagnet, residing in the covalent insulating regime and exhibiting soft magnetism with quenched spin moments [Fig. 1.2] [61, 62]. We explore the potential for room-temperature 2D magnetism in SrRu<sub>2</sub>O<sub>6</sub>, alongside the emergent physics it offers.



## CHAPTER 2

### COMPUTATIONAL METHODS

*" All models are approximations. Essentially, all models are wrong, but some are useful. The practical question is how wrong do they have to be to not be useful"*

– George E.P. Box

This chapter provides an overview of some of the computational techniques utilized in this thesis. It begins by addressing the challenges associated with solving the quantum many-body problem. Key approximations that have contributed to the development of density functional theory (DFT) are examined. We then look into the methods for calculating isotropic Heisenberg exchange using energy-mapping method and magnetic-coupling tensor using the four-state energy method. In the end, we describe the Monte Carlo simulations which utilizes these coupling parameters to determine magnetic transition temperatures based on macroscopic thermodynamic observables.

## 2.1 The quantum many-body problem

The hydrogen atom, a two-body system, is the only quantum mechanical problem with an exact solution. In contrast, even for helium, the solutions are only approximate. Solid-state systems consist of many ions and electrons with interactions such as ion-ion, electron-electron and ion-electron making it an even more challenging problem. The many-body Hamiltonian for the system is:

$$H = - \sum_I \frac{\hbar^2}{2M} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \quad (2.1)$$

where  $I(i)$  denotes an ion (electron),  $M(m)$  stands for the mass of the ion (electron), and  $\mathbf{R}(\mathbf{r})$  refers to the position of the ion (electron). The first two terms of the Hamiltonian correspond to the kinetic energy of the ions and electrons, respectively. The third and fourth terms describe the Coulomb interaction energy between the ions and electrons. The final term represents the electron-ion interaction. Relativistic effects, such as spin-orbit coupling, are not considered in this formulation. The solution to this system is derived using the Schrödinger equation:

$$H\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}) \quad (2.2)$$

The many-body wave function, denoted as  $\psi$  and the eigenvalue of the system, represented as  $E$ , describe the quantum state of the system. However, solving for these exactly is nearly impossible, as the problem involves an overwhelming number of quantum variables, often on the order of avogadro number ( $10^{23}$ ). This complexity arises from the intricate many-body interactions, which must be decoupled into independent equations. Consequently, approximate methods become indispensable for tackling such systems.

The ionic and electronic contributions to the Hamiltonian can be separated due to the significant mass difference between ions and electrons, with ions being much heavier ( $10^3 - 10^5$  times more) and moving more slowly. This allows the ions to be treated as stationary while electrons respond instantaneously to ionic motion. Known as the Born-Oppenheimer approximation or adiabatic approximation, this separation enables the electrons to experience a static potential created by fixed ions [63]. Thus, the total wavefunction can be divided into ionic and electronic parts, the effective electronic Hamiltonian becomes:

$$H = - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + V_{ion} \quad (2.3)$$

As in Eq.2.1, the first term is the electron kinetic energy, the second term is the complex many-body interactions between electrons, the third term is the electron-ion Coulomb attraction. The final term is the static energy between the ions. The many-body energy is the most challenging term, and physicists usually approach it by employing a mean-field approximation.

Hartree decoupled the many-body electron wavefunction into a product of single-electron wavefunctions [64]:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \varphi_1(\mathbf{r}_1) \varphi_2(\mathbf{r}_2) \dots \varphi_i(\mathbf{r}_i) \dots \varphi_N(\mathbf{r}_N) \quad (2.4)$$

where  $N$  is the number of electrons in the system. The many-body Hamiltonian operator is then applied to this wavefunction:

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{ion}(\mathbf{r}_i) + e^2 \sum_{j \neq i} \int \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \varphi_i(\mathbf{r}) = E_i \varphi_i(\mathbf{r}) \quad (2.5)$$

This is referred to as the Hartree equation, where  $|\varphi(\mathbf{r})|^2 = \rho(\mathbf{r})$  represents the electron density. Equation 2.5 is then solved using the variational principle, minimizing the total energy with respect to either the wavefunction or the density:

$$E = \sum_i E_i - \frac{e^2}{2} \iint \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2.6)$$

where  $E$  is the total energy and the second term represents the electron-electron interaction that has been counted twice, also referred to as the Hartree energy. However, the equation is incomplete, as electrons are fermionic particles and must be described by an anti-symmetric wavefunction to comply with the Pauli exclusion principle. Fock solved this problem by expressing  $\Phi$  in terms of a Slater determinant [65]. This led to the Hartree-Fock equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(\mathbf{r}) + e^2 \sum_j \int \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \phi_i(\mathbf{r}) - e^2 \sum_j \int \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \phi_j(\mathbf{r}) = E_i \phi_i(\mathbf{r}) \quad (2.7)$$

The fourth term, known as the Fock exchange, is a purely quantum mechanical contribution arising from many-body interactions. The Fock exchange causes same-spin electrons to avoid each other, forming an exchange hole that reduces their Coulomb repulsion. The Hartree-Fock approximation ignores energies beyond the exchange interaction, such as electronic correlation. This results in an inaccurate prediction of bond-energies and an inflated estimation of band gaps. However, the Hartree-Fock equation can provide qualitatively valid insights, helping us understand the general behavior of materials.

## 2.2 Density Functional Theory (DFT)

The Density Functional Theory is the most widely used computational approach for studying the electronic structure of matter. The Hartree-Fock method, even when formulated in the second quantization framework, remains computationally

expensive. DFT defined the physical properties as a functional of electron density, reducing the number of variables in the equation and making the eigenvalue problem solvable for systems with a large number of atoms.

The Hohenberg-Kohn theorem rigorously proved that the electron density can be the fundamental variable in describing the electronic structure of a system [25]. It establishes that the ground-state electron density  $\rho(\mathbf{r})$  of a bound system of interacting electrons uniquely determines the external potential except for an inconsequential additive constant. Since the wavefunction depends on the density, the energy functional  $E_v[\rho]$  and other properties are uniquely determined as functionals of the density. Hohenberg and Kohn further proved that the electron density that minimizes the energy functional is the density corresponding to the ground state.

The procedure for solving the energy functional was provided by the Kohn-Sham approach [26]. They assumed a system of non-interacting electrons subjected to an external potential, designed in such a way that its density matches the ground-state density of the interacting real system. The Kohn-Sham energy functional is written as :

$$E_{KS}[\rho] = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(r) + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_x[\rho] + E_c[\rho] \quad (2.8)$$

The first term represents the kinetic energy of the non-interacting electrons, the second term is the potential energy in the external potential, the third term corresponds to the Hartree energy and the final two terms account for the exchange and correlation energies. Using the variational principle, the energy functional is minimized with respect to density  $\rho(\mathbf{r})$  and single-particle wavefunctions  $\phi(\mathbf{r})$  (also called Kohn-Sham orbitals), enabling the self-consistent determination of the



ground-state properties.

## 2.3 Exchange-Correlation Functional

The exchange and correlation energy terms in Eq.2.8 are combined into a single entity known as the exchange-correlation functional. The correlation energy represents the discrepancy in the kinetic energy calculation between the real system and the non-interacting system, while  $E_x[\rho]$  is the difference between the many-body energy and the Hartree-Fock exchange energy. The majority of the effort is focused on developing the exchange-correlation functional, as no exact expression for it exists. It must be accurate, computationally efficient, and yield results that closely match experimental data. The exchange-correlation energy effectively reduces the Coulombic repulsion between electrons, which is why it is modeled as a 'hole'. It also must account for the correction of the self-energy interaction, which is incorrectly included in the Hartree expression. We now discuss some of the commonly used approaches for functionals.

### 2.3.1 Local Density Approximation (LDA)

The Local Density Approximation (LDA) assumes that the exchange-correlation energy at each spatial point is solely a function of the local electron density. This approach enhances computational efficiency, but it may fail to account for non-local effects, particularly in systems with significant density fluctuations. Despite these shortcomings, LDA is commonly used as an initial approximation and yields reasonable results for systems with relatively uniform electron densities (e.g. ideal metals like Na). The functional is written as :

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) E_{xc}^{homo}(\rho(\mathbf{r})) d\mathbf{r} \quad (2.9)$$

Here  $E_{xc}^{homo}$  is the exchange-correlation energy in a uniform electron density  $\rho(\mathbf{r})$ . The correlations were modeled initially by Hedin and Lundqvist [66] and later by Perdew and Zunger [67]. However, LDA suffers from self-interaction and overemphasizes electron delocalization, resulting in underestimations of band gaps and magnetic moments.

### 2.3.2 Generalized Gradient Approximation (GGA)

The GGA approach extends the LDA approach to include both local density and density gradients, thereby capturing regions of steep density variations. The expression is as follows:

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) E_{xc}^{homo}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) d\mathbf{r} \quad (2.10)$$

The gradient term amplifies exchange interactions in areas of greater electron density. This aligns with the expectation that exchange interactions outweigh correlation effects in these density regimes. GGA approaches LDA behavior at low densities. In general, GGA provides improved binding energies but overestimates bond lengths. Unless otherwise specified, the Perdew-Burke-Ernzerhof (PBE) functional, a stable and efficient version of the GGA, has been employed in most of the calculations presented in this thesis [68].

### 2.3.3 DFT+ $U$

To address the inadequate treatment of electron correlations or onsite Coulombic repulsions within orbitals in standard DFT, a corrective framework known as DFT+ $U$  is implemented. The Hubbard repulsions described in Eq. 1.2 can be significant, especially for the strongly correlated  $d$  and  $f$  electrons of transition metals. This approach aids in localizing spins to achieve accurate magnetic moments and

ensures proper band gap predictions in Mott or spin-orbital Mott insulators. The total energy becomes:

$$E^{DFT+U}[\rho(\mathbf{r}), n_d] = E^{DFT}[\rho(\mathbf{r})] + E^U[n_d] - E^{double}[n_d] \quad (2.11)$$

The first term is the standard DFT energy, the second term is the Hubbard repulsion dependent on the  $d$  (or  $f$ ) electron density  $n_d$  and the last term is a double-counting correction energy for the repulsive interaction. In this thesis, we employ the Liechtenstein approach, which separately accounts for onsite-Coulombic interactions  $U$  and Hund's coupling  $J_H$ , as well as the Dudarev approach, where the effective parameter  $U - J_H$  is utilized [69, 70].

### 2.3.4 Hybrid Functional

Hybrid functionals provide an improved approximation for exchange-correlation energy by incorporating a portion of the exact exchange from Hartree-Fock (HF) theory while retaining the correlation energy from density functional approximations like LDA or GGA. The Heyd-Scuseria-Ernzerhof (HSE) hybrid functional partitions the short-range (SR) HF exchange while screening the long-range (LR) HF exchange contributions [71].

$$E_{xc}^{HSE} = \alpha E_x^{SR-HF}(r, r'; \omega) + (1 - \alpha) E_x^{SR-DFT}(r; \omega) + E_x^{LR-DFT}(r; \omega) + E_c^{DFT}(r) \quad (2.12)$$

Here  $\alpha$  and  $\omega$  represent the mixing and range separation parameters, respectively. Specifically, in the case of HSE06, the range separation parameter is fixed at  $\omega = 0.2 \text{ \AA}^{-1}$ , while the mixing coefficient  $\alpha$  is set to 0.25. This implies that one-fourth of the SR-HF exchange is combined with three-fourths of the SR-DFT

exchange, while the correlation energy is fully derived from DFT. This method significantly enhances the accuracy of electronic structure calculations, making it particularly effective for band gap predictions in both bulk and low-dimensional materials.

### 2.3.5 $r^2$ SCAN meta-GGA

The GGA functional suffers from the notorious self-interaction error. Moreover, it is inherently a local functional, which results in unreliable performance across different density regimes. Meta-GGA functionals incorporate the kinetic energy density  $\tau$ , which introduces a degree of non-locality [72]. This enables meta-GGAs to better capture the characteristics of various chemical bonds, including covalent, metallic, and weak interactions, surpassing the accuracy of LDAs and GGAs. The energy is expressed as:

$$E_{xc}^{meta-GGA}[\rho] = \int E_{xc}(\rho(r), \nabla\rho(r), \tau(r)) dr \quad (2.13)$$

where the kinetic energy density  $\tau$  is derived from the Kohn-Sham single-particle wavefunctions:

$$\tau = \frac{1}{2} \sum_{\text{occupied}} |\nabla\phi(r)|^2 \quad (2.14)$$

Meta-GGA functionals are designed to satisfy exact constraints while minimizing adjustable parameters. Non-empirical functionals strictly adhere to these constraints, ensuring broad applicability. The "empirical" functionals on the other hand, introduce additional flexibility by allowing certain constraints to be relaxed, enabling parameter optimization but may lack reliability beyond their training sets.

The strongly constrained and appropriately normed (SCAN) functional en-

forces all 17 known constraints, offering high accuracy across diverse systems [73]. It effectively predicts structural and energetic properties of ice, silicon, and  $\text{MnO}_2$  and captures complex electronic and magnetic behaviors in superconductors and iridates. Although SCAN is highly accurate, its reliance on dense numerical grids reduces computational efficiency, and issues with XC potential divergence complicate pseudopotential generation.

A regularized version of SCAN ( $r$ SCAN) was developed to enhance numerical stability while making minimal changes to the original functional [74]. This modification improved pseudopotential generation and stability; however, later studies revealed a decline in transferability, particularly affecting atomization energy accuracy [75].

The restored-regularized SCAN ( $r^2$ SCAN) combines SCAN's rigorous constraint adherence with  $r$ SCAN's improved numerical stability, ensuring both accuracy and computational efficiency [76]. Thus,  $r^2$ SCAN offers a refined meta-GGA functional optimized for reliable large-scale simulations. In Chapter 4, we employ the  $r^2$ SCAN functional to investigate its effectiveness in determining the magnetic and electronic properties of the unconventional compound  $\text{SrRu}_2\text{O}_6$ .

## 2.4 Energy-Mapping analysis

The energy-mapping analysis is a widely used method for extracting magnetic interactions from DFT calculations [77]. It can be used to compute scalar isotropic-Heisenberg couplings. Subsequently, these interaction parameters are used to estimate magnetic-phase transition temperatures through Monte Carlo simulations. These couplings can also be applied to calculate the spin-wave energy spectra or to fit existing experimental magnonic spectra within the framework of linear spin-wave theory [78]. In this thesis, we employed this method to calculate the follow-

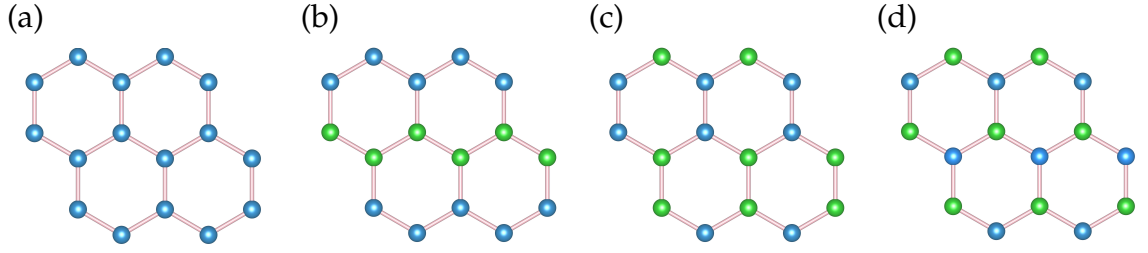


Figure 2.1: A subset of possible magnetic structures on a honeycomb lattice, the blue (green) balls denote up (down) spins : a) FM, b) zigzag AFM, c) stripy AFM and d) neel AFM

ing long-range interacting Hamiltonian:

$$H = -\frac{1}{2} \sum_{\langle i,j \rangle} J_1 \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2} \sum_{\langle\langle i,j \rangle\rangle} J_2 \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2} \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} J_3 \mathbf{S}_i \cdot \mathbf{S}_j + E_0 \quad (2.15)$$

Here  $J_1$ ,  $J_2$  and  $J_3$  are the 1<sup>st</sup> NN (nearest neighbour), 2<sup>nd</sup> NN and 3<sup>rd</sup> NN Heisenberg exchanges respectively.  $\mathbf{S}_i$  is the spin on magnetic atom at site  $i$ . The 1/2 factor accounts for the double counting of coupling energies in DFT.  $E_0$  represents the non-magnetic energy of the crystal, determined by its geometry but not the spin arrangement. An effective AFM interaction (FM interaction) would result in a negative value (positive value) of  $J$ . Based on the number of variables (four in Eq. 2.15 :  $J_1$ ,  $J_2$ ,  $J_3$  and  $E_0$ ), several magnetic excited state energies are computed within DFT. The energies are expressed in terms of the Heisenberg couplings and spins, where the prefactor of each term corresponds to the signed difference between the number of FM and AFM bonds/couplings at a given separation, along with a factor of 1/2. On the left-hand side, DFT energies are normalized per magnetic atom.

As an example, we consider the honeycomb lattice. It has three 1<sup>st</sup> NNs, six 2<sup>nd</sup> NNs and three 3<sup>rd</sup> NNs. Expressing the energies for a subset of possible configurations [Fig.2.1]:

$$\begin{aligned}
\frac{E_{FM}}{f} &= [-3J_1 - 6J_2 - 3J_3] \frac{S^2}{2} + E_0 \\
\frac{E_{zigzag}}{f} &= [-J_1 + 2J_2 + 3J_3] \frac{S^2}{2} + E_0 \\
\frac{E_{stripy}}{f} &= [J_1 + 2J_2 - 3J_3] \frac{S^2}{2} + E_0 \\
\frac{E_{neel}}{f} &= [3J_1 - 6J_2 + 3J_3] \frac{S^2}{2} + E_0
\end{aligned} \tag{2.16}$$

Here,  $E_{FM}$ ,  $E_{zigzag}$ ,  $E_{stripy}$ , and  $E_{neel}$  represent the energies of the FM, zigzag-AFM, stripy-AFM, and Neel-AFM structures, respectively. The variable  $f$  denotes the number of magnetic atoms in the supercell used to calculate the energies. To eliminate  $E_0$ , the ground-state energy equation is subtracted from the others. This results in a system of three linear equations, which are solved using standard linear algebra to obtain  $J_1$ ,  $J_2$ , and  $J_3$ . Similarly, the inter-planar coupling ( $J_\perp$ ) can be determined by considering FM and AFM inter-planar coupled ground-state structures. The single-ion anisotropy (Eq. 1.1) is obtained by subtracting the energies of the in-plane and out-of-plane aligned spin structures of the ground state, then dividing by  $f$  and  $S^2$ . Thus, the energy-mapping method proves to be an effective and simple tool for calculating many essential magnetic interaction parameters.

## 2.5 Four-State Energy method

In general, exchange interactions may be anisotropic, varying depending on the direction. This is particularly true for frustrated magnets, such as Kitaev spin liquid candidates. It is also crucial in systems with Dzyaloshinskii–Moriya interaction (DMI), which induces spin canting (weak ferromagnetism), plays a key role in hosting magnetic skyrmions and accounts for the magnetoelectric effect. The anisotropic couplings stem from spin-orbit coupling (SOC), which breaks the symmetry of the system.

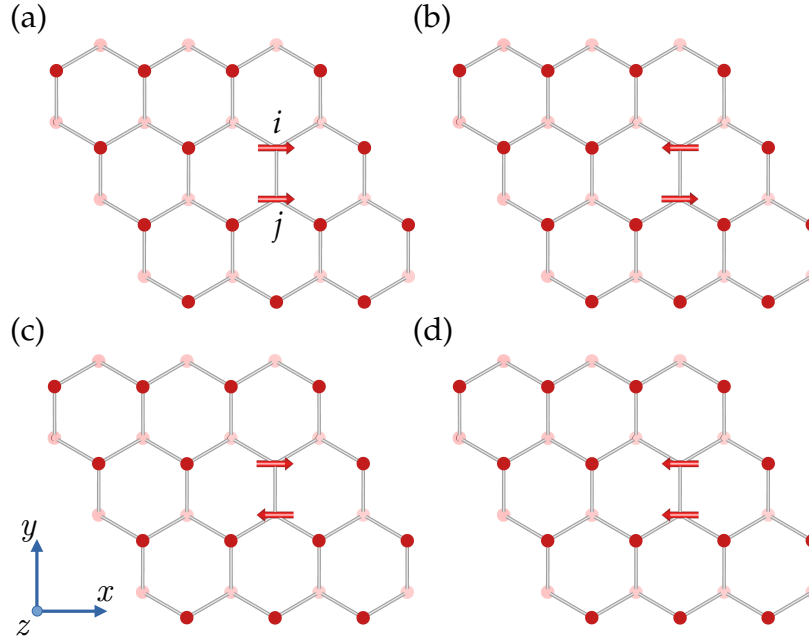


Figure 2.2: Demonstrating the four-state energy method: Calculation of  $J^{xx}$  in a honeycomb lattice. The dark red (light red) dots are the spins aligned in the  $+z$  direction ( $-z$  direction). Two spins  $i$  and  $j$  under consideration (near middle denoted by red arrows) are lying along the  $x$ -axis. Rest of the spins are arranged in the ground-state configuration of the material, which is the Néel AFM state in this case. Spins  $i$  and  $j$  are manipulated in four different configurations: a)  $+x$  and  $+x$ , b)  $-x$  and  $+x$ , c)  $+x$  and  $-x$  and d)  $-x$  and  $-x$ . The energies of these configurations are calculated to determine  $J_{xx}$ .

Based on the three orthogonal directions ( $x$ ,  $y$  and  $z$ ), the anisotropic exchange can be expressed in the form of a  $3 \times 3$  tensor:

$$J = \begin{bmatrix} J^{xx} & J^{xy} & J^{xz} \\ J^{yx} & J^{yy} & J^{yz} \\ J^{zx} & J^{zy} & J^{zz} \end{bmatrix}$$

This corresponds to the following Hamiltonian:

$$H = \sum_{i,j} \sum_{\alpha\beta} J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta \quad (2.17)$$

Here  $\alpha$  and  $\beta$  span the  $x$ ,  $y$  and  $z$  directions, while  $i$  and  $j$  denote two magnetic sites.

Rearranging the terms to separate out the interaction between the magnetic



spins  $i$  and  $j$  from the interactions with other spins:

$$H = \sum_{\alpha\beta} J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta + \sum_{k \neq i,j} \sum_{\alpha\beta} J_{ik}^{\alpha\beta} S_i^\alpha S_k^\beta + \sum_{k \neq i,j} \sum_{\alpha\beta} J_{kj}^{\alpha\beta} S_k^\alpha S_j^\beta + \sum_{k \neq i,j; m \neq i,j} \sum_{\alpha\beta} J_{km}^{\alpha\beta} S_k^\alpha S_m^\beta \quad (2.18)$$

The 1<sup>st</sup> term is solely the anisotropic interaction between spins  $i$  and  $j$ , the 2<sup>nd</sup> term is the interaction of spin  $i$  with all other spins (except  $j$ ), the 3<sup>rd</sup> term is the interaction of spin  $j$  with all other spins (except  $i$ ) while the 4<sup>th</sup> term is the interaction of rest of the spins among themselves [27, 28, 79]. Only the first term needs to be computed. The phrase four-state energy method originates from the need to compute the energies of four states to eliminate the unnecessary terms in equation 2.18 while calculating the first term [27, 28, 79].

As an example, we calculate  $J^{xx}$  on a honeycomb lattice by considering spins  $i$  and  $j$  (red arrows in Fig.2.2). We represent the magnitude of the 2<sup>nd</sup> term as  $K_1$ , the 3<sup>rd</sup> term as  $K_2$  and the last term as  $E_{\text{other}}$ . The spins of the rest of the structure is fixed as in the ground state (assuming Neel AFM in this case), ensuring they remain perpendicular to both spins  $i$  and  $j$ , while manipulating only the spins  $i$  and  $j$ . The energies of the following four states are computed, as illustrated in Fig.2.2:

- (i)  $i$  along  $[1,0,0]$ ,  $j$  along  $[1,0,0]$ ;  $E_1 = J_{ij}^{xx} S^2 + K_1 + K_2 + E_{\text{other}}$
- (ii)  $i$  along  $[-1,0,0]$ ,  $j$  along  $[1,0,0]$ ;  $E_2 = -J_{ij}^{xx} S^2 - K_1 + K_2 + E_{\text{other}}$
- (iii)  $i$  along  $[1,0,0]$ ,  $j$  along  $[-1,0,0]$ ;  $E_3 = -J_{ij}^{xx} S^2 + K_1 - K_2 + E_{\text{other}}$
- (iv)  $i$  along  $[-1,0,0]$ ,  $j$  along  $[-1,0,0]$ ;  $E_4 = J_{ij}^{xx} S^2 - K_1 - K_2 + E_{\text{other}}$

Thus,

$$J^{xx} = \frac{E_1 - E_2 - E_3 + E_4}{4S^2} \quad (2.19)$$

In a similar fashion  $J^{xy}$  can be found by manipulating the spin  $i$  along  $x$ -axis and the spin  $j$  along  $y$ -axis while keeping rest of the spins along  $z$ -axis. For calculating  $J^{yz}$ , the spin  $i$  is manipulated along  $y$ -axis and the spin  $j$  along  $z$ -axis while keeping rest of the spins along  $x$ -axis ( $\perp$  to  $i$  and  $j$ ). In most systems, the  $J$ -tensor is symmetric, implying that only 6 elements need to be calculated.

To calculate the Kitaev frustration, symmetric off-diagonal exchange and isotropic Heisenberg coupling, as described in eq.1.4, two distinct approaches are used. In the first approach, the  $J$ -tensor is determined in global cartesian coordinates and then diagonalized to extract the relevant parameters, as illustrated in Ref.[80]. In the second approach, the crystal structure is rotated such that the new  $x$ ,  $y$ , and  $z$  directions align with the Kitaev easy-axes [Fig.1.4]. One can then directly use simplified equations (B2a-B2c) in Ref.[79], to extract the Hamiltonian parameters. Therefore, the four-state energy method is a powerful technique for determining complex anisotropic interactions, relying solely on DFT-calculated energies.

## 2.6 Monte Carlo simulation

The Monte Carlo method is a set of techniques that use random sampling to estimate deterministic values or properties of a system or solve complex problems. It is particularly useful for systems with a large number of variables or intricate probabilistic behaviors, where direct analytical solutions are infeasible. One of the earliest documented works on the Monte Carlo method is likely the publication by Metropolis and Ulam [81]. The Monte Carlo method is widely applied across a multitude of areas today, including calculating thermodynamic observables in a statistical system, evaluating complex integrals, functional optimization, modeling financial systems and fitting curves to experimental data points. In this thesis we used Monte Carlo simulations to find magnetic phase transtion temperatures

from the paramagnetic state to an ordered phase, based on the input Hamiltonian parameters.

Consider a statistical system of particles in thermal equilibrium. The probability of occurrence of a microstate  $\mathbf{x}_i$  at a temperature  $T = 1/(k_B \beta)$  is given as:

$$P(\mathbf{x}_i) = \frac{1}{Z} \exp[-\beta H(\mathbf{x}_i)] \quad (2.20)$$

where  $Z = \sum_{i=1}^N \exp[-\beta H(\mathbf{x}_i)]$  is the canonical partition function over  $N$  states.

The thermal average of any observable  $M$  is given as :

$$\langle M \rangle = \lim_{N \rightarrow \infty} \overline{M}_N = \frac{1}{Z} \sum_{i=1}^N M(\mathbf{x}_i) \exp[-\beta H(\mathbf{x}_i)] \quad (2.21)$$

In the Ising-model,  $\mathbf{x}_i = (S_1, S_2, S_3, \dots, S_n)$ , where  $n$  is the total number of spins. Each  $\mathbf{x}_i$  represents a point in a high-dimensional space, with the number of dimensions determined by  $n$ . If this high-dimensional space were sampled uniformly, it would be computationally infeasible to calculate for the exponentially large number of phase points and many of the points would lie on the surface of the hypercube [82]. Therefore, the points can be selected randomly, using simple sampling. However, simple-sampling can be inefficient in high-dimensional spaces as many points are wasted in regions of low importance, resulting in slow convergence. Thus, importance sampling is used, where the points  $\mathbf{x}_i$  are not entirely random, but are preferentially selected from the regions of phase space that are most relevant at the given temperature  $T$ .

Metropolis and co-workers [83] developed an algorithm based on the Markov process where each state  $\mathbf{x}_{i+1}$  would depend on the previous state  $\mathbf{x}_i$ , with the two states being linked by the transition probability  $W(\mathbf{x}_i \rightarrow \mathbf{x}_{i+1})$ . By enforcing the principle of detailed balance, the algorithm ensures that equilibrium is eventually reached after a sufficient number of transitions:

$$P(\mathbf{x}_i)W(\mathbf{x}_i \rightarrow \mathbf{x}_j) = P(\mathbf{x}_j)W(\mathbf{x}_j \rightarrow \mathbf{x}_i) \quad (2.22)$$

The Metropolis procedure to simulate the Ising-model is as follows:

1. Start with an arbitrary initial state  $\mathbf{x}_i = (S_1, S_2, S_3, \dots, S_n)$
2. Select randomly with equal probability one of the spins  $S_k$  in this microstate and flip it :  $S_k = S \rightarrow S_k = -S$ . Let this trial microstate be  $\mathbf{x}_j$ .
3. Calculate  $\Delta E = E(\mathbf{x}_i) - E(\mathbf{x}_j)$
4. If  $\Delta E \leq 0$ , accept the trial state :  $\mathbf{x}_{i+1} = \mathbf{x}_j$
5. If  $\Delta E > 0$ , draw a random number  $\xi$  between 0 and 1:
  - (a) If  $\xi \leq \exp(-\beta\Delta E)$ , accept the trial state :  $\mathbf{x}_{i+1} = \mathbf{x}_j$
  - (b) If  $\xi > \exp(-\beta\Delta E)$ , reject the trial state :  $\mathbf{x}_{i+1} = \mathbf{x}_i$

Next, a neighboring spin of  $S_k$  is considered and the process is repeated (2-5). A Monte Carlo sweep is completed by repeatedly applying this procedure until the system reaches equilibrium. Once equilibrium is achieved, thermodynamic observables, such as the specific heat,  $C_V = \frac{\partial E}{\partial T} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}$ , magnetization  $M$  and susceptibility  $\chi$ , can be calculated. A large number of Monte Carlo sweeps ( $\sim 10^6$ ) are carried out to achieve proper equilibrium, following the Law of Large Numbers. It is essential to use a sufficiently large ensemble of spins to achieve a sharper transition (finite-size scaling). By computing these thermodynamic variables over a range of temperatures, we can identify the corresponding phase transition.

In the Heisenberg model, spins have three degrees of freedom, unlike the Ising model where spins are constrained to only one direction. As a result, the spin in step 2 is reoriented in any arbitrary direction. To ensure a uniform distribution of spin orientations and prevent clustering at the poles of the sphere, the spin

coordinates are generated using the Marsaglia procedure [84]. To generate pseudo-random numbers for the simulation, we employed the advanced Mersenne-Twister generator, which is natively available in both Fortran and C++ [85].

Monte Carlo simulation is a pivotal tool in our study, as it enables us to determine the phase transition temperatures. This step is essential for generating a comprehensive description of the material's magnetic properties.

## CHAPTER 3

# ROBUST MAGNETISM AND PHASE TRANSITIONS IN ULTRATHIN QUANTUM SPIN LIQUID $\text{Na}_2\text{IrO}_3$ FLAKES

The quest for quantum spin liquids has garnered significant attention due to their rich physics and disruptive prospects in quantum communication and computation. Spin-orbit coupling, electron correlation, and structural distortion play critical roles in the candidate materials that eventually order antiferromagnetically at low temperatures. We introduce quantum electron confinement to the existing complexity and explore the interplay between Heisenberg and Kitaev interactions in ultrathin  $\text{Na}_2\text{IrO}_3$  layers using first-principles calculations. The zigzag antiferromagnetic state in the monolayer is reinforced and pushed further away from the Kitaev spin liquid state due to the increased strength of Heisenberg and off-diagonal exchange interactions. In contrast, the carrier-doped flakes undergo a Mott insulator-to-metal transition accompanied by an antiferromagnetic to ferromagnetic transition. These findings present exciting prospects for comprehending magnetism in a novel two-dimensional framework of non-van der Waals correlated oxide flakes. This work has appeared in [Physical Review B 110, L020403 \(2024\)](#).

## 3.1 Introduction

Quantum spin liquid (QSL) is an exotic state of matter where highly correlated spins evade symmetry-breaking phase transition down to the lowest temperatures [32–36]. QSLs exhibit long-range entanglement, topological order, emergent

gauge fields and fractional excitations that attracted enormous attention in quantum condensed matter physics. In 1973, Anderson proposed a two-dimensional QSL state in a triangular  $S = 1/2$  Heisenberg spin system interacting antiferromagnetically [37]. The conjectured resonating valence bond ground state consists of a quantum superposition of spin singlets, and the elementary excitations are the fractionalized  $S = 1/2$  spinons that can propagate in the lattice. However, the detection of these fractionalized excitations in real materials remains inconclusive despite extensive efforts [86–91]. In contrast, the Kitaev QSL state is an exact solution to a model Hamiltonian with bond-specific  $S = 1/2$  nearest-neighbour Ising interactions,  $K_\gamma S_i^\gamma S_j^\gamma$ , where  $\gamma$  denotes different bonds [41]. In this model, the spin fractionalizes into itinerant and localized Majorana fermions.

Realizing Kitaev QSL state in real materials is challenging due to the existence of additional spin interactions, such as the Heisenberg exchange [46–48, 92, 93]. In this context, spin-orbit entangled pseudospins on a honeycomb lattice can generate Kitaev interaction in the edge-shared octahedral Mott insulators. The interplay between correlation and spin-orbit coupling makes Ir<sup>4+</sup> oxides and Ru<sup>3+</sup> chlorides the primary candidate materials for hosting the Kitaev QSL state [45, 50, 94–96]. However, magnetic ordering is observed at low temperatures in two-dimensional honeycomb iridates and RuCl<sub>3</sub>, [50, 94–96] while the existence of the QSL state in H<sub>3</sub>LiIrO<sub>6</sub> remains a topic of debate [45]. Nevertheless, the ordering temperature is an order of magnitude lower than the energy scale of magnetic interactions, indicating the presence of magnetic frustration.

Among the iridates, Na<sub>2</sub>IrO<sub>3</sub> has received considerable attention since it was envisioned for realizing Kitaev physics [46, 47]. Due to the extended Ir–5d orbitals, iridates reside far away from the Mott insulating limit,  $U \gg W$ , with  $U$  and  $W$  being the electron correlation and electronic bandwidth, respectively. However, owing to strong spin-orbit coupling  $\lambda_{\text{Ir}} \sim 400$  meV, Na<sub>2</sub>IrO<sub>3</sub> is a weak spin-orbital

entangled Mott insulator similar to Sr<sub>2</sub>IrO<sub>3</sub> [97–101]. The half-filled  $j_{\text{eff}} = 1/2$  narrow band splits due to electron correlation, and the singly-occupied Kramers doublet describes the low-energy physics. Consequently, the delicate interplay between comparable  $U$ ,  $W$ , and  $\lambda$  becomes intriguing.

Given the spin-orbital nature, the interactions between  $j_{\text{eff}} = 1/2$  pseudospins are highly anisotropic, [46, 47] and the conventional Heisenberg exchange is suppressed according to the Jackeli-Khaliullin (JK) mechanism [46, 47]. The hopping between the adjacent  $j_{\text{eff}} = 1/2$  and virtual  $j_{\text{eff}} = 3/2$  ( $m_j = \pm 3/2$ ) orbitals dominates, leading to anisotropic Ising ferromagnetic interaction due to Hund’s coupling. The three bonds emerging from each metal site accommodate Kitaev interaction for edge-shared octahedra. The easy-axes of the  $j_{\text{eff}} = 1/2$  pseudospin are perpendicular to Ir–O<sub>2</sub>–Ir bond planes, and thus the Ising axes are orthogonal to each other for the three bonds. However, trigonal distortions of the cubic octahedral environment lift the  $t_{2g}$  orbital degeneracy and partially quench the orbital angular momentum, leading to a decrease in the Kitaev interaction and an increase in Heisenberg exchange [92, 102]. Accordingly, at temperatures below 15 K, the bulk Na<sub>2</sub>IrO<sub>3</sub> exhibits antiferromagnetic (AFM) ordering, forming a zigzag spin structure that is consistent with a large Kitaev exchange [94, 103, 104]. Thus, a Heisenberg-Kitaev model is deemed appropriate [47, 92].

We explore magnetism in ultrathin layers of Na<sub>2</sub>IrO<sub>3</sub> within the first-principles calculations. Such ultrathin flakes have recently been synthesised through chemical exfoliation, presenting a promising avenue for investigating frustrated magnetism in two-dimensional systems with strong correlation and spin-orbit coupling. Surprisingly, we find that magnetism not only survives but is reinforced up to the monolayer limit. Similar to the bulk counterpart, the ultrathin and passivated Na<sub>2</sub>IrO<sub>3</sub> flakes exhibit a Mott-insulating zigzag AFM ground state. The present investigation focuses on the evolution of different magnetic interactions



from the bulk crystal to the monolayer. Further, chemically exfoliated flakes may be charge-doped, and our findings suggest that it drives an intriguing magnetic phase transition along with a Mott insulator-to-metal transition. These results present an exciting opportunity for further exploration.

## 3.2 Computational Details

We conduct first-principles calculations using density functional theory, as implemented in the Vienna *ab initio* simulations package [105, 106]. The projector augmented wave formalism is employed to describe wave functions, utilizing a plane-wave basis and a kinetic energy cut-off of 475 eV [107]. The Perdew-Burke-Ernzerhof functional is employed to account for the exchange-correlation energy [68]. Additionally, on-site Coulomb interactions ( $U_{\text{Ir}} = 1$  eV) and Hund's exchange ( $J_{\text{H}} = 0.5$  eV) for the Ir-*d* electrons are included [69]. Some calculations are repeated with different Hubbard correlations  $U_{\text{Ir}}$  between 1 eV to 3 eV, yielding qualitatively similar results. Expectedly, an increase in  $U_{\text{Ir}}$  results in a larger band gap and a slight increase in orbital moment. Further, switching to local density approximation for the exchange-correlation energy leads to qualitatively similar results, albeit with a slight reduction in both band gap and Ir-moments. The first Brillouin zone is discretized using a  $\Gamma$ -centred Monkhorst-Pack *k*-grid of  $7 \times 4 \times 7$  for the bulk and  $7 \times 4 \times 1$  for the two-dimensional flakes [108]. For faster convergence, we optimized the crystal and magnetic structures sequentially. Initially, we conducted a comprehensive structural relaxation involving the lattice and ionic coordinates, followed by magnetic optimization. A straightforward magneto-structural optimization consistently renders quantitatively similar results across all cases. Relativistic calculations (GGA + SO +  $U_{\text{Ir}}$  +  $J_{\text{H}}$ ) are subsequently conducted in a self-consistent manner to examine spin-orbit-induced ef-

fects. We ensure that all force components remain below  $5 \times 10^{-3}$  eV/Å, and the total energy convergence threshold is set at  $10^{-8}$  eV. Charge-neutral flakes are designed by surface passivation of Na<sub>3</sub>-layers with hydrogen (H). For partially passivated and charge-neutral flakes, H-atoms are initially permitted to relax above the frozen Na<sub>3</sub> and NaIr<sub>2</sub>O<sub>6</sub> layers, followed by the relaxation of all atoms. The entire slab undergoes relaxation in flakes of varying thicknesses. A perpendicular vacuum space of at least 20 Å is included to minimize interactions between periodic images of the two-dimensional flakes. Anisotropy energies are computed by rotating the geometric structure around the *b*-axis while constraining the direction of the Ir-spins. We calculate the magnetic interaction parameters using the modified four-state energy method [28, 79]. Here, the structure is rotated to align the axes with the three orthogonal Ir–O bond directions of the IrO<sub>6</sub> octahedra, while the magnetic moments are constrained to follow these directions. To prevent spurious interactions between the ordered and manipulated spins, a  $2 \times 2 \times 1$  supercell is utilized. To evaluate dynamical stability, phonon band structures are computed through the finite difference method within the supercell approach. Force constants are initially determined using the Phonopy code, [109] which incorporates the acoustic-sum-rule only. However, additional consideration of the rotational sum rules, as implemented in the Hiphive code, effectively eliminates the spurious phonon instability [110]. Phonon calculations employ an elevated kinetic energy cut-off of 700 eV. The Néel temperature is determined using Heisenberg-Kitaev Monte Carlo simulations with  $10^4$  spins within the SpinW code [111]. At every temperature,  $10^6$  Monte Carlo steps are executed to ensure thermal equilibrium.

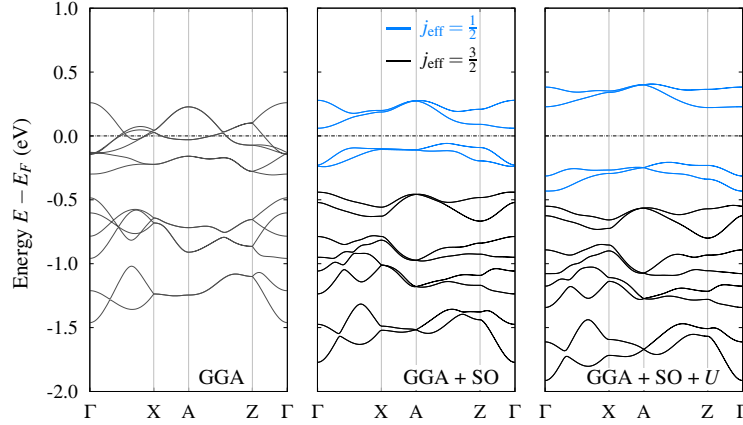


Figure 3.1: The Ir  $5d-t_{2g}$  band structure is obtained using non-magnetic GGA, magnetic GGA + SO and GGA + SO +  $U_{\text{Ir}}$  ( $U_{\text{Ir}} = 1$  eV,  $J_H = 0.5$  eV). Both structural distortions and SO coupling play critical roles. Na<sub>2</sub>IrO<sub>3</sub> is described as a relativistic Mott insulator since SO coupling opens up an insulating gap between the occupied and unoccupied  $j_{\text{eff}} = 1/2$  bands. This gap increases further with the inclusion of  $U_{\text{Ir}}$ . Remarkably, the calculated gap agrees well with experimental data [97, 112, 113].

### 3.3 Relativistic Mott insulating bulk

Bulk Na<sub>2</sub>IrO<sub>3</sub> crystallizes in the monoclinic  $C2/m$  phase, and the calculated lattice parameters ( $a = 5.45$  Å,  $b = 9.43$  Å,  $c = 5.64$  Å) agree with the experimental data [Table 3.1] [51]. The crystal structure comprises two-dimensional layers of edge-shared IrO<sub>6</sub> octahedra that construct a honeycomb Ir-lattice in the  $ab$ -plane, with Na atoms at the centre. These layers are stacked along the  $c$ -axis by alternating with pure Na-layers. Since the  $5d$  orbitals are more extended than the  $3d$  orbitals, the resonant inelastic X-ray scattering (RIXS) data corroborates a much larger octahedral crystal field splitting  $\Delta_{\text{OC}}$  about 3 eV in Ir-compounds [112]. Thus, with  $\Delta_{\text{OC}} \sim 3.4$  eV in Na<sub>2</sub>IrO<sub>3</sub>, the  $5d^5$  electrons of Ir<sup>4+</sup> ions exist in the low-spin  $t_{2g}^5$  configuration, and the state can alternatively be described with one  $t_{2g}$  hole. The dispersion of the Ir  $5d-t_{2g}$  manifold is broad, around 2 eV, and is impacted by structural distortion. This leads to narrower  $t_{2g}$  sub-bands, with  $W$  in the range of 0.5-0.6 eV [Figure 3.1]. A metallic solution characterized by a high density

of states at the Fermi level is obtained using GGA, and it remains metallic even with the inclusion of the Hubbard correlation  $U_{\text{Ir}}$  term in the calculation. An insulating gap appears only when the spin-orbit coupling is introduced [Figure 3.1]. With the strong spin-orbit coupling, the degeneracy of the threefold Ir- $t_{2g}^5$  orbitals is further lifted, resulting in states with effective angular momentum  $j_{\text{eff}} = 3/2$  and  $j_{\text{eff}} = 1/2$ . While the  $j_{\text{eff}} = 3/2$  manifold is completely filled, the half-filled  $j_{\text{eff}} = 1/2$  splits into lower and upper Hubbard bands due to electron correlation. Thus, Na<sub>2</sub>IrO<sub>3</sub> is a relativistic Mott insulator [Figure 3.1]. The insulating gap increases from 120 meV in GGA + SO to 430 meV as an additional on-site Coulomb interaction,  $U_{\text{Ir}} = 1$  eV, is incorporated into the calculation [Figure 3.1]. The results are consistent with the angle-resolved photoemission spectroscopy, optical conductivity, and RIXS data, [97, 112, 113] and previous theoretical estimations [Table 3.1] [97, 104, 113–115]. The effective correlation, which is determined from the occupied and unoccupied  $j_{\text{eff}} = 1/2$  states, ranges from 0.3 to 0.6 eV for  $U_{\text{Ir}}$  values of 0 to 1 eV, consistent with the experimental estimation of 0.52 eV [99]. The bandwidths of the  $t_{2g}$  subbands are further affected by the SO coupling and become narrower  $\sim 200$  meV near the Fermi level, compatible with the ARPES experiment [97]. Therefore, we conclude that Na<sub>2</sub>IrO<sub>3</sub> resides at the borderline of Mott criterion,  $U > W$ .

Structural distortions play a central role in determining the quantum state. The cubic symmetry of the IrO<sub>6</sub> octahedra is broken as trigonal and orthorhombic distortions are inherited, [51, 103] and the Ir–O–Ir angles  $\theta_{\text{Ir}}$  become more than 90°. The computed average  $\theta_{\text{Ir}} \sim 100.3^\circ$  agrees with the measured range 98–100° [51]. The crystal-field splitting  $\Delta_t$  of the  $j_{\text{eff}} = 3/2$  states, induced by the trigonal distortion, is determined to be 110 meV in high-resolution RIXS measurements [112]. The present result of  $\Delta_t \sim 170$  meV corroborates the experimental data, and since  $\Delta_t < \lambda_{\text{Ir}}$ , the microscopic model with  $j_{\text{eff}}$  picture remains valid. Further, the spin-

Table 3.1: Calculated structural, electronic, and magnetic parameters for the bulk Na<sub>2</sub>IrO<sub>3</sub> are in good agreement with various experimental results. A meticulous comparison with experimental bulk data establishes a robust theoretical framework for the unexplored realm of ultrathin flakes.

| (I) Structural properties                                                        |                                         |              |
|----------------------------------------------------------------------------------|-----------------------------------------|--------------|
|                                                                                  | Experiment                              | Current work |
| $a$ (Å)                                                                          | 5.43 [51]                               | 5.45         |
| $b$ (Å)                                                                          | 9.40 [51]                               | 9.43         |
| $c$ (Å)                                                                          | 5.61 [51]                               | 5.64         |
| $\delta_{\text{off}}$ (%)                                                        | 0.86 [51]                               | 0.69         |
| $d_{\text{Ir-O}}$ (Å)                                                            | 2.07 [51]                               | 2.05         |
| $\angle \text{O-Ir-O}$ (°)                                                       | 94.0 [51]                               | 93.7         |
| $\angle \text{Ir-O-Ir}$ (°)                                                      | 98.5 [51]                               | 100.3        |
| (II) Electronic properties                                                       |                                         |              |
| Band gap $E_g$ (meV)                                                             | 340 (ARPES) [97]                        | 428          |
|                                                                                  | 320 (optical) [113]                     |              |
|                                                                                  | 420 (RIXS) [112]                        |              |
| Effective correlation (eV)                                                       | 0.52 [99]                               | 0.60         |
| Bandwidth of $t_{2g}$ sub-bands (meV)                                            | 100 [97]                                | $\sim 200$   |
| Trigonal distortion $\Delta_t$ (meV)                                             | 110 [112]                               | 170          |
| Spin-orbit excitation<br>( $j_{\text{eff}}-3/2 \rightarrow j_{\text{eff}}-1/2$ ) | 0.7-0.8 [112]                           | 0.7          |
| (III) Magnetic properties                                                        |                                         |              |
| Magnetic ordering                                                                | Zigzag AFM [51, 103, 104]<br>13.3 [104] | Zigzag AFM   |
| Neel temperature $T_N$ (K)                                                       | 15 [44, 51, 94]<br>18 [103]             | 18           |
| Magnetic moment ( $\mu_B/\text{Ir}$ )                                            | 0.22 [103]                              | 0.28         |
| Magnetic moment lies in                                                          | $ac$ plane [44, 103, 104]               | $ac$ plane   |
| Moment relative to $a$ -axis, $\theta_{\mu_s}^a$ (°)                             | -                                       | 70           |
| (IV) Parameters of HK Hamiltonian                                                |                                         |              |
| $J_1/K$                                                                          | -0.38 [93]                              | -0.23        |
|                                                                                  | -0.17 [116]                             |              |
| $J_1/\Gamma$                                                                     | 3.0 [116]                               | 2.1          |
| $J_1/J_3$                                                                        | 1.6 [116]                               | 0.5          |

Table 3.2: Electronic and magnetic parameters for the bulk Na<sub>2</sub>IrO<sub>3</sub> in various magnetically ordered states. The relative energy of different magnetic structures is indicated by  $\Delta_{\text{GS}}$ . The  $\mu_s$  and  $\mu_o$  lie in the  $a$ - $c$  plane at an angle  $\theta$ . Calculated band gaps  $E_g$  are also tabulated.

|                                                                     | AFM        |               |             | FM         |
|---------------------------------------------------------------------|------------|---------------|-------------|------------|
|                                                                     | Zigzag     | Stripy        | Néel        |            |
| $\Delta_{\text{GS}}$ (meV/Ir)                                       | 0          | 5.4           | 6.3         | 4.1        |
| $\mu_s$ ( $\mu_B$ /Ir)                                              | 0.28       | 0.19          | 0.10        | 0.37       |
| $\mu_o$ ( $\mu_B$ /Ir)                                              | 0.33       | 0.32          | 0.34        | 0.35       |
| $\theta_{\mu_s}^a, \theta_{\mu_o}^a, \theta_{\mu_j}^a$ ( $^\circ$ ) | 70, 51, 60 | -50, -24, -34 | -11, -4, -6 | 89, 88, 88 |
| $E_g$ (meV)                                                         | 428        | 216           | 411         | 198        |

orbit excitation ( $j_{\text{eff}}-3/2 \rightarrow j_{\text{eff}}-1/2$ ) energy of 0.7 eV within GGA + SO +  $U_{\text{Ir}}$  compares well with the RIXS peak located at 0.7-0.8 eV [112].

According to the JK mechanism, the magnetic superexchange interactions between Ir<sup>4+</sup> ions with  $j_{\text{eff}} = 1/2$  pseudospins are essentially of Kitaev type for edge-shared, undistorted octahedra [46, 47]. Trigonal distortion significantly influences the quantum state by lifting the  $t_{2g}$  degeneracy, leading to partial quenching of orbital momentum in bulk Na<sub>2</sub>IrO<sub>3</sub>. The distorted edge-shared octahedra disrupts the JK mechanism, triggering superexchange interactions. These interactions result in magnetic ordering below 15 K, [94, 103, 104] as the channels for nearest neighbour Heisenberg and off-diagonal interactions are introduced, and longer-ranged interactions are considered. The inelastic neutron scattering, [51] X-ray diffraction, [103] and RIXS experiments [104] indicate an AFM zigzag ordering. In concurrence, we find that the zigzag AFM ground state is 4 meV/Ir lower than the ferromagnetic (FM) case, while the stripe and Néel AFM states remain 5 and 6 meV/Ir higher in energy [Table 3.2]. The spin moment of 0.28  $\mu_B$ /Ir is significantly smaller than expected for the  $j_{\text{eff}} = 1/2$  system, in consensus with the experimental result [103]. Such reduction in the spin moment is also observed in other Ir<sup>4+</sup> compounds, Sr<sub>2</sub>IrO<sub>4</sub>, Ba<sub>2</sub>IrO<sub>3</sub>, and  $\beta$ -Li<sub>2</sub>IrO<sub>3</sub> [117–119]. The reduction in the spin

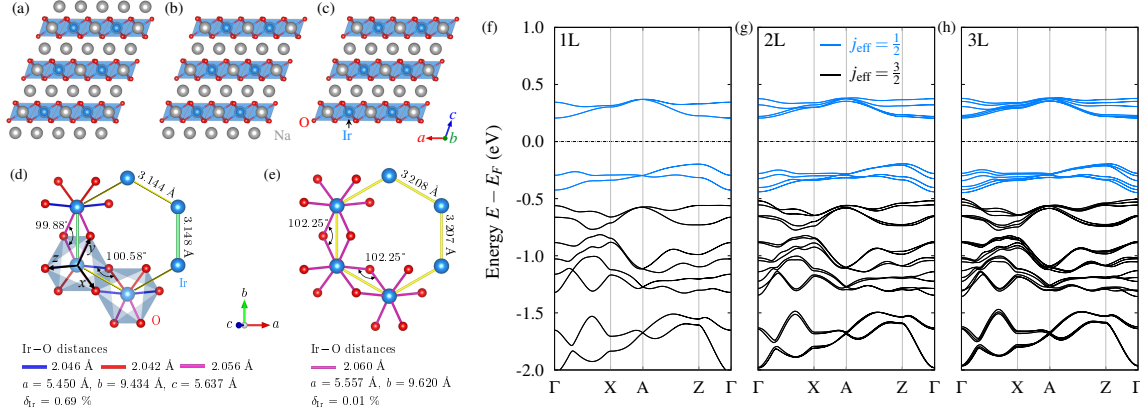


Figure 3.2: Crystal structure and electronic band structure of ultrathin flakes are illustrated. (a)-(c) Various surface terminations are possible for the ultrathin flakes, shown for three-layer (3L)  $\text{Na}_2\text{IrO}_3$ . The bulk structure consists of alternating stacking of honeycomb  $\text{NaIr}_2\text{O}_6$  layers separated by hexagonal  $\text{Na}_3$  layers. Flakes with and without the pure  $\text{Na}_3$  termination are equally probable. Flake where (a) both sides  $[\text{Na}_3] \cdots [\text{Na}_3]$ , (b) one side  $[\otimes] \cdots [\text{Na}_3]$  and (c) none of the sides  $[\otimes] \cdots [\otimes]$  are terminated with  $\text{Na}_3$ -layer. Chemically passivated flakes are also explored, though not depicted. Similar structures are studied for monolayers and bilayers. Local structural details of the honeycomb  $\text{NaIr}_2\text{O}_6$  layer are represented in (d) for the bulk and (e) for the passivated monolayer,  $[\text{H}-\text{Na}_3|\text{NaIr}_2\text{O}_6|\text{Na}_3-\text{H}]$ . Na-atoms are omitted for clarity. Magnetic axes,  $\{\alpha, \beta, \gamma\} = \{x, y, z\}$ , are along three nearest-neighbour Ir-O bonds. Bonds of the same color indicate equivalent Ir-O distances. As the thickness decreases from the bulk to the passivated monolayer, the in-plane lattice parameters increase, resulting in uniform Ir-O bonds, Ir-O-Ir angles, and Ir-Ir distances. Consequently, the Ir-off-centering distortion  $\delta_{\text{Ir}}$  becomes negligible in the monolayer. Electronic band structures of passivated flakes are shown in (f)-(h), which remain spin-orbit coupled Mott insulator. Essential electronic structure parameters such as band gaps, bandwidths and electron correlation remain equivalent to those of the bulk  $\text{Na}_2\text{IrO}_3$ .

moment is attributed to the  $5d$ - $2p$  hybridization and small exchange splitting in the  $5d$  bands. While the orbital moment  $\mu_o \sim 0.34 \mu_B/\text{Ir}$  is equivalent across the magnetic states, the spin moment is highly dependent,  $\mu_s \sim 0.1, 0.2$ , and  $0.4 \mu_B/\text{Ir}$  for Néel, stripe, and FM arrangements [Table 3.2]. Further,  $\mu_s$  and  $\mu_o$  moments are weakly noncollinear and lie in the  $ac$ -plane at an angle with the crystallographic  $a$  axis, which is in qualitative agreement with the experimental [44] and earlier theoretical results [Table 3.2] [120].

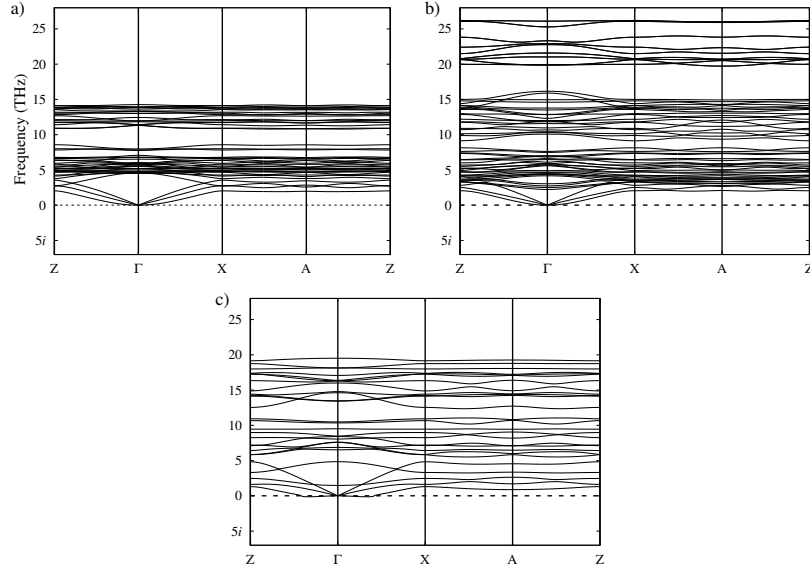


Figure 3.3: Phonon band structures of (a) electron-doped monolayer  $[\text{Na}_3|\cdots|\text{Na}_3]$ , (b) passivated neutral monolayer  $[\text{H}-\text{Na}_3|\cdots|\text{Na}_3-\text{H}]$ , and (c) hole-doped monolayer  $[\otimes|\cdots|\otimes]$ . Phonon band structures are computed utilizing acoustic and rotational sum rules within the hiPhive code, [110] demonstrating the dynamic stability of the flakes. Nevertheless, during calculations with the Phonopy code, [109] localized regions of phonon instability in the flexural acoustic modes were detected. This occurrence is attributed to the exclusive reliance on acoustic sum rules for force constant calculations. However, integrating the rotational sum rule into the calculations effectively eliminates this spurious instability. Furthermore, in 2D materials, the presence of an extremely small ( $\ll 1$  THz) unstable flexural phonon is often regarded as spurious. This minor instability in the flexural acoustic modes near the  $\Gamma$  point is highly sensitive to calculation parameters, such as supercell size and  $\mathbf{k}$ -point sampling.

### 3.4 Ultrathin $\text{Na}_2\text{IrO}_3$ flakes

Exploring ultrathin layers of  $\text{Na}_2\text{IrO}_3$  could provide fascinating insights, as they offer additional complexity due to the quantum electron confinement, in addition to the existing electron correlation and spin-orbit coupling. These layers have recently been chemically exfoliated, and a comprehensive theoretical exploration of the same is highly relevant. Through chemical exfoliation, the weaker Na–O bonds between the  $\text{Na}_3$  and  $\text{NaIr}_2\text{O}_6$  layers are cleaved. As a result, the flakes with and without the pure Na-layer terminations are equally likely, [121, 122] and we study all such possibilities, some of which are shown in Figure 3.2(a)-(c). Ul-



Table 3.3: Bader charge analysis of the passivated flakes compared to the bulk. The numbers represent the average magnitude and the nature of the charge per atom. Results indicate that the magnetic honeycomb NaIr<sub>2</sub>O<sub>6</sub> sublayers in these flakes have identical charge distribution as in bulk and are charge neutral.

|              | Na     | Ir     | O      |
|--------------|--------|--------|--------|
| Bulk         | +0.856 | +1.439 | −1.049 |
| 3L-surface   | +0.853 | +1.432 | −1.053 |
| 3L-mid-layer | +0.858 | +1.434 | −1.048 |
| 2L           | +0.860 | +1.436 | −1.049 |
| 1L           | +0.864 | +1.423 | −1.047 |

trathin layers are cleaved parallel to the honeycomb IrO layers resulting in two-dimensional flakes in the crystallographic *ab*-plane. The exfoliation energy of the Na<sub>3</sub> layer was determined to be 154 meV Å<sup>−2</sup>, comparable to that of already exfoliated transition metal carbides [123–125]. The phonon dispersions, as determined using acoustic and rotational sum rules for the force constants, [110] indicate that ultrathin non-van der Waals flakes in neutral and charge-doped states exhibit dynamic stability [Figure 3.3]. Since exfoliated flakes are either Na-rich or Na-deficient, they are electron- or hole-doped at the surface and will have an intriguing effect on their physical properties.

### 3.4.1 Charge-neutral flakes

We begin by analyzing ultrathin layers that are terminated with Na<sub>3</sub> layers on both sides, which are further H-passivated, creating a structure of [H–Na<sub>3</sub> | ··· | Na<sub>3</sub>–H]. Bader charge analysis demonstrates that the magnetic honeycomb NaIr<sub>2</sub>O<sub>6</sub> sublayers in these flakes have identical charge distribution as in bulk Na<sub>2</sub>IrO<sub>3</sub> and are charge neutral [Table 3.3]. The in-plane lattice parameters increase consistently due to thickness reduction and are 2% longer in the monolayer than in bulk [Figure 3.2(d)–(e)]. The lattice distortions are also affected as the Ir-off-centring distortion  $\delta_{\text{Ir}}$  substantially decreases from 0.69% in bulk to 0.01% in the passivated

Table 3.4: Structural parameters of the passivated flakes compared to the bulk. The Ir off-centering distortion is calculated as,  $\delta_{\text{off}} = \left( \frac{d_{\text{Ir-O}}^{\text{long}}}{d_{\text{Ir-O}}^{\text{short}}} - 1 \right) \times 100$ . Here,  $d_{\text{Ir-O}}^{\text{long}}$  ( $d_{\text{Ir-O}}^{\text{short}}$ ) are the long (short) Ir-O bonds in the basal plane. [126]

|            | Lattice Parameters (Å) |      |      | $\delta_{\text{off}}(\%)$ | $d_{\text{Ir-O}}(\text{Å})$ | $\angle \text{O-Ir-O}$ | $\angle \text{Ir-O-Ir}$ |
|------------|------------------------|------|------|---------------------------|-----------------------------|------------------------|-------------------------|
|            | $a$                    | $b$  | $c$  |                           |                             |                        |                         |
| Bulk [51]  | 5.43                   | 9.40 | 5.61 | −0.86                     | 2.068                       | 94°                    | 99°                     |
| Bulk (DFT) | 5.45                   | 9.43 | 5.64 | 0.69                      | 2.048                       | 94°                    | 100°                    |
| 3L         | 5.50                   | 9.51 | —    | 0.36                      | 2.054                       | 94°                    | 101°                    |
| 2L         | 5.51                   | 9.55 | —    | 0.36                      | 2.056                       | 94°                    | 102°                    |
| 1L         | 5.56                   | 9.62 | —    | 0.01                      | 2.060                       | 95°                    | 102°                    |

monolayer [Table 3.4]. In contrast, in the monolayer, trigonal distortion increases  $\theta_{\text{Ir}} \sim 102.3^\circ$  [Table 3.4]. The overall electronic structure of the passivated flakes remains similar to that of the bulk and retains the relativistic Mott insulating state with about 400 meV band gaps [Figure 3.2(f)-(h)]. Calculated  $\Delta_{\text{OC}} = 3.4$  eV, the effective correlation calculated from the upper and lower Hubbard bands of 0.6 eV and bandwidths near the Fermi level, 160–250 meV, also remain similar to bulk values.

Surface passivated ultrathin flakes with one to three NaIr<sub>2</sub>O<sub>6</sub> sublayers remain magnetic and exhibit a zigzag AFM configuration, similar to the bulk [Table 3.5]. These findings demonstrate that the conventional notion of diminishing ordering with decreasing thickness is not applicable in this context [24]. This is particularly unexpected given that the bulk material orders only below 15 K. Further, the zigzag ordered Ir-moments exhibit a curious characteristic of not aligning with any of the crystallographic axes. In passivated monolayer and optimized bulk lattice, the Ir moments are situated in the  $ac$ -plane at an angle of approximately 75° and 70°, respectively, with respect to the crystallographic  $a$ -axis [Figure 3.4]. In comparison, calculations reveal that these angles are somewhat smaller for Na<sub>2</sub>IrO<sub>3</sub> with experimental lattice. Moreover, the  $\mu_s$  and  $\mu_o$  moments exhibit a weakly non-

Table 3.5: Magnetic and electronic properties of the passivated layers. Remarkably, magnetism is preserved in the ultrathin passivated flakes, with the magnetic ground state remaining same as that of the bulk phase, i.e. the zigzag antiferromagnetic configuration. The magnetic moments and band gaps in the passivated flakes closely resemble those of the bulk phase.

|    |                                                   | AFM    |          |        | FM        |          |
|----|---------------------------------------------------|--------|----------|--------|-----------|----------|
|    |                                                   | Zigzag | Stripy   | Néel   | Inter-AFM | Inter-FM |
| 3L | $\Delta_{GS}$ (meV/Ir)                            | 0      | 3.8      | 25.5   | 2.3       | 3.2      |
|    | $\mu_s$ ( $\mu_B$ /Ir)                            | 0.28   | 0.15     | 0.22   | 0.38      | 0.38     |
|    | $\mu_o$ ( $\mu_B$ /Ir)                            | 0.32   | 0.34     | 0.33   | 0.34      | 0.34     |
|    | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ ( $^\circ$ ) | 73, 51 | -44, -22 | 90, 89 | 88, 86    | 89, 88   |
|    | $E_g$ (meV)                                       | 401    | 339      | 308    | 257       | 217      |
| 2L | $\Delta_{GS}$ (meV/Ir)                            | 0      | 3.2      | 25.5   | 2.3       | 3.0      |
|    | $\mu_s$ ( $\mu_B$ /Ir)                            | 0.28   | 0.14     | 0.22   | 0.38      | 0.38     |
|    | $\mu_o$ ( $\mu_B$ /Ir)                            | 0.32   | 0.34     | 0.32   | 0.33      | 0.33     |
|    | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ ( $^\circ$ ) | 73, 50 | -34, -23 | 90, 89 | 89, 88    | 89, 89   |
|    | $E_g$ (meV)                                       | 400    | 413      | 308    | 259       | 228      |
| 1L | $\Delta_{GS}$ (meV/Ir)                            | 0      | 5.2      | 26.5   | 1.7       |          |
|    | $\mu_s$ ( $\mu_B$ /Ir)                            | 0.28   | 0.19     | 0.22   | 0.39      |          |
|    | $\mu_o$ ( $\mu_B$ /Ir)                            | 0.31   | 0.32     | 0.31   | 0.31      |          |
|    | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ ( $^\circ$ ) | 74, 49 | -49, -21 | 90, 90 | 90, 90    |          |
|    | $E_g$ (meV)                                       | 404    | 123      | 300    | 256       |          |

Table 3.6: Structural details of the doped 1L flakes. The bond length,  $d_{Ir-O}$ , decreases in the hole-doped structures whereas it increases for the electron-doped structures with respect to the passivated monolayer. An opposite trend is seen for the angle,  $\angle O-Ir-O$ .

|                                | $a$ (Å) | $b$ (Å) | $\delta_{off}$ (%) | $d_{Ir-O}$ (Å) | $\angle O-Ir-O$ | $\angle Ir-O-Ir$ |
|--------------------------------|---------|---------|--------------------|----------------|-----------------|------------------|
| $[Na_3   \cdots   Na_3]$       | 5.49    | 9.51    | 0.00               | 2.107          | 93 $^\circ$     | 97 $^\circ$      |
| $[H-Na_3   \cdots   Na_3]$     | 5.50    | 9.51    | 0.01               | 2.083          | 94 $^\circ$     | 99 $^\circ$      |
| $[H-Na_3   \cdots   Na_3-H]$   | 5.56    | 9.62    | 0.01               | 2.060          | 95 $^\circ$     | 102 $^\circ$     |
| $[H-Na_3   \cdots   \otimes]$  | 5.39    | 9.33    | -0.03              | 1.994          | 93 $^\circ$     | 103 $^\circ$     |
| $[\otimes   \cdots   \otimes]$ | 5.24    | 9.07    | 0.00               | 1.941          | 93 $^\circ$     | 102 $^\circ$     |

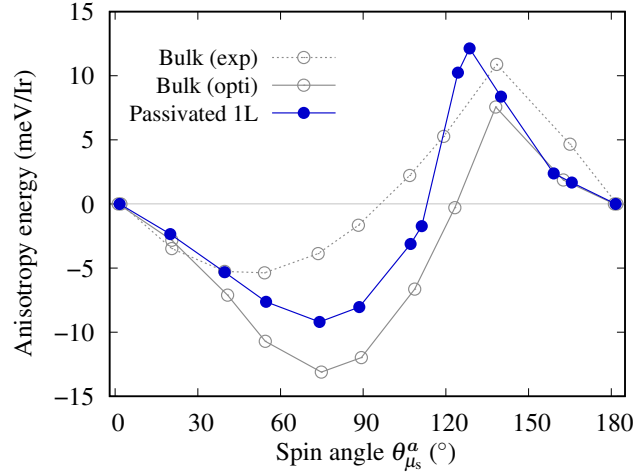


Figure 3.4: The magnetic anisotropy energy in the crystallographic  $ac$  plane is illustrated as the spin moment rotates at an angle  $\theta_{\mu_s}^a$  with respect to the  $a$ -axis. The calculations are performed using GGA + SO +  $U_{\text{Ir}}$  +  $J_{\text{H}}$  approach in the zigzag AFM order, and the obtained energies are presented relative to the energy with the moment oriented along the  $a$ -axis. The moments in the Mott insulating zigzag AFM ground state are aligned at an angle with the  $a$ -axis.

collinear behavior with mutual angles that are below  $10^\circ$ . These observations agree with both experimental [44] and theoretical results [120]. The passivated monolayer flake exhibits a similar trend as the bulk [Figure 3.4], although with a greater degree of noncollinearity between the spin and orbital moments, which is approximately  $25^\circ$ .

### 3.4.2 Charge-doped flakes

We now focus on the unpassivated flakes, which can be represented in several ways based on their surface terminations. Moreover, partial passivation enables control over the charge carrier density, which induces intriguing phase transitions. Both electron and hole doping drive the Mott insulator to metal transition and trigger AFM to FM phase transition.

The charge-doped flakes exhibit a reduction in their in-plane lattice parameters, with a more pronounced dependence in the hole-doped flakes [Table 3.6].

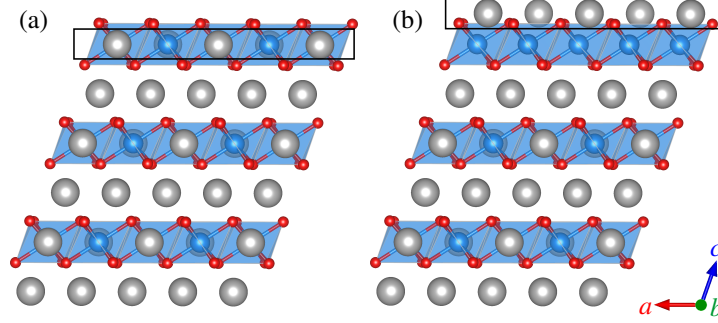


Figure 3.5: In flakes lacking Na<sub>3</sub> termination, the Na-atoms within the adjacent magnetic NaIr<sub>2</sub>O<sub>6</sub> sublayer become volatile and protrude vertically. (a) An illustrative example of a [H–Na<sub>3</sub>] ··· [⊗] trilayer is depicted, with H-atoms in the bottom H–Na<sub>3</sub> layer omitted for clarity. (b) Upon relaxation, the Na-atoms from the top NaIr<sub>2</sub>O<sub>6</sub> layer (highlighted with a rectangular box) experience an out-of-plane displacement of 1.6 Å.

Carrier density affects the structural parameters such as Ir–O bonds, O–Ir–O, and Ir–O–Ir angles. In flakes lacking the Na termination, Na-atoms from the adjacent NaIr<sub>2</sub>O<sub>6</sub> magnetic layer undergo an out-of-plane displacement of 1.6 Å [Figure 3.5], signifying the Na volatility previously observed in experiments [121, 127].

The introduction of charge carriers reveals the emergence of a metallic FM state [Figure 3.6, 3.7], which becomes increasingly stable with higher density, as illustrated in Figure 3.8. However, there is no evidence of magnetism in the high electron-doped [Na<sub>3</sub>|NaIr<sub>2</sub>O<sub>6</sub>|Na<sub>3</sub>] monolayer. The moments are correlated with the carrier density. As the carrier density increases,  $\mu_o$  decreases, and the effect is more prominent for hole doping, which simultaneously suppresses  $\mu_s$  [Figure 3.7, Table 3.7]. Consequently, effective spin-orbit coupling is reduced. At intermediate hole-doping, the lower Hubbard band of  $j_{\text{eff}}=1/2$  is partially filled, leading to a concurrent decrease in both moments. It is important to highlight that in the presence of charge carriers,  $\mu_s$  aligns with the *c*-direction and is collinear with  $\mu_o$ . This behavior differs from what is observed in the bulk and neutral monolayer.

Magnetism in the bilayer and trilayer is intricate [Figure 3.9], with a simultaneous presence of Mott insulating AFM and metallic FM orders in distinct sublayers depending on carrier density. The charge-neutral magnetic NaIr<sub>2</sub>O<sub>6</sub> sublayer re-

Table 3.7: Magnetic properties of doped 1L flakes with different terminations. The negative (positive) sign in  $\delta$  indicates an electron (hole) doped surface. The magnetic ground state transitions to the ferromagnetic phase upon doping. In the doped structures, the spin moment decreases, while the orbital moment shows a significant quenching, especially in the hole-doped system.

|    |                                                | Zigzag AFM                               | FM       | $\delta_{e/h}$ (cm <sup>-2</sup> ) |
|----|------------------------------------------------|------------------------------------------|----------|------------------------------------|
| 1L | [H–Na <sub>3</sub>   ...   Na <sub>3</sub> ]   | $\Delta_{GS}$ (meV/Ir)                   | 1.44     | 0.0                                |
|    |                                                | $\mu_s$ ( $\mu_B$ /Ir)                   | 0.17     | 0.24                               |
|    |                                                | $\mu_o$ ( $\mu_B$ /Ir)                   | 0.24     | 0.28                               |
|    |                                                | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ (°) | 55, 46   | 89, 88                             |
|    | [H–Na <sub>3</sub>   ...   Na <sub>3</sub> –H] | $\Delta_{GS}$ (meV/Ir)                   | 0        | 1.7                                |
|    |                                                | $\mu_s$ ( $\mu_B$ /Ir)                   | 0.28     | 0.39                               |
|    |                                                | $\mu_o$ ( $\mu_B$ /Ir)                   | 0.31     | 0.31                               |
|    |                                                | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ (°) | 74, 49   | 90, 90                             |
|    | [H–Na <sub>3</sub>   ...   ⊗]                  | $\Delta_{GS}$ (meV/Ir)                   | 1.4      | 0.0                                |
|    |                                                | $\mu_s$ ( $\mu_B$ /Ir)                   | 0.07     | 0.14                               |
|    |                                                | $\mu_o$ ( $\mu_B$ /Ir)                   | 0.05     | 0.07                               |
|    |                                                | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ (°) | 36, 137  | 91, 91                             |
|    | [⊗   ...   ⊗]                                  | $\Delta_{GS}$ (meV/Ir)                   | 9.5      | 0.0                                |
|    |                                                | $\mu_s$ ( $\mu_B$ /Ir)                   | 0.24     | 0.23                               |
|    |                                                | $\mu_o$ ( $\mu_B$ /Ir)                   | 0.04     | 0.01                               |
|    |                                                | $\theta_{\mu_s}^a, \theta_{\mu_o}^a$ (°) | 133, 120 | 92, 76                             |

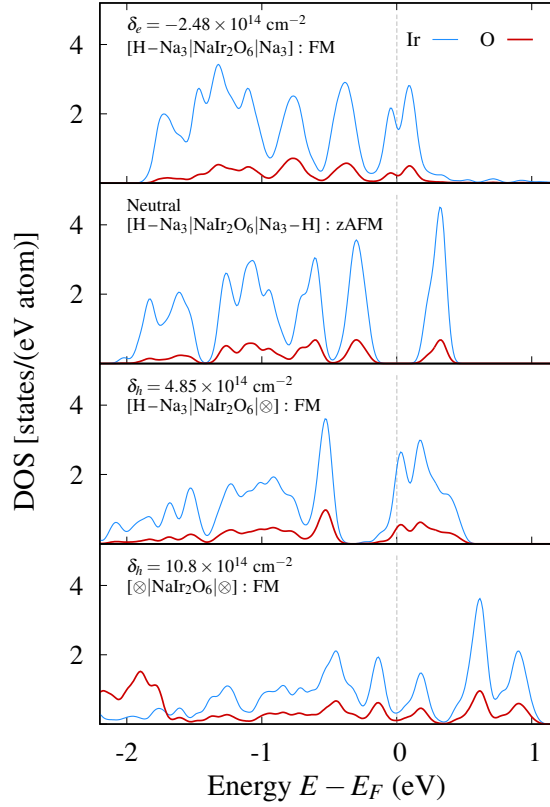


Figure 3.6: We computed the density of states (DOS) for the monolayer with different surface terminations, representing scenarios of electron doping, neutrality, and hole doping. The presence of charge carriers leads to metallic behavior, while the neutral monolayer exhibits relativistic Mott insulator characteristics.

mains in an AFM Mott insulating state but transitions to a metallic FM state with the addition of extra electrons or holes [Figure 3.10, 3.11]. For example, the passivated bilayer  $[H-Na_3|\cdots|Na_3-H]$  exhibits a Mott insulating behavior, whereas a metallic FM|FM state arises when both sides of the bilayer are terminated with or without the Na<sub>3</sub>-layers, corresponding to electron and hole doping, respectively [Figure. 3.10]. Similarly, in bilayers with a passivated Na<sub>3</sub>-H layer on one side and carrier doping on the other, the systems stabilize in AFM|FM phase [Figure 3.10]. Consistent observations are made in the trilayers with various terminations. Trilayers with and without Na<sub>3</sub>-layers on both sides, representing electron-doped  $[Na_3|\cdots|Na_3]$  and hole-doped  $[\otimes|\cdots|\otimes]$ , give rise to a [FM|AFM|FM] magnetic configuration [Figure 3.11]. Comprehensive details of the magnetic properties of

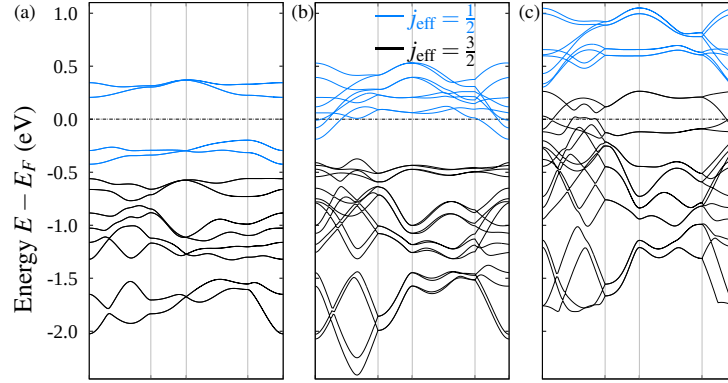


Figure 3.7:  $j_{\text{eff}} = 3/2$  and  $j_{\text{eff}} = 1/2$  resolved band structures of (a) Passivated monolayer  $[\text{H}-\text{Na}_3|\cdots|\text{Na}_3-\text{H}]$ , (b) Partially-hole doped monolayer  $[\text{H}-\text{Na}_3|\cdots|\otimes]$  and (c) Fully-hole doped monolayer  $[\otimes|\cdots|\otimes]$  Intermediate hole doping transitions  $\text{Ir}-d^5$  states towards  $\text{Ir}-d^{5-\delta}$  (where  $\delta < 1$ ). For instance, in the hole-doped monolayer, the  $j_{\text{eff}} = 1/2$  state remains partially occupied rather than completely empty. Conversely, in the case of extreme hole doping, the  $j_{\text{eff}} = 1/2$  state becomes completely empty, while the  $j_{\text{eff}} = 3/2$  state is partially unoccupied.

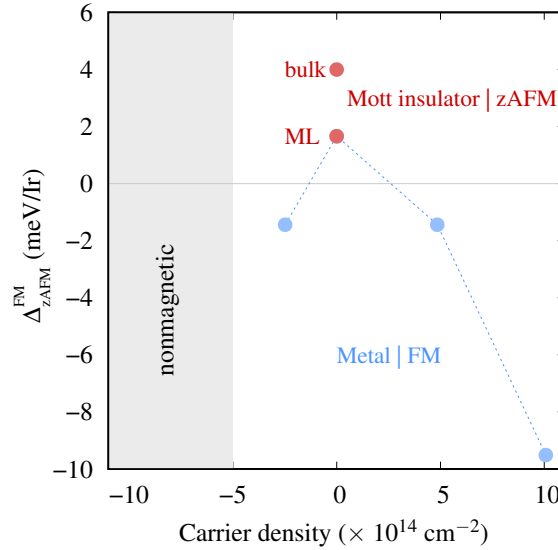


Figure 3.8: Variation of carrier density leads to changes in the relative energy  $\Delta_{\text{ZAFM}}^{\text{FM}}$  between the FM and the zigzag AFM phases. The monolayer undergoes electronic and magnetic phase transitions under the influence of charge carriers. These structures correspond to those depicted in Figure 3.6.

bilayers and trilayers are provided in Tables 3.8 and 3.9.

Naturally carrier-doped multilayer flakes hold promise for diverse applications in spin-based devices, including magnetic tunnel junctions, magnetic sensors, spin filters, valves, and memory devices. However, it is crucial to highlight that devices



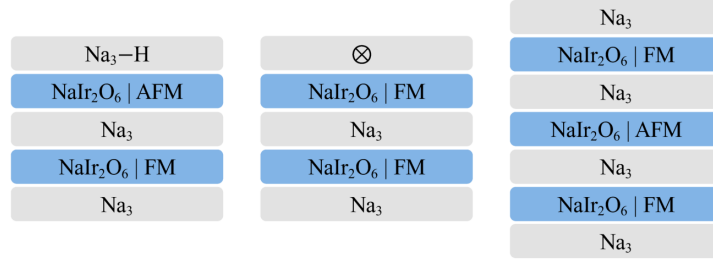


Figure 3.9: Magnetic ordering in the  $\text{NaIr}_2\text{O}_6$  sublayers is dictated by the adjacent termination layer,  $\text{Na}_3$ , passivated  $\text{Na}_3\text{—H}$  or the absence of  $\text{Na}_3$ -layer denoted by  $\otimes$ . These termination layers correspond to the electron-doped, neutral, and hole-doped magnetic  $\text{NaIr}_2\text{O}_6$  sublayers, respectively. We studied all possible terminations, the schematic illustrates a selection of them. The bilayer  $[\text{H—Na}_3|\cdots|\text{Na}_3]$  exhibits an AFM|FM arrangement, whereas the bilayer  $[\otimes|\cdots|\text{Na}_3]$  demonstrates FM|FM ordering. The trilayer  $[\text{Na}_3|\cdots|\text{Na}_3]$  displays a FM|AFM|FM configuration. The corresponding density of states are presented in Figures 3.10 and 3.11.

integrating  $\text{Na}_2\text{IrO}_3$  flakes will be limited to operation exclusively at cryogenic temperatures. Therefore, future research should emphasise the exploration of new materials capable of producing ultrathin flakes that can maintain such electronic and magnetic features at elevated temperatures, in pursuit of practical applications.

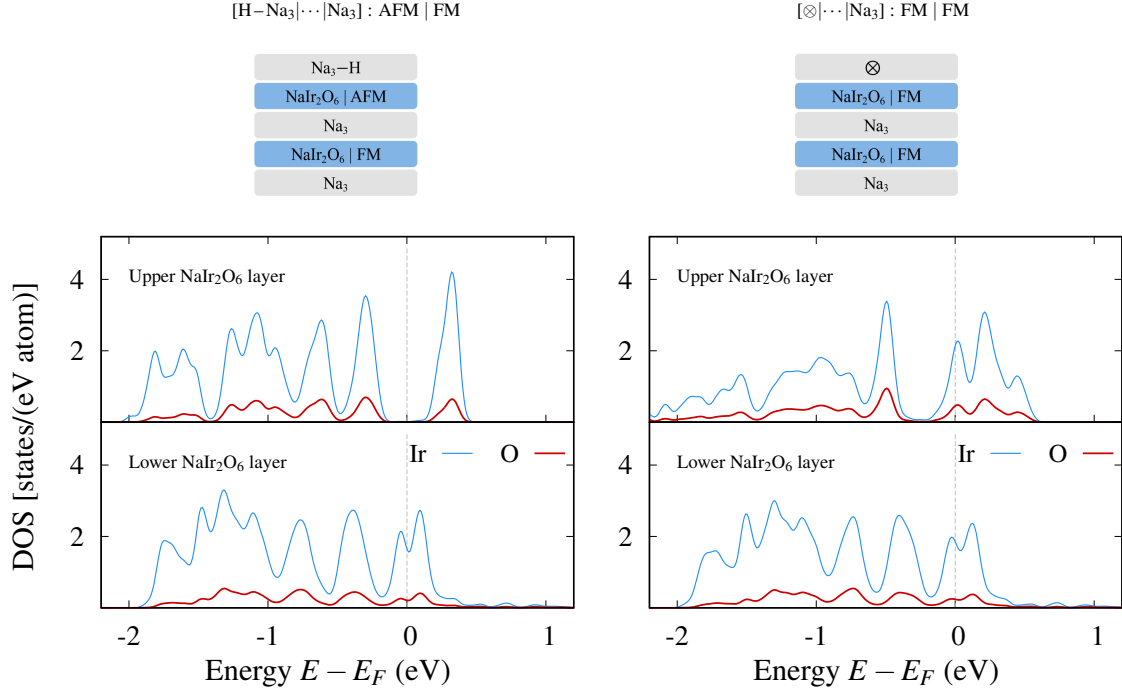


Figure 3.10: Density of states for the  $[\text{H}-\text{Na}_3] \cdots [\text{Na}_3]$  (left) and  $[\otimes] \cdots [\text{Na}_3]$  (right) bi-layers. The passivated  $\text{H}-\text{Na}_3$  terminations signify charge neutrality in the neighboring  $\text{NaIr}_2\text{O}_6$  sublayer, which remains a Mott-insulator. The presence (absence) of  $\text{Na}_3$  termination results in electron (hole) doping in the adjacent  $\text{NaIr}_2\text{O}_6$  sublayer, leading to metallic FM phase. Absence of  $\text{Na}_3$  is denoted by  $\otimes$ . The magnetic properties are listed in Table 3.8

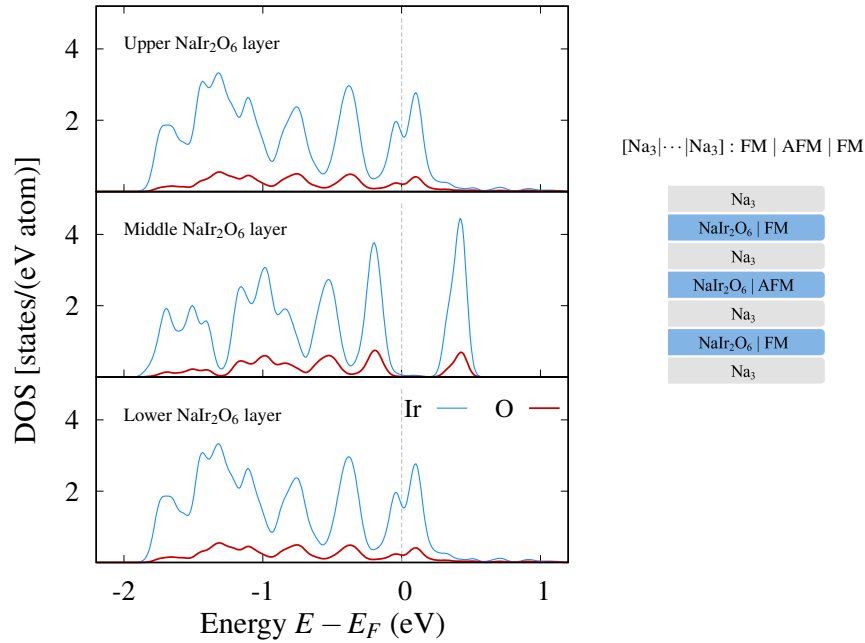


Figure 3.11: The density of states for the trilayer  $[\text{Na}_3] \cdots [\text{Na}_3]$  is displayed. The charge carrier-induced magnetic and electronic phase transitions are observed in the  $\text{NaIr}_2\text{O}_6$  sub-layers at the surface. The middle layer maintains the AFM Mott insulating state. The magnetic properties are listed in Table 3.9

Table 3.8: Magnetic properties of doped 2L flakes for all possible terminations. For example, [Na<sub>3</sub>|...|Na<sub>3</sub>] represents the [Na<sub>3</sub>|NaIr<sub>2</sub>O<sub>6</sub>|Na<sub>3</sub>|NaIr<sub>2</sub>O<sub>6</sub>|Na<sub>3</sub>] flake. As the moments and angles vary with the adjacent termination, they are quoted in the same sequence as the flake.  $\Delta_{\text{GS}}$  is in meV/Ir,  $\mu_s$  and  $\mu_o$  are in  $\mu_B/\text{Ir}$  and angles  $\theta_{\mu_s}^a$  and  $\theta_{\mu_o}^a$  are in degrees ( $^\circ$ )

|    |                                             | GS                   | Zigzag AFM | $\delta_{e/h}$ (cm <sup>-2</sup> ) |
|----|---------------------------------------------|----------------------|------------|------------------------------------|
| 2L | [Na <sub>3</sub>  ... Na <sub>3</sub> ]     | FM FM                | —          |                                    |
|    |                                             | $\Delta_{\text{GS}}$ | 0.0        | 1.4                                |
|    |                                             | $\mu_s$              | 0.25, 0.25 | 0.15, 0.15                         |
|    |                                             | $\mu_o$              | 0.29, 0.29 | 0.24, 0.24                         |
|    |                                             | $\theta_{\mu_s}^a$   | 82, 82     | 53, 53                             |
|    |                                             | $\theta_{\mu_o}^a$   | 80, 80     | 44, 44                             |
|    | [H—Na <sub>3</sub>  ... Na <sub>3</sub> ]   | AFM FM               | —          |                                    |
|    |                                             | $\Delta_{\text{GS}}$ | 0.0        | 0.7                                |
|    |                                             | $\mu_s$              | 0.28, 0.23 | 0.28, 0.12                         |
|    |                                             | $\mu_o$              | 0.32, 0.27 | 0.32, 0.23                         |
|    |                                             | $\theta_{\mu_s}^a$   | 74, 83     | 74, 55                             |
|    |                                             | $\theta_{\mu_o}^a$   | 50, 79     | 51, 41                             |
|    | [H—Na <sub>3</sub>  ... Na <sub>3</sub> —H] | AFM AFM              | —          |                                    |
|    |                                             | $\Delta_{\text{GS}}$ | 0.0        | —                                  |
|    |                                             | $\mu_s$              | 0.28, 0.28 |                                    |
|    |                                             | $\mu_o$              | 0.32, 0.32 | Neutral                            |
|    |                                             | $\theta_{\mu_s}^a$   | 73, 73     |                                    |
|    |                                             | $\theta_{\mu_o}^a$   | 50, 50     |                                    |
|    | [H—Na <sub>3</sub>  ... ⊗]                  | AFM FM               | —          |                                    |
|    |                                             | $\Delta_{\text{GS}}$ | 0.0        | 0.5                                |
|    |                                             | $\mu_s$              | 0.29, 0.16 | 0.28, 0.17                         |
|    |                                             | $\mu_o$              | 0.30, 0.07 | 0.30, 0.07                         |
|    |                                             | $\theta_{\mu_s}^a$   | 78, 88     | 78, 105                            |
|    |                                             | $\theta_{\mu_o}^a$   | 51, 88     | 50, 68                             |
|    | [⊗ ... ⊗]                                   | FM FM                |            |                                    |
|    |                                             | $\Delta_{\text{GS}}$ | 0.0        | 1.0                                |
|    |                                             | $\mu_s$              | 0.11, 0.11 | 0.09, 0.09                         |
|    |                                             | $\mu_o$              | 0.07, 0.07 | 0.05, 0.05                         |
|    |                                             | $\theta_{\mu_s}^a$   | 92, 92     | 90, 90                             |
|    |                                             | $\theta_{\mu_o}^a$   | 115, 115   | 98, 98                             |

Table 3.9: Magnetic properties of the doped 3L flakes with all possible terminations. A similar convention is followed as in 2L flakes.  $\Delta_{\text{GS}}$  is in meV/Ir,  $\mu_s$  and  $\mu_o$  are in  $\mu_B/\text{Ir}$  and angles  $\theta_{\mu_s}^a$  and  $\theta_{\mu_o}^a$  are in degrees ( $^\circ$ )

|    |                                                          | GS                   | Zigzag AFM       | $\delta_{e/h} (\text{cm}^{-2})$ |
|----|----------------------------------------------------------|----------------------|------------------|---------------------------------|
|    |                                                          | FM AFM FM            | —                |                                 |
| 3L | $[\text{Na}_3   \cdots   \text{Na}_3]$                   | $\Delta_{\text{GS}}$ | 0.0              | 0.5                             |
|    |                                                          | $\mu_s$              | 0.25, 0.30, 0.25 | 0.15, 0.30, 0.15                |
|    |                                                          | $\mu_o$              | 0.29, 0.33, 0.29 | 0.23, 0.33, 0.23                |
|    |                                                          | $\theta_{\mu_s}^a$   | 80, 75, 80       | 55, 75, 55                      |
|    |                                                          | $\theta_{\mu_o}^a$   | 78, 55, 78       | 45, 55, 45                      |
|    |                                                          |                      |                  | $-2.44 \times 10^{14}$          |
|    | $[\text{H}-\text{Na}_3   \cdots   \text{Na}_3]$          | AFM AFM FM           | —                |                                 |
|    |                                                          | $\Delta_{\text{GS}}$ | 0.0              | 0.4                             |
|    |                                                          | $\mu_s$              | 0.28, 0.29, 0.23 | 0.28, 0.29, 0.13                |
|    |                                                          | $\mu_o$              | 0.32, 0.32, 0.27 | 0.32, 0.32, 0.23                |
|    |                                                          | $\theta_{\mu_s}^a$   | 73, 73, 83       | 73, 74, 54                      |
|    |                                                          | $\theta_{\mu_o}^a$   | 51, 52, 80       | 51, 52, 42                      |
|    | $[\text{H}-\text{Na}_3   \cdots   \text{Na}_3-\text{H}]$ | AFM AFM AFM          | —                |                                 |
|    |                                                          | $\Delta_{\text{GS}}$ | 0.0              | —                               |
|    |                                                          | $\mu_s$              | 0.28, 0.28, 0.28 |                                 |
|    |                                                          | $\mu_o$              | 0.32, 0.32, 0.32 | Neutral                         |
|    |                                                          | $\theta_{\mu_s}^a$   | 73, 73, 73       |                                 |
|    |                                                          | $\theta_{\mu_o}^a$   | 51, 51, 51       |                                 |
|    | $[\text{H}-\text{Na}_3   \cdots   \otimes]$              | AFM AFM FM           | —                |                                 |
|    |                                                          | $\Delta_{\text{GS}}$ | 0.0              | 0.2                             |
|    |                                                          | $\mu_s$              | 0.28, 0.29, 0.14 | 0.28, 0.29, 0.10                |
|    |                                                          | $\mu_o$              | 0.33, 0.33, 0.08 | 0.33, 0.33, 0.04                |
|    |                                                          | $\theta_{\mu_s}^a$   | 71, 73, 88       | 71, 73, 65                      |
|    |                                                          | $\theta_{\mu_o}^a$   | 51, 53, 88       | 51, 54, 105                     |
|    | $[\otimes   \cdots   \otimes]$                           | FM AFM FM            | —                |                                 |
|    |                                                          | $\Delta_{\text{GS}}$ | 0.0              | 0.5                             |
|    |                                                          | $\mu_s$              | 0.13, 0.28, 0.13 | 0.02, 0.29, 0.02                |
|    |                                                          | $\mu_o$              | 0.07, 0.35, 0.07 | 0.01, 0.35, 0.01                |
|    |                                                          | $\theta_{\mu_s}^a$   | 90, 72, 90       | 50, 72, 50                      |
|    |                                                          | $\theta_{\mu_o}^a$   | 89, 55, 89       | 116, 55, 116                    |

### 3.5 Extended Heisenberg-Kitaev model

Significant lattice distortion away from the ideal cubic octahedral environment renders conventional Heisenberg exchange, and a pure Kitaev Hamiltonian is inadequate to describe the physics. Instead, an extended Heisenberg-Kitaev (HK) model is appropriate for describing magnetism in spin-liquid candidate materials [46–48, 92, 93]. Many variants of the HK model have been assumed in the literature; we consider a minimal HK Hamiltonian of the form,

$$H = \sum_{\langle ij \rangle \in \alpha\beta(\gamma)} \left[ J_1 \mathbf{S}_i \cdot \mathbf{S}_j + K S_i^\gamma S_j^\gamma + \Gamma \left( S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha \right) \right] + \sum_{\langle\langle ij \rangle\rangle} J_3 \mathbf{S}_i \cdot \mathbf{S}_j,$$

where  $J_1$  and  $J_3$  are the first and third neighbour Heisenberg interactions,  $K$  is Kitaev exchange and  $\Gamma$  is the symmetric off-diagonal exchange.  $\mathbf{S}$  are the Ir<sup>4+</sup> Kramers doublet pseudospin ( $J_{\text{eff}} = 1/2$ ). Other symmetric off-diagonal exchange can also be considered and has the form,  $\Gamma' \left( S_i^\beta S_j^\gamma + S_i^\gamma S_j^\beta + S_i^\gamma S_j^\alpha + S_i^\alpha S_j^\gamma \right)$ .  $\{\alpha, \beta, \gamma\} = \{x, y, z\}$  are three nearest-neighbour bonds [Figure 3.2(d)]. The non-Kitaev terms in the Hamiltonian trigger a phase transition at 15 K to a zigzag AFM state [94, 103, 104]. Stronger  $J_1, J_3, \Gamma$  and  $\Gamma'$  will drive the system further away from the quantum spin liquid state. Therefore, exploring the evolution of exchange interactions from bulk Na<sub>2</sub>IrO<sub>3</sub> to a single layer of spin-orbit coupled correlated electrons is intriguing.

We determine the parameters of the HK Hamiltonian using the four-state method [Table 3.10] [28, 79]. The Kitaev interaction in bulk Na<sub>2</sub>IrO<sub>3</sub> is ferromagnetic and serves as the dominant energy scale, whereas the nearest-neighbor  $J_1$  interaction is antiferromagnetic and notably weaker,  $|J_1| \ll K$  [Table 3.10]. These results are consistent with *ab initio* calculations [48, 79, 128, 129] and the exchange interactions extracted from the experimental data [93, 116]. Moreover, anisotropy in the magnetic

Table 3.10: Heisenberg exchange couplings ( $J_1$  and  $J_3$ ), off-diagonal exchanges ( $\Gamma$  and  $\Gamma'$ ), and Kitaev interaction in meV were calculated for bulk Na<sub>2</sub>IrO<sub>3</sub>, passivated charge neutral monolayer, ML: [H–Na<sub>3</sub>|NaIr<sub>2</sub>O<sub>6</sub>|Na<sub>3</sub>–H], and hole-doped monolayer, h-ML: [ $\otimes$ |NaIr<sub>2</sub>O<sub>6</sub>| $\otimes$ ]. The calculated Néel temperature  $T_N$  for the bulk exhibits excellent agreement with experimental data, [94, 103, 104] confirming the accuracy of the calculations. Remarkably, while the zAFM magnetism strengthens in the charge-neutral monolayer, a magnetic phase transition occurs in the case of hole-doping.

|      |      | $J_1$  | $K$    | $\Gamma$ | $\Gamma'$ | $J_3$ | $T_{N/C}$ |
|------|------|--------|--------|----------|-----------|-------|-----------|
| Bulk | zAFM | 7.22   | –31.26 | 3.52     | –3.24     | 3.56  | 18 K      |
| ML   | zAFM | 6.96   | –29.50 | 10.00    | –5.96     | 6.14  | 32 K      |
| h-ML | FM   | –12.56 | 1.82   | 0.21     | –0.50     | –2.79 | 29 K      |

susceptibility suggests the presence of symmetric off-diagonal exchange, [48, 94] and fitting with experimental data indicates a non-negligible contribution when  $K \gg |J_1|$ . In the case of bulk Na<sub>2</sub>IrO<sub>3</sub>, we have determined the ratio of  $\Gamma / (3J_1 + K)$  to be approximately  $-0.37$ , in good agreement with the previously predicted value of  $-0.3$  [48]. The stabilization of the zigzag AFM phase in honeycomb iridates has been attributed to the third-neighbour Heisenberg exchange  $J_3$ , arising from an inversion centre and finite M–L–L–M hopping in the system [102, 116, 129]. Like  $J_1$ , we observe  $J_3$  to be sizeable and antiferromagnetic, with  $J_3 \sim \Gamma$  and  $J_3 / J_1 \sim 0.5$ . Furthermore, we computed the off-diagonal exchange  $\Gamma'$ , which is ferromagnetic unlike  $\Gamma$ , but comparable in strength,  $|\Gamma'| \sim |\Gamma|$ . Hence, despite having a significant Kitaev interaction, the bulk Na<sub>2</sub>IrO<sub>3</sub> orders in the zigzag AFM phase, driven by the considerable AFM Heisenberg exchanges  $J_1$ ,  $J_3$ , as well as the off-diagonal exchanges  $\Gamma$  and  $\Gamma'$  [Table 3.10]. The corresponding  $T_N$  is determined through Heisenberg-Kitaev Monte Carlo simulations involving  $10^4$  spins and utilizing the parameters from Table 3.10, yielding excellent agreement with the experimental data [94, 103, 104].

The passivated monolayer maintains electronic equivalence to the bulk and retains its spin-orbit coupled Mott insulating nature. Nevertheless, the HK inter-

action parameters exhibit intriguing characteristics in monolayer due to specific structural alterations. Proceeding from the bulk to monolayer, the nature of interactions remains unaltered, FM  $K$  and  $\Gamma'$ ; while  $J_1$ ,  $J_3$  and  $\Gamma$  are AFM [Table 3.10]. The magnitudes of Kitaev  $K$  and Heisenberg  $J_1$  remain consistent [Table 3.10]. In contrast, the symmetric off-diagonal interactions  $\Gamma, \Gamma'$  and third neighbour  $J_3$  notably escalate in the passivated monolayer, resulting in  $|K/J_1| \sim 4.2$ ,  $J_3/J_1 \sim 0.9$ , and  $|\Gamma| > |J_3| \sim |\Gamma'|$ .  $\Gamma$  and  $\Gamma'$  are determined by competing metal-metal, ligand-assisted, and distortion-mediated hopping processes [102]. In Na<sub>2</sub>IrO<sub>3</sub>, where ligand-assisted hopping predominates, [128] a simultaneous increase in the Ir–O–Ir angle and trigonal distortion, as measured by the O–Ir–O angle [Table 3.6], in the monolayer contributes to the enhanced strength of  $\Gamma$  and  $\Gamma'$ . As a result, the monolayer exhibits a pronounced stabilization of the zigzag AFM phase, as evidenced by a substantial rise in  $T_N$  [Table 3.10]. The complex magnetism described here contrasts with that of non-Kitaev 2D magnets [24]. Analogously, a recent study on RuCl<sub>3</sub> has showcased an enhancement in off-diagonal exchanges through lattice distortion [130].

A microscopic analysis of the magnetic phase transition reveals an intriguing picture in the hole-doped metallic flake [Table 3.10]. Contrary to the charge-neutral flakes and bulk material, the Heisenberg interactions become ferromagnetic and dominate over the antiferromagnetic Kitaev interaction, where  $K \ll |J_1|$ . Hole-doping quenches the orbital moment, leading to a significant decrease in spin-orbit coupling [Table 3.7]. Consequently, both the Kitaev and off-diagonal interactions experience substantial reductions [Table 3.10], while the ferromagnetic  $J_1$  and  $J_3$ , with  $|K/J_1| \sim 0.14$  and  $J_3/J_1 \sim 0.22$ , govern the physics. The corresponding Curie temperature  $T_C$  is relatively high at 29 K.

The preceding discussion suggests that quantum electron confinement does not alter the Mott-insulating electronic or zigzag AFM magnetic state. However,

the two-dimensional nature of the flakes induces structural distortions that significantly influence the microscopic magnetic interaction parameters [Table 3.10]. Electronic and magnetic phase transitions in carrier-doped flakes are primarily driven by doping and lattice distortions rather than electron confinement.

### 3.6 Summary

We rigorously explore magnetism in ultrathin flakes of correlated oxide Na<sub>2</sub>IrO<sub>3</sub>, considering its proximity to a quantum spin-liquid state in bulk. Remarkably, magnetism persists even at the monolayer limit, with heightened Heisenberg and off-diagonal exchange interactions robustly reinforcing the zigzag AFM state. Enhanced magnetism in the two-dimensional limit contrasts with the conventional trend observed in van der Waals magnets. Passivated flakes retain their Mott insulator characteristic, while naturally carrier-doped flakes undergo an insulator-to-metal transition. This electronic transition is also accompanied by an antiferromagnetic to ferromagnetic transition. Hence, multilayer flakes show potential as low-temperature spin devices. These findings open avenues for comprehending and harnessing two-dimensional magnetism in non-van der Waals correlated oxides and underscore the importance of experimental evaluation for both magnetism and device applications.





## CHAPTER 4

### HIGH TEMPERATURE ANTIFERROMAGNETISM IN ULTRATHIN $\text{SrRu}_2\text{O}_6$ NANO-SHEETS

The quest for room-temperature nanoscale magnets remains a central challenge, driven by their promising applications in quantum technologies. Layered  $4d$  and  $5d$  transition metal oxides with high magnetic ordering temperatures offer significant potential in this context. We explore ultrathin  $\text{SrRu}_2\text{O}_6$  nanosheets using first-principles calculations, complemented by the classical Heisenberg Monte Carlo simulations. Remarkably, these nanosheets exhibit robust antiferromagnetic ordering with Néel temperatures exceeding 430 K, despite the enhanced spin fluctuations characteristic of two-dimensional systems. Surface-termination-induced intrinsic charge doping introduces complexity to the magnetism, resulting in an insulator-to-metal transition and renormalized Néel temperatures in doped systems. A detailed microscopic analysis reveals distinct mechanisms underlying the magnetic behavior in electron- and hole-doped nanosheets. These findings provide a foundation for advancing theoretical and experimental studies in the largely unexplored realm of correlated oxides at the two-dimensional limit. This work has appeared in [Physical Review B 111, 134409 \(2025\)](#)

## 4.1 Introduction

Ruthenates present a rich platform for exploring exotic physics owing to the intricate interplay between competing electronic correlations, spin-orbit (SO) coupling and the dispersion of Ru-4d orbitals, which governs the electron kinetic energy. The Ruddlesden-Popper series of ruthenate perovskites  $(\text{Ca/Sr})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ , display a diverse range of intriguing phenomena [131, 132]. For instance,  $\text{Sr}_2\text{RuO}_4$  ( $n = 1$ ) is among the first non-copper-based materials to exhibit triplet superconductivity, though its classification remains debated [133–136]. In the  $n = 2$  phase,  $\text{Sr}_3\text{Ru}_2\text{O}_7$  exhibits borderline ferromagnetism (FM) with non-Fermi liquid characteristics, while  $\text{Ca}_3\text{Ru}_2\text{O}_7$  is a metallic A-type antiferromagnet (AFM) over a narrow temperature range [137–142]. At low temperatures,  $\text{Sr}_4\text{Ru}_3\text{O}_{10}$  ( $n = 3$ ) features a unique FM configuration with alternating in-plane and out-of-plane Ru-spin orientations [143, 144]. The infinite-layer  $\text{SrRuO}_3$  ( $n = \infty$ ) is an itinerant ferromagnet with intriguing transport properties, transitioning from a Fermi liquid state at low temperatures to a bad metal state at higher temperatures [145–147]. In the realm of exotic quantum phases,  $\alpha\text{-RuCl}_3$  exhibits behaviour characteristic of a proximate Kitaev spin liquid, featuring fractional excitations [148–151].

While most ruthenates exhibit the  $\text{Ru}^{4+}$  oxidation state, the  $\text{Ru}^{5+}$  oxides reveal intriguing properties. For example,  $\text{SrRu}_2\text{O}_6$  is an antiferromagnet with an exceptionally high Néel temperature,  $T_N \sim 560$  K [61, 62, 152, 153]. Unlike the cubic lattice and corner-sharing  $\text{RuO}_6$  octahedra in perovskites,  $\text{SrRu}_2\text{O}_6$  adopts a structure with edge-shared octahedra arranged in a honeycomb Ru lattice. This configuration features dual Ru–O–Ru superexchange pathways and a  $\text{Ru}^{5+}\text{-}4d^3$  electronic configuration. Such high-temperature antiferromagnets are rare in compounds lacking 3d transition elements, with notable exceptions such as  $\text{SrTcO}_3$ ,  $\text{CaTcO}_3$ , and  $\text{NaOsO}_3$  [154–156]. Compared to these perovskites,  $\text{SrRu}_2\text{O}_6$  is distinctive due

to its quasi-two-dimensional magnetic structure, where magnetic Ru<sub>2</sub>O<sub>6</sub> sheets are separated by Sr layers along the perpendicular direction. Despite weak interlayer coupling, neglected in some theoretical studies, [61, 157] the material exhibits an unexpectedly high ordering temperature. Another remarkable feature is its reduced magnetic moment of about  $1.4\mu_B$ , [61, 62] significantly smaller than the expected  $3\mu_B$  for a half-filled  $t_{2g}$  configuration. This reduction is attributed to strong covalency between Ru- $d$  and O- $p$  orbitals. Furthermore, while SrRu<sub>2</sub>O<sub>6</sub> is classified as a band insulator, the underlying transport mechanism and the role of defects remain subjects of ongoing debate [157–161].

Contrary to the electronic structure, the magnetic properties of bulk SrRu<sub>2</sub>O<sub>6</sub> are well characterized [61, 62, 152, 153]. However, an intriguing question arises regarding the evolution of its high-temperature magnetism as the material is thinned to the monolayer limit, particularly in light of the growing interest in two-dimensional (2D) magnetism. It would be fascinating to determine whether high-temperature antiferromagnetism persists in the 2D regime. The recent hydrothermal synthesis of ultrathin SrRu<sub>2</sub>O<sub>6</sub> flakes has sparked further interest in exploring the magnetic properties of 4d oxides in their 2D form. The exfoliation of chemically bonded compounds is challenging and rarely achieved, [56–59] unlike the van der Waals (vdW) materials. While most non-vdW metal-oxide magnets consist of 3d transition metals, [57–59] 2D ruthenates are particularly intriguing due to the complex interplay between electron correlations, SO coupling, and electronic bandwidth. Moreover, the surfaces of non-vdW oxides often undergo reconstruction due to the presence of dangling bonds, which can significantly impact their properties. The nature of the surface termination can disrupt charge neutrality, leading to inherent carrier doping. This combination of surface reconstruction and natural doping introduces additional layers of complexity that can be further exploited to realize novel properties [162]. In this study, we investigate the evolution of mag-

netism in  $\text{SrRu}_2\text{O}_6$  as the layer thickness is reduced to the 2D limit and examine the impact of carrier doping on its magnetic properties.

From a technological perspective, antiferromagnetic spintronics offers significant advantages over traditional ferromagnetic systems [163–165]. The absence of stray fields, ultrafast spin dynamics, and the potential for electrical manipulation render AFM materials highly promising for next-generation technologies. In this context, 2D materials and their heterostructures provide an ideal platform for exploring novel magnetic properties. While ferromagnetic 2D materials have garnered significant attention, antiferromagnetic 2D materials have not elicited the same level of excitement [166–169]. Nonetheless, the technological relevance of 2D magnetism hinges on achieving magnetic order above room temperature, a challenge that has proven difficult to overcome [170–172]. In this context, ultrathin oxide flakes that exhibit high-temperature antiferromagnetism in their bulk form present significant potential. This study explores the microscopic magnetic exchange interactions and demonstrates that ultrathin  $\text{SrRu}_2\text{O}_6$  flakes retain room-temperature antiferromagnetism. This finding paves the way for further experimental investigations and potential applications.

## 4.2 Methodology

First-principles calculations are conducted using density functional theory, [25, 26] as implemented in the Vienna *ab initio* simulation package [106, 173, 174]. The wave functions are represented using the projector-augmented wave formalism, [107] with a plane-wave basis set energy cut-off of 600 eV. The exchange-correlation energy is treated using the Perdew-Burke-Ernzerhof functional [68]. Unless otherwise specified, all results incorporate SO coupling in the calculations. To make a comparison, select calculations are also performed with the range-

separated Heyd-Scuseria-rnzerhof (HSE06) hybrid functional [71] and the recently developed  $r^2$ -SCAN meta-GGA functional [76]. The bulk SrRu<sub>2</sub>O<sub>6</sub> is modelled using a  $1 \times 2 \times 2$  supercell to capture different magnetic configurations, including antiferromagnetic interlayer coupling. This approach allows for a comprehensive analysis of the magnetic interactions. For ultrathin nanosheets, a vacuum space of 20 Å is incorporated to minimize interactions between periodic images. A  $\Gamma$ -centered  $8 \times 4 \times 4$  Monkhorst-Pack  $k$ -mesh is employed for the bulk calculations, [108] while a finer  $10 \times 5 \times 1$   $k$ -mesh is utilized for the ultrathin nanosheets to ensure accurate sampling of the Brillouin zone in both cases. Although the Hubbard-type on-site Coulomb interaction  $U$  is not explicitly included in our primary calculations to describe the Ru-4*d* electrons, selected computations are repeated with  $U_{\text{Ru}} \leq 1.8$  eV to assess its potential effects [70]. The lattice parameters and ionic positions for both the bulk and nanosheets, across various magnetic configurations, are optimized until all force components are reduced below a threshold of 0.01 eV/Å. Although ultrathin flakes have been experimentally synthesized, we assess their dynamic stability by calculating the phonon band structure using the finite difference method. Larger  $2 \times 4 \times 1$  supercells are employed, and the force constants are derived using the Phonopy code [109]. A stricter convergence criterion with force components reduced below 0.001 eV/Å, along with an increased kinetic energy cut-off of 700 eV, is employed for phonon calculations. The magnetism is modelled using the classical Heisenberg Hamiltonian, with exchange parameters derived from first-principles calculations. Magnetic ordering temperatures are determined via Monte Carlo simulations using the Vampire Code, [175] where over  $10^4$  spins are included to minimize finite-size effects. At each temperature,  $1.5 \times 10^6$  Monte Carlo steps are employed to ensure thermal equilibrium.

## 4.3 Results and Discussion

We start by analyzing the bulk properties of SrRu<sub>2</sub>O<sub>6</sub>, comparing the results with both experimental data and previous theoretical results. Subsequently, we employ the same theoretical framework to explore ultrathin flakes and investigate the effect of charge carrier doping.

### 4.3.1 Insulating AFM bulk

Bulk SrRu<sub>2</sub>O<sub>6</sub> crystallizes in the trigonal  $P\bar{3}1m$  phase, with calculated parameters of  $a = 5.31$  Å, and  $c = 5.20$  Å, which are in good agreement with experimental data [61, 62]. The crystal structure consists of quasi-2D layers of edge-sharing RuO<sub>6</sub> octahedra, forming a honeycomb Ru-lattice in the  $ab$ -plane. These magnetic layers are stacked along the  $c$ -axis, separated by alternating Sr layers.

The electronic structure of bulk SrRu<sub>2</sub>O<sub>6</sub> remains widely debated and is not the primary focus of this study. Using the PBE-GGA exchange-correlation functional, [68] the non-magnetic bulk SrRu<sub>2</sub>O<sub>6</sub> reveals a small band gap of 40 meV at the Fermi level, indicating a normal insulating state [Figure 4.1(a)]. Upon introducing magnetism, the band gap increases with the Ru magnetic moment, [158] reaching 0.41 eV [Figure 4.1(b)]. The overall electronic structure remains largely unchanged as SO coupling is introduced, though the energy gap is slightly reduced by 30 meV [Figure 4.1(c)], corroborating earlier calculations [158, 159, 176]. Calculations were repeated with an added Hubbard correlation  $U_{\text{Ru}}$  between 1.3 and 1.8 eV, resulting in a significantly larger gap, ranging from 0.86 to 1.03 eV. Additionally, advanced exchange-correlation functionals like  $r^2$ SCAN meta-GGA [76] and hybrid HSE functionals [71] produced higher gaps of 0.87 eV and 2.5 eV, respectively. This behaviour aligns with that of a band insulator, where an existing

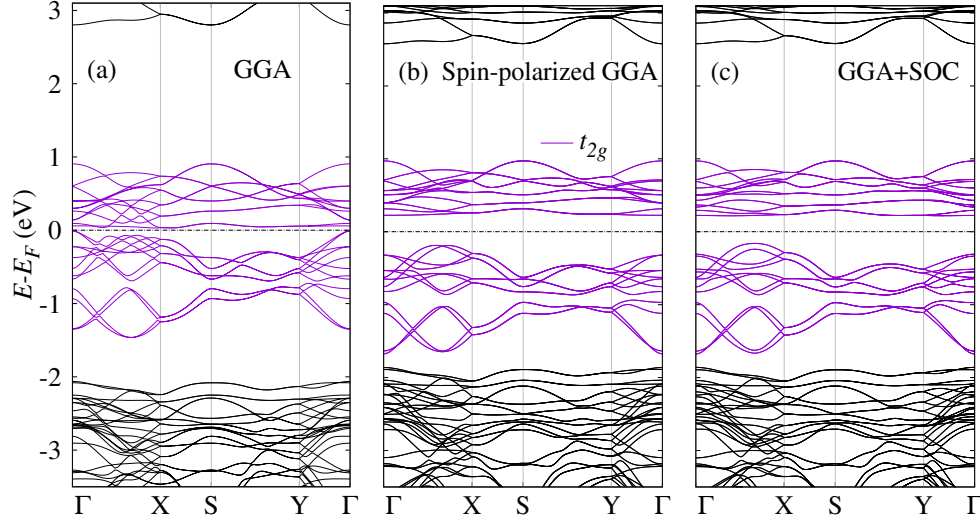


Figure 4.1: The electronic band structure of bulk SrRu<sub>2</sub>O<sub>6</sub> at various theoretical hierarchy reveals key features. The trigonal structural distortion splits the  $t_{2g}$  manifold into an  $a_{1g}$  singlet and  $e'_g$  doublets. A non-magnetic gap of 40 meV, as shown in (a), indicates the band-insulating nature. (b) When magnetism is incorporated, the gap increases, but SO coupling has a negligible effect, as demonstrated in (c). The unoccupied  $e_g$  bands appear approximately 2.5 eV above the Fermi level.

non-magnetic gap is enhanced by magnetism, electron correlation, and relativistic effects. However, resistivity measurements in the high-temperature range indicate an activated gap of 36 meV, significantly smaller than the theoretical gap predicted in this study and in previous reports [61, 62, 158–160, 176]. The electron transport mechanism over a wide temperature range remains unclear, but it is suggested that the unusually small energy gap may arise from disorder-induced localized states in experimental samples. Further theoretical and experimental investigations are necessary to resolve this discrepancy.

The nominal valence of Ru<sup>5+</sup> in a large octahedral crystal field,  $\Delta_{OC} \sim 3$  eV, leads to half-filled  $4d-t_{2g}^3$  orbitals, which exhibit a broad dispersion exceeding 2.5 eV. Trigonal compression of the RuO<sub>6</sub> octahedra along the  $c$ -axis [177], manifested by the O–Ru–O bond angle of 94.4°, further splits the  $t_{2g}$  manifold into a singlet  $a_{1g}$  and a doubly degenerate  $e'_g$  by  $\Delta_t \sim 0.6$  eV [Figure 4.1(b) and Table 4.1]. These findings are consistent with resonant inelastic X-ray scattering (RIXS) data [157].



Table 4.1: Trigonal distortion  $\Delta_t$ , bandwidths of  $t_{2g}$  subbands, effective correlation and electronic bandgaps computed using non-magnetic and magnetic GGA calculations, both with and without SO coupling. Values are provided for bulk SrRu<sub>2</sub>O<sub>6</sub>.

| Parameters                          | Non-magnetic GGA | Magnetic GGA | GGA + SO coupling |
|-------------------------------------|------------------|--------------|-------------------|
| $W_{t_{2g}}$ (eV)                   | 2.37             | 2.65         | 2.65              |
| Trigonal distortion $\Delta_t$ (eV) | 0.68             | 0.64         | 0.64              |
| Occupied $W_{a_{1g}}$ (eV)          | 0.74             | 0.74         | 0.73              |
| Occupied $W_{e'_g}$ (eV)            | 0.69             | 0.68         | 0.71              |
| Unoccupied $W_{a_{1g}}$ (eV)        | 0.33             | 0.36         | 0.29              |
| Unoccupied $W_{e'_g}$ (eV)          | 0.66             | 0.46         | 0.47              |
| Effective correlation (eV)          | 0.54             | 0.93         | 0.91              |
| Band gap $E_g$ (meV)                | 40               | 413          | 380               |

We further note that the  $a_{1g}$  and  $e'_g$  states have a mixed character, in agreement with previous studies [Figure 4.2] [159, 160]. The subbands are narrower, with widths of  $W_{a_{1g}} \sim 0.74$  eV and  $W_{e'_g} \sim 0.68$  eV [Figure 4.1(b)], and remain unaffected by the introduction of SO coupling [Figure 4.1(c)]. In contrast, the empty  $t_{2g}$  states above the Fermi level are flatter with reduced widths of  $W_{a_{1g}} \sim 0.36$  eV and  $W_{e'_g} \sim 0.46$  eV, suggesting lower kinetic energy, which supports the localized-itinerant picture discussed in the literature [158–161]. The effective correlation calculated

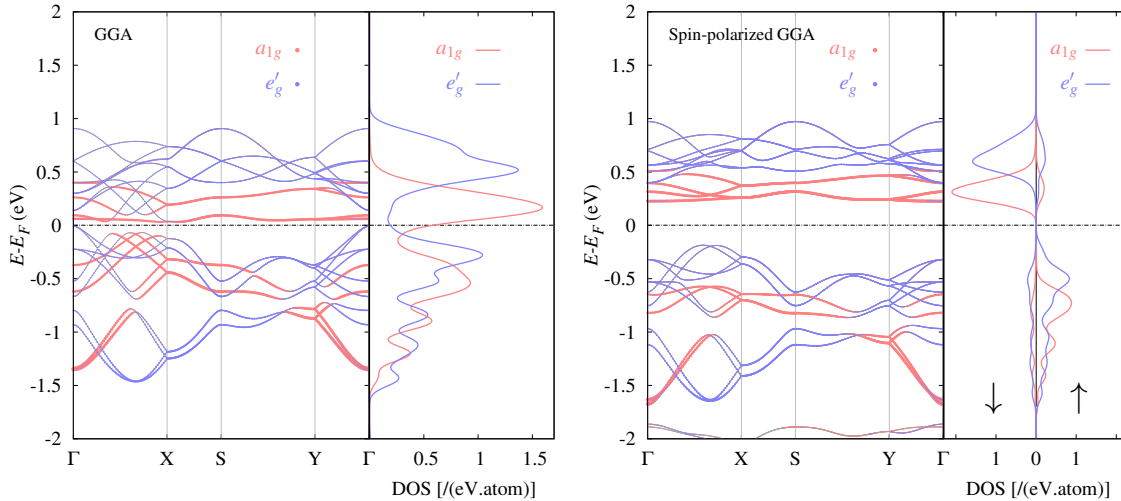


Figure 4.2: The band dispersion projected onto the  $a_{1g}$  and  $e'_g$  orbitals, along with the corresponding density of states (DOS), are calculated for bulk SrRu<sub>2</sub>O<sub>6</sub> [177]. In both, non-magnetic and magnetic calculations we observe hybridization between  $a_{1g}$  and  $e'_g$  states, which is slightly weaker in the conduction band [159, 160].

from the occupied and unoccupied  $t_{2g}$  states near the Fermi level is about 0.93 eV. This places SrRu<sub>2</sub>O<sub>6</sub> near the fluctuating limit of  $U \sim W$ , similar to what has been argued for antiferromagnetic SrTcO<sub>3</sub>, which exhibits high  $T_N \sim 1023$  K [154, 178]. Consequently, bulk SrRu<sub>2</sub>O<sub>6</sub> is also expected to have a high ordering temperature.

Consistent with experimental predictions, [61, 62] present calculations indicate a G-type AFM ordering in bulk SrRu<sub>2</sub>O<sub>6</sub>, having both in-plane and out-of-plane AFM interactions. Within the edge-shared octahedral cage of O atoms, with a Ru–O–Ru bond angle of 103°, the Ru- $t_{2g}^3$  electrons interact through competing processes that contribute to the exchange interactions [62, 179]. The combined effects of direct exchange and superexchange mechanisms result in AFM interactions, in accordance with the Goodenough-Kanamori-Anderson (GKA) rules [180]. Specifically, the nearest-neighbour superexchange is dominated by virtual  $d_{xz} - d_{yz}$  and  $d_{xy} - d_{xy}$  hoppings, while second-neighbour  $d_{xz} - d_{yz}$  and  $d_{xy} - d_{yz}$  hoppings, as well as third-neighbour  $d_{xy} - d_{xy}$  hoppings, further contribute to the resultant AFM interaction. The other magnetic configurations, such as ferromagnetic (FM, 0.24 eV/Ru), zigzag-AFM (0.15 eV/Ru), and stripe-AFM (0.09 eV/Ru), are energetically less favorable. This demonstrates relatively soft magnetism for a 4d system, as indicated by the modest energy difference between the magnetic and non-magnetic states, which is 0.26 eV/Ru.

The Ru spin moment,  $m_{s|\text{Ru}} = 1.36\mu_B$ , is significantly lower than the expected value for a half-filled  $t_{2g}$  ( $S = 3/2$ ) system. This reduction is attributed to the strong hybridization between Ru- $d$  and O- $p$  states, aligning with the experimentally observed ordered magnetic moment of 1.3–1.4 $\mu_B$  [61, 62]. However, strong hybridization does not necessarily imply a weak coupling nature, as previously discussed. While the local moments in  $t_{2g}^3$  perovskites are also reduced, the de-

gree of reduction and the underlying physics differ across systems. For instance, SrMnO<sub>3</sub> ( $T_N = 260$  K,  $m_{s|\text{Mn}} = 2.6\mu_B$ ) falls in the strong coupling regime with  $U/W \gg 1$ , [181] while NaOsO<sub>3</sub> ( $T_N = 410$  K,  $m_{s|\text{Os}} = 1\mu_B$ ) is in the weak coupling limit with  $U/W \ll 1$  [156, 182]. On the other hand, SrTcO<sub>3</sub> ( $T_N = 1023$  K,  $m_{s|\text{Tc}} = 2.1\mu_B$ ) resides at the boundary between these two extremes with  $U/W \sim 1$  [154]. Furthermore, the reduction in  $m_{s|\text{Ru}}$  is notably more severe compared to quasi-one-dimensional Li<sub>3</sub>RuO<sub>4</sub> [183] and other mixed-metal oxides containing Ru<sup>5+</sup> cations [184, 185]. The reduction in local moment observed in SrRu<sub>2</sub>O<sub>6</sub> aligns with the interplay between electron correlation and bandwidth, characterized by  $U \sim W$ , resulting in significant hybridization between Ru-4*d* and O-2*p* orbitals. As expected in a half-filled  $t_{2g}^3$  electronic configuration, the SO coupling in SrRu<sub>2</sub>O<sub>6</sub>, with  $\lambda < 200$  meV, does not play a dominant role in describing the electronic structure, resulting in vanishing orbital moment,  $m_{s|\text{Ru}} < 0.02\mu_B$ . However, SO coupling plays a prime role in magnetism by inducing uniaxial spin anisotropy.

The electronic structure of the one- to three-layer SrRu<sub>2</sub>O<sub>6</sub> nanosheets generally mirrors that of the bulk, retaining their insulating nature. However, the reduced dimensionality introduces quantum confinement effects, which result in a substantial increase in the band gap, reaching approximately 450 meV. This enhancement underscores the influence of confinement on the electronic properties of ultrathin layers, making them distinct from their bulk counterpart.

To gain deeper insights into the microscopic nature of magnetism in bulk SrRu<sub>2</sub>O<sub>6</sub> and ultrathin nanosheets, we employ the anisotropic Heisenberg model on the

honeycomb Ru lattice, [171, 172]

$$H = -\frac{1}{2} \sum_{\langle i,j \rangle} J_1 \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2} \sum_{\langle\langle i,j \rangle\rangle} J_2 \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{2} \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} J_3 \mathbf{S}_i \cdot \mathbf{S}_j \\ - \frac{1}{2} \sum_{\langle i,j \rangle} J_{\perp} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i A_z S_i^z S_i^z$$

Here,  $J_1$ ,  $J_2$ , and  $J_3$  represent the first, second, and third nearest-neighbour intralayer isotropic exchange interactions, respectively, while  $J_{\perp}$  denotes the inter-layer interaction between Ru-spins  $\mathbf{S}_i$ . The magnetic exchange coupling is FM for positive  $J$  and negative for AFM interaction. Although SO coupling does not influence the electronic structure, it plays a crucial role in the magnetism of SrRu<sub>2</sub>O<sub>6</sub> through on-site anisotropy, particularly in the ultrathin limit. The on-site anisotropy  $A_z < 0$  characterizes in-plane and  $A_z > 0$  represents out-of-plane magnetization.  $A_z$  is calculated as the energy difference between the in-plane and out-of-plane magnetization,  $A_z = (E_{[100]} - E_{[001]})/S^2$ . Such a magnetic model has been employed to describe 2D magnetic insulators, offering not only a quantitative framework but also the ability to predict the experimental evolution of magnetism under electrical gating [171, 172]. Isotropic interactions are calculated by energy mapping across various ordered phases, including FM, G-type AFM, C-type AFM, in-plane zigzag-AFM, and in-plane stripe-AFM configurations.

Calculations reveal strong in-plane AFM correlations compared to the weaker out-of-plane interactions [Table 4.2]. The robust in-plane magnetism is primarily governed by AFM superexchange coupling between Ru spins, mediated by oxygen and further enhanced by the strong Ru–O covalency. The honeycomb  $J_1$ - $J_2$ - $J_3$  model provides an excellent fit, with the magnetism predominantly described by the first-neighbour AFM interaction,  $J_1 = 163$  meV, which corresponds to  $J_1 S^2 = 75$  meV, and in good agreement with experimental estimates derived from magnon dispersion [157]. While  $J_3/J_1 = 0.07$  remains moderate, the second-

Table 4.2: Heisenberg exchange interactions are derived from first-principles calculations. The magnetism in charge-neutral nanosheets is primarily governed by intralayer AFM  $J_1$ , AFM  $J_3$ , and out-of-plane magnetic anisotropy, resulting in high-temperature antiferromagnetic ordering in two dimensions, as calculated through Heisenberg Monte Carlo simulations. However, charge doping adversely affects the Néel temperature  $T_N$ . Electron doping significantly impacts the on-site anisotropy, flipping it to an in-plane orientation. In contrast, in hole-doped sublayers, both intralayer  $J_2$  and  $J_3$  transition to strong ferromagnetic interactions, accompanied by a substantial reduction in the Ru spin moment, significantly influencing the magnetic ordering.

|                                                        | Exchange interactions (meV) |       |       |           | $A_z$ | $m_{\text{s} \text{Ru}}$ | $m_{\text{o} \text{Ru}}$ | $T_N$ |
|--------------------------------------------------------|-----------------------------|-------|-------|-----------|-------|--------------------------|--------------------------|-------|
|                                                        | $J_1$                       | $J_2$ | $J_3$ | $J_\perp$ | (meV) | ( $\mu_B$ )              | ( $\mu_B$ )              | (K)   |
| Bulk $\text{SrRu}_2\text{O}_6$                         | -163.2                      | -0.1  | -12.2 | -0.85     | 3.5   | 1.36                     | 0.02                     | 501   |
| 3L-[H-Sr] $\cdots$ [Sr-H]                              | -163.1                      | -0.5  | -10.0 | -0.28     | 3.6   | 1.36                     | 0.02                     | 452   |
| 2L-[H-Sr] $\cdots$ [Sr-H]                              | -162.1                      | -0.8  | -10.6 | -0.14     | 3.7   | 1.36                     | 0.02                     | 445   |
| 1L-[H-Sr  $\text{Ru}_2\text{O}_6$  Sr-H]               | -163.0                      | -1.8  | -9.5  | —         | 3.9   | 1.36                     | 0.02                     | 431   |
| 1L-[H-Sr  $\text{Ru}_2\text{O}_6$  Sr]                 | -136.0                      | -25.2 | -9.7  | —         | -3.8  | 1.03                     | 0.04                     | 73    |
| 1L-[Sr  $\text{Ru}_2\text{O}_6$  Sr]                   | -90.0                       | 4.6   | -9.8  | —         | -14.9 | 1.01                     | 0.08                     | 195   |
| 1L-[H-Sr  $\text{Ru}_2\text{O}_6$   $\otimes$ ]        | -198.7                      | 47.7  | 88.5  | —         | 3.2   | 0.32                     | 0.01                     | 23    |
| 2L-[ $\otimes$   $\text{Ru}_2\text{O}_6$   $\otimes$ ] | -200.1                      | 50.3  | 86.8  | -10.2     | 3.7   | 0.32                     | 0.01                     | 29    |
| 2L-[Sr  $\text{Ru}_2\text{O}_6$  Sr]                   | -131.6                      | -24.5 | -13.9 | 0.22      | -3.8  | 1.02                     | 0.04                     | 91    |

neighbour interaction  $J_2$  is negligible [Table 4.2]. With a much weaker interplane exchange of  $J_\perp = 0.85$  meV, the magnetism in bulk  $\text{SrRu}_2\text{O}_6$  is effectively 2D in nature. Calculated positive on-site anisotropy of  $A_z = 3.5$  meV indicates an easy-axis magnetism, consistent with experimental predictions [62, 157]. Heisenberg Monte Carlo simulations, incorporating these exchange parameters, yield a Néel temperature of 501, which is in close agreement with the experimental value of 565 K [61, 62, 152, 153]. The microscopic magnetic picture presented here is consistent with previous theoretical calculations [61, 62]. However, the calculated  $T_N$  is highly sensitive to the spin model and the crystal structure used to derive the exchange interactions.

Calculations for bulk  $\text{SrRu}_2\text{O}_6$  are repeated using various descriptions of exchange-correlation functionals, but the results deviate significantly from experimental observations [Table 4.3]. For instance, the electronic band gap increases to 0.93 eV as electron correlation is supplemented with a Hubbard-like Coulomb interac-

Table 4.3: Structural, electronic and magnetic properties of bulk SrRu<sub>2</sub>O<sub>6</sub>, calculated using various treatments of the exchange-correlation energy, are compared with existing experimental and theoretical results. The calculated energies of various magnetic configurations are reported for a supercell with four Ru atoms. The G-type AFM ordering with the Ru-spins aligned in-plane (out-of-plane) is denoted with G-AFM<sub>x</sub> (G-AFM<sub>z</sub>). The spin-moment  $\mu_s$  is consistently antiparallel to the orbital moment  $\mu_o$ . Exchange interactions are derived using the energy-mapping method, and the corresponding Néel temperature  $T_N$  is determined via Heisenberg Monte Carlo simulations.

|                        | Hiley et al. [61] | $U = 0$ eV | $U = 1.5$ eV | HSE   | $r^2$ SCAN |
|------------------------|-------------------|------------|--------------|-------|------------|
| FM                     | 614               | 969        | 1093         | 687   | 888        |
| Zigzag                 | 385               | 598        | 593          | 429   | 475        |
| Stripy                 | 194               | 366        | 284          | 211   | 228        |
| G-AFM <sub>z</sub>     | 0                 | 0          | 0            | 0     | 0          |
| G-AFM <sub>x</sub>     | 6.5               | 7.3        | 9.8          | 9.8   | 4.9        |
| C-AFM                  | 2.0               | 3.1        | 2.8          | 1.6   | 2.0        |
| $\mu_s$ ( $\mu_B$ /Ru) | 1.4               | 1.36       | 1.77         | 2.03  | 1.80       |
| $\mu_o$ ( $\mu_B$ /Ru) | –                 | 0.02       | 0.02         | 0.03  | 0.01       |
| $J_1$ (meV)            | –50.0             | –163.2     | –112.3       | –55.1 | –87.1      |
| $J_2$ (meV)            | –1.4              | –0.1       | –8.6         | –1.4  | –7.0       |
| $J_3$ (meV)            | –0.6              | –12.2      | –4.4         | –0.6  | –3.7       |
| $J_\perp$ (meV)        | –1.4              | –0.9       | –0.5         | –0.2  | –0.3       |
| $A_z$ (meV)            | 1.9               | 3.5        | 2.4          | 2.4   | 1.5        |
| $T_N$ (K)              | 563               | 501        | 370          | 285   | 288        |
| Band Gap (meV)         | 36                | 380        | 928          | 2540  | 867        |
| $a = b$ (Å)            | 5.21              | 5.31       | 5.32         | 5.28  | 5.24       |
| $c$ (Å)                | 5.23              | 5.20       | 5.21         | 5.25  | 5.27       |

tion ( $U_{Ru}=1.5$  eV). A similar enhancement is observed with the regulated-restored  $r^2$ SCAN meta-GGA, and the hybrid HSE06 functional. While the G-type AFM ground state is well reproduced, these descriptions of exchange-correlation significantly overestimate the Ru magnetic moment. Moreover, the calculated Néel temperatures are significantly lower than experimental values, mainly due to a reduction in the AFM  $J_1$ , resulting from a decreased energy difference between the G-AFM ground state and the stripy AFM excited state.

### 4.3.2 Two-dimensional SrRu<sub>2</sub>O<sub>6</sub> sheets

Having explored the bulk properties, it is intriguing to investigate SrRu<sub>2</sub>O<sub>6</sub> sheets in the 2D limit [Figure 4.3(a)]. Given the quasi-2D nature of magnetism in the

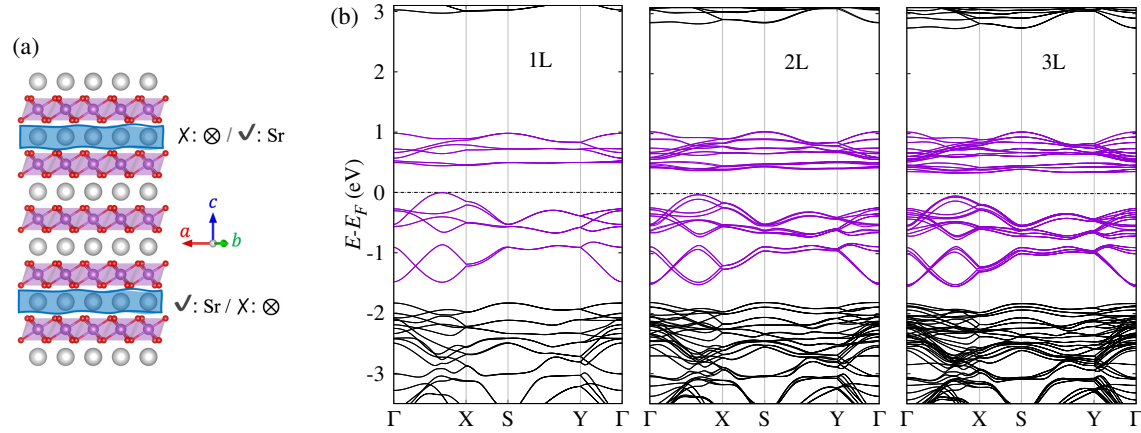


Figure 4.3: (a) Bulk  $\text{SrRu}_2\text{O}_6$  consists of two-dimensional  $\text{Ru}_2\text{O}_6$  sublayers formed by edge-sharing octahedra within the  $ab$ -plane, stacked along the  $c$ -axis and separated by alternating Sr layers. The Sr–O bonds, not shown for clarity, are weaker and can be chemically cleaved, resulting in ultrathin flakes. Cleaving may occur at any Sr-layer, highlighted in blue in the figure, leading to nanosheets with varying thicknesses. Flakes with ( $\checkmark$ : Sr) and without ( $\times$ :  $\text{Ru}_2\text{O}_6$ ) Sr termination have equal likelihood, giving rise to different types of flakes classified by their terminations. (b) Charge-neutral nanosheets are modelled by hydrogen passivating the surfaces of flakes terminated by Sr layers on both sides,  $[\text{H}-\text{Sr}|\cdots|\text{Sr}-\text{H}]$ . The electronic structure of the one- to three-layer nanosheets generally mirrors that of the bulk, retaining their insulating nature. However, the reduced dimensionality introduces quantum confinement effects, which results in an increased band gap of 450 meV.

bulk, the key question is whether these 2D sheets can sustain an above-room-temperature AFM state. The added complexities of quantum confinement, surface reconstruction, and self-doped charge carriers make this exploration more compelling.

Bulk  $\text{SrRu}_2\text{O}_6$  is a layered compound with alternating triangular Sr layers and honeycomb  $\text{Ru}_2\text{O}_6$  layers stacked along the  $c$ -axis [Figure 4.3(a)]. We find that the Sr–O bonds are about ten times weaker than the Ru–O bonds. Consequently, the Sr–O bonds are easily cleaved, leaving behind nanosheets of magnetic  $\text{Ru}_2\text{O}_6$  layers in the  $ab$ -plane, separated by nonmagnetic Sr layers. Since ultrathin sheets with or without Sr-layer termination are equally likely, these 2D sheets become charge-doped at the surface. A deficiency or excess of Sr from the stoichiometric composition results in hole or electron doping at the surface of the flakes, re-

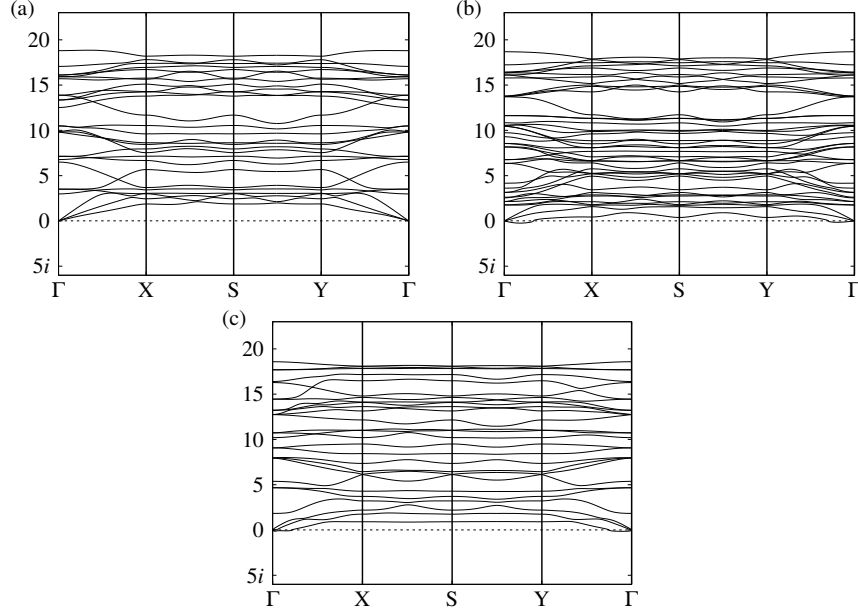


Figure 4.4: Phonon bandstructure of (a) Bulk, (b)  $[\text{H-Sr}] \cdots [\text{Sr-H}]$  passivated monolayer, and (c)  $[\text{Sr}] \cdots [\otimes]$  monolayer. The absence of imaginary modes indicates the dynamical stability of the oxide nanosheets.

spectively. Driving the ultrathin sheets away from the charge neutral point could induce emergent physics, similar to observations in  $\text{Na}_2\text{IrO}_3$  flakes [162]. In the monolayer limit of  $\text{Na}_2\text{IrO}_3$ , the Kitaev spin liquid state is disrupted, and carrier doping induces electronic and magnetic phase transitions, resulting in a spin-only ferromagnetic phase.

The exfoliation energy for  $\text{SrRu}_2\text{O}_6$  is calculated to be  $76 \text{ meV}/\text{\AA}^2$ , which is significantly lower than that of  $\text{Na}_2\text{IrO}_3$ , where the  $\text{Na-O}$  bonds are cleaved. Furthermore, this exfoliation energy is lower than that of metal carbides and nitrides, known as MXenes, [53, 186, 187] which have already been experimentally cleaved, but is still higher than conventional vdW layered systems [188]. The calculated phonon dispersions show that both neutral and charge-doped ultrathin non-vdW flakes are dynamically stable [Figure 4.4]. A flexural phonon mode with a small frequency is observed near the Brillouin zone centre, a feature commonly seen in vdW 2D materials and is attributed to numerical convergence [189, 190]. These results are further corroborated by the recent successful synthesis of ultra-



Table 4.4: Bader charge analysis of the passivated and charge-doped flakes compared to the bulk [191]. The numbers represent the average magnitude and the nature of the charge per atom. Results indicate that the passivated honeycomb  $\text{SrRu}_2\text{O}_6$  flakes have identical charge distribution as in bulk and are charge neutral.

|                                  | Sr                    | Ru                    | O                     |
|----------------------------------|-----------------------|-----------------------|-----------------------|
| Bulk                             | +1.68                 | +1.93                 | -0.93                 |
| 3L-[H-Sr]...[Sr-H]               | +1.82   +1.69   +1.82 | +2.04   +2.06   +2.04 | -0.96   -0.97   -0.96 |
| 2L-[H-Sr]...[Sr-H]               | +1.76   +1.76         | +2.05   +2.05         | -0.96   -0.96         |
| 2L-[Sr]...[Sr]                   | +1.69   +1.69         | +1.86   +1.86         | -1.04   -1.04         |
| 2L-[H-Sr]...[Sr]                 | +1.74   +1.69         | +2.02   +1.94         | -0.97   -1.05         |
| 2L-[ $\otimes$ ]...[ $\otimes$ ] | +1.70                 | +2.11   +2.11         | -0.85   -0.85         |
| 1L-[H-Sr]...[Sr-H]               | +1.79                 | +2.07                 | -0.96                 |

thin  $\text{SrRu}_2\text{O}_6$  nanosheets using a scalable liquid exfoliation technique [60]. Comprehensive structural characterizations were conducted using a variety of complementary experimental methods. The nanosheet thickness ranges from 1.3 to 2.2 nm, corresponding to three to five monolayers in the experiment. Nevertheless, the electronic and magnetic characterization of these nanosheets remains challenging, underscoring the critical importance of theoretical investigations.

Table 4.5: Structural parameters for bulk  $\text{SrRu}_2\text{O}_6$  and charge-neutral, electron-doped, and hole-doped monolayer nanosheets are calculated using the PBE exchange-correlation functional without on-site Coulomb corrections.

|                            | Bulk  | [Sr]...[Sr] | [H-Sr]...[Sr] | [H-Sr]...[Sr-H] | [H-Sr]...[ $\otimes$ ] | [ $\otimes$ ]...[ $\otimes$ ] |
|----------------------------|-------|-------------|---------------|-----------------|------------------------|-------------------------------|
| $a = b$ (Å)                | 5.31  | 5.44        | 5.42          | 5.29            | 5.26                   | 5.24                          |
| $c$ (Å)                    | 5.20  | —           | —             | —               | —                      | —                             |
| $d_{\text{Ru-O}}$ (Å)      | 1.96  | 2.01        | 1.99          | 1.95            | 1.93                   | 1.91                          |
| $d_{\text{Ru-Ru}}$ (Å)     |       |             |               |                 |                        |                               |
| 1 <sup>st</sup> NN         | 3.07  | 3.14        | 3.13          | 3.05            | 3.04                   | 3.02                          |
| 2 <sup>nd</sup> NN         | 5.31  | 5.44        | 5.42          | 5.29            | 5.26                   | 5.24                          |
| 3 <sup>rd</sup> NN         | 6.13  | 6.28        | 6.26          | 6.10            | 6.08                   | 6.05                          |
| $\angle\text{O-Ru-O}$ (°)  | 94.4  | 92.2        | 94.7          | 94.2            | 94.1                   | 93.5                          |
| $\angle\text{Ru-O-Ru}$ (°) | 103.2 | 103.1       | 103.5         | 102.7           | 104.3                  | 104.8                         |

### 4.3.3 Charge-neutral nanosheets

We begin by investigating ultrathin layers comprising one to three monolayers, each terminated with Sr layers on both sides and further hydrogen-passivated,

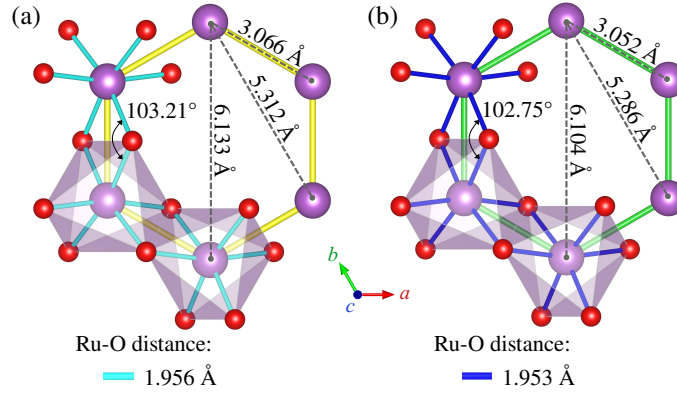


Figure 4.5: The structural comparison between (a) bulk  $\text{SrRu}_2\text{O}_6$  and (b) the hydrogen-passivated charge-neutral monolayer reveals key differences and similarities. The honeycomb Ru lattice and edge-sharing octahedral geometry remain evident in both cases. In the monolayer, a minor contraction of the in-plane lattice parameter is observed, impacting the Ru–Ru distances. However, the Ru–O bonds remain largely unaffected in the passivated nanosheets.

forming  $[\text{H}-\text{Sr}] \cdots [\text{Sr}-\text{H}]$  structures. Bader charge analysis reveals that the magnetic honeycomb  $\text{Ru}_2\text{O}_6$  sublayers in these nanosheets retain an identical charge distribution to that of bulk  $\text{SrRu}_2\text{O}_6$ , confirming the charge neutrality of these flakes [Table 4.4]. The in-plane lattice parameter shows minimal variation with thickness [Figure 4.5 and Table 4.5], being only 0.5% shorter in the monolayer compared to the bulk. As a result, the Ru–Ru distances within the honeycomb lattice are also slightly reduced in the flakes. Other structural parameters remain unchanged, including Ru–O bond distance and the degree of trigonal distortion.

The overall electronic structure of the nanosheets closely resembles that of the bulk, preserving the normal insulating state [Figure 4.3(b)]. However, in the monolayer limit, the band gap increases to 450 meV, a change attributed to quantum confinement effects rather than structural modifications, which are found to be negligible. Key electronic parameters, including  $\Delta_{\text{OC}}$ ,  $\Delta_t$ , electron correlation, and bandwidths  $W_{a_{1g}}$  and  $W_{e'_g}$ , remain unchanged in the nanosheets [Figure 4.3(b)]. Consequently, both the spin and orbital moments remain unaltered in the ultrathin nanosheets [Table 4.6].

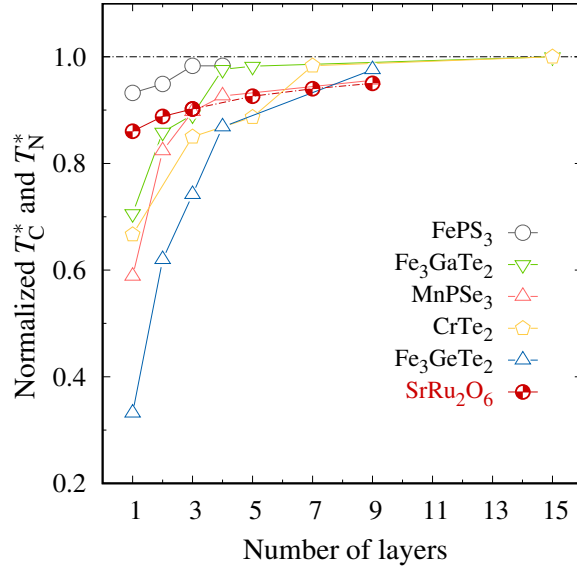


Figure 4.6: The thickness-dependent evolution of magnetism in ultrathin  $\text{SrRu}_2\text{O}_6$  nanosheets is compared to other 2D vdW magnets, with their ordering temperatures normalized to bulk values. The results for the passivated nanosheets calculated using the parameters in Table 4.2 are compared with  $\text{FePS}_3$ , [166]  $\text{Fe}_3\text{GaTe}_2$ , [192]  $\text{MnPSe}_3$ , [193]  $\text{CrTe}_2$ , [194] and  $\text{Fe}_3\text{GeTe}_2$  [170]. The  $T_N$  for five- to nine-layer nanosheets (dotted line) are calculated using the interpolated exchange parameters. Although magnetic ordering temperatures are renormalized in the 2D limit due to enhanced thermal spin fluctuations, the extent of this reduction varies significantly across materials, driven by differences in SO coupling and interlayer exchange interactions.

Remarkably, magnetism in  $\text{SrRu}_2\text{O}_6$  2D nanosheets remains robust, even at the monolayer limit, which consists of a single  $\text{Ru}_2\text{O}_6$  sublayer. Similar to the bulk, the ultrathin films exhibit a G-type AFM structure, with the monolayer retaining the corresponding Néel AFM order. The retention of high-temperature magnetism in ultrathin flakes is surprising, considering the bulk exhibits quasi-2D magnetism with weak interlayer coupling  $J_\perp$ . Typically, the ordering temperature undergoes significant renormalization in the 2D limit [Figure 4.6], as observed in vdW magnets [166, 170, 192–195]. However, the renormalization of  $T_N$  in  $\text{SrRu}_2\text{O}_6$  nanosheets is significantly weaker [Figure 4.6].

Similar to its bulk counterpart, magnetism in the nanosheets is primarily governed by AFM  $J_1$  interactions and magnetic anisotropy oriented perpendicular to the honeycomb lattice [Table 4.6]. Classical Heisenberg Monte Carlo simulations

Table 4.6: Comprehensive details of magnetic and electronic properties of passivated and charge-doped monolayers. The energies of various magnetic configurations are reported for a supercell with four Ru atoms.

|                                                   | [Sr] $\cdots$ [Sr] | [H–Sr] $\cdots$ [Sr] | [H–Sr] $\cdots$ [Sr–H] | [H–Sr] $\cdots$ [ $\otimes$ ] |
|---------------------------------------------------|--------------------|----------------------|------------------------|-------------------------------|
| $a = b$ (Å)                                       | 5.44               | 5.42                 | 5.29                   | 5.26                          |
| FM                                                | 311                | 461                  | 951                    | 35                            |
| Zigzag                                            | 206                | 181                  | 586                    | 62                            |
| Stripy                                            | 143                | 68                   | 339                    | 13                            |
| G-AFM <sub>z</sub>                                | 15.5               | 4.0                  | 0                      | 0                             |
| G-AFM <sub>x</sub>                                | 0                  | 0                    | 7.1                    | 0.3                           |
| $\mu_s$ ( $\mu_B$ /Ru)                            | 1.01               | 1.03                 | 1.36                   | 0.32                          |
| $\mu_o$ ( $\mu_B$ /Ru)                            | 0.08               | 0.04                 | 0.02                   | 0.01                          |
| $\mu_o$ relative to $\mu_s$                       | $\uparrow\uparrow$ | $\uparrow\uparrow$   | $\uparrow\downarrow$   | $\uparrow\downarrow$          |
| $J_1$ (meV)                                       | −90                | −136                 | −163                   | −199                          |
| $J_2$ (meV)                                       | 4.6                | −25.2                | −1.8                   | 47.7                          |
| $J_3$ (meV)                                       | −9.8               | −9.7                 | −9.5                   | 88.5                          |
| $A_z$ (meV)                                       | −14.9              | −3.8                 | 3.9                    | 3.2                           |
| $T_N$ (K)                                         | 195                | 73                   | 431                    | 23                            |
| Band Gap (meV)                                    | 188                | metallic             | 446                    | metallic                      |
| $\delta_{e^-/h^+}$ ( $10^{14}$ cm <sup>−2</sup> ) | −5.33              | −3.53                | neutral                | 3.34                          |

indicate a Néel temperature of 431 K for the passivated monolayer, making it the 2D antiferromagnet with the highest known ordering temperature. This surpasses not only experimentally synthesized materials [166–168] but also those identified through computational screening [169]. In comparison, ternary MPS<sub>3</sub> compounds, which share the  $P\bar{3}1m$  space group, exhibit significantly lower ordering temperatures. For instance, FePS<sub>3</sub> demonstrates Ising antiferromagnetism with an in-plane zigzag magnetic order below 118 K, [166] while MnPS<sub>3</sub> is a Heisenberg antiferromagnet that exhibits out-of-plane Néel order below 78 K [195]. Compared to the bulk, the moderate reduction in the monolayer, with  $T_N^{\text{ML}} = 0.86T_N^{\text{bulk}}$  is primarily attributed to the complete loss of magnetic interactions in the perpendicular direction, resulting in enhanced spin fluctuations. Additionally, a slight increase in the AFM  $J_2$  further contributes to the decrease in  $T_N$ , as AFM  $J_2$  hinders Néel ordering on a honeycomb lattice. The interlayer coupling  $J_\perp$  remains AFM in ultrathin sheets, and it increases with layer thickness. This results in a moderate increase in

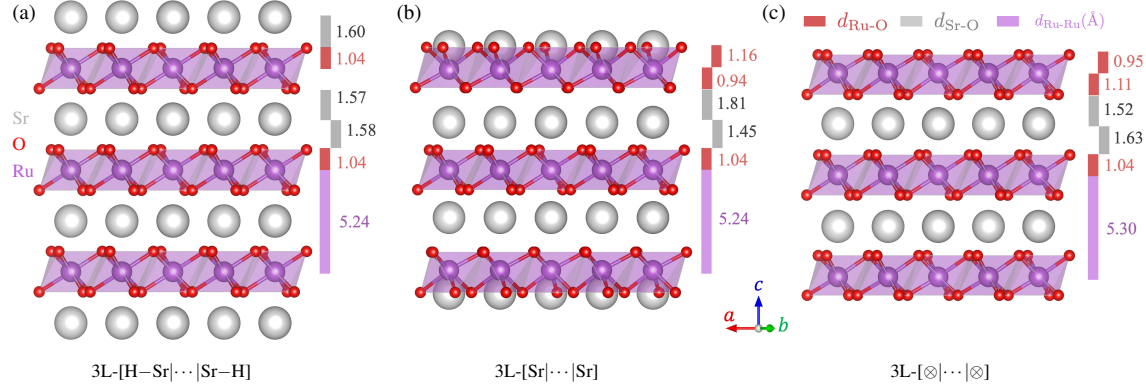


Figure 4.7: The type of surface termination determines the charge carriers infused into the adjacent  $\text{Ru}_2\text{O}_6$  sublayer, which in turn drives structural reconstruction and significantly influences the electronic and magnetic properties of the nanosheets. For instance, a comparison of structural reconstructions in three-layer nanosheets highlights these effects. (a) The passivated, charge-neutral nanosheet  $3\text{L}[\text{H}-\text{Sr}|\cdots|\text{Sr}-\text{H}]$  closely resembles the bulk structure without significantly altering the interplanar distances, as indicated by the colour bars. Passivating H-atoms are not shown for clarity. (b) However, in the electron-doped  $3\text{L}[\text{Sr}|\cdots|\text{Sr}]$  flake, the exposed Sr layer induces severe structural reconstruction, with the dangling Sr layer plunging into the adjacent  $\text{Ru}_2\text{O}_6$  sublayer. This results in significant changes to the interplanar distances, particularly  $d_{\text{Sr}-\text{O}}$  and  $d_{\text{Ru}-\text{O}}$ . (c) In contrast, the structural reconstruction is relatively less pronounced in the hole-doped trilayer  $[\otimes]|\cdots|[\otimes]$  nanosheet.

the  $T_N$  in the two- and three-layer nanosheets [Table 4.2 and Figure 4.6]

Table 4.7: Structural parameters of neutral and charge-doped bilayer nanosheets are reported. The magnetic  $\text{Ru}_2\text{O}_6$  sublayers exhibit distinct relaxations influenced by their adjacent terminations and the nature of charge doping.

|                                          | $[\text{Sr} \cdots \text{Sr}]$ | $[\text{H}-\text{Sr} \cdots \text{Sr}]$ | $[\text{H}-\text{Sr} \cdots \text{Sr}-\text{H}]$ | $[\text{H}-\text{Sr} \cdots [\otimes]]$ | $[\otimes] \cdots [\otimes]$ |
|------------------------------------------|--------------------------------|-----------------------------------------|--------------------------------------------------|-----------------------------------------|------------------------------|
| $a = b$ (Å)                              | 5.44                           | 5.36                                    | 5.30                                             | 5.28                                    | 5.27                         |
| $d_{\text{Ru}-\text{O}}$ (Å)             | 1.99                           | (1.96   1.98)                           | 1.96                                             | (1.95   1.93)                           | 1.93                         |
| $d_{\text{Ru}-\text{Ru}}$ (Å)            |                                |                                         |                                                  |                                         |                              |
| 1 <sup>st</sup> NN                       | 3.14                           | 3.09                                    | 3.06                                             | 3.05                                    | 3.04                         |
| 2 <sup>nd</sup> NN                       | 5.44                           | 5.36                                    | 5.30                                             | 5.28                                    | 5.27                         |
| 3 <sup>rd</sup> NN                       | 6.28                           | 6.19                                    | 6.12                                             | 6.10                                    | 6.08                         |
| $\angle\text{O}-\text{Ru}-\text{O}$ (°)  | 94.8                           | (94.7   93.7)                           | 94.3                                             | (94.1   94.1)                           | 94.1                         |
| $\angle\text{Ru}-\text{O}-\text{Ru}$ (°) | 103.8                          | (103.9   102.5)                         | 102.9                                            | (102.7   104.5)                         | 104.3                        |

Table 4.8: The structural parameters of neutral and charge-doped trilayer nanosheets are presented, revealing that the magnetic Ru<sub>2</sub>O<sub>6</sub> sublayers undergo varying relaxations depending on the adjacent terminations and the type of charge doping.

|                            | [Sr]...[Sr]         | [H-Sr]...[Sr]       | [H-Sr]...[Sr-H]     | [H-Sr]...[O]        | [O]...[O]           |
|----------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| $a = b$ (Å)                | 5.39                | 5.34                | 5.30                | 5.28                | 5.28                |
| $d_{\text{Ru-O}}$ (Å)      | (1.99 1.97 1.99)    | (1.96 1.96 1.98)    | (1.96 1.96 1.96)    | (1.95 1.95 1.93)    | (1.93 1.95 1.93)    |
| $d_{\text{Ru-Ru}}$ (Å)     |                     |                     |                     |                     |                     |
| 1 <sup>st</sup> NN         | 3.11                | 3.08                | 3.06                | 3.05                | 3.05                |
| 2 <sup>nd</sup> NN         | 5.39                | 5.34                | 5.30                | 5.28                | 5.28                |
| 3 <sup>rd</sup> NN         | 6.22                | 6.16                | 6.12                | 6.10                | 6.10                |
| $\angle\text{O-Ru-O}$ (°)  | (94.2 94.8 94.2)    | (94.7 94.5 93.3)    | (94.3 94.3 94.3)    | (94.1 94.1 94.1)    | (94.1 94.1 94.1)    |
| $\angle\text{Ru-O-Ru}$ (°) | (103.0 104.4 103.0) | (103.7 103.6 102.2) | (102.9 102.9 102.9) | (102.6 102.8 104.5) | (104.4 102.7 104.4) |

#### 4.3.4 Charge-carrier doped nanosheets

The non-vdW flakes become charge-doped depending on surface termination, which may severely impact their electronic and magnetic properties, as reported for Na<sub>2</sub>IrO<sub>3</sub> nanosheets [162]. In the case of SrRu<sub>2</sub>O<sub>6</sub>, the Sr-terminated layer electron-dopes the adjacent Ru<sub>2</sub>O<sub>6</sub> magnetic sublayer. In contrast, the oxygen-terminated layer hole-dopes it in the absence of a Sr sublayer. Further, partial passivation allows for control over carrier density in the active magnetic layer.

A clear trend in the in-plane lattice parameter  $a$  is observed in the ultrathin flakes, independent of their thickness [Table 4.5, 4.7 and 4.8]. The calculated  $a$  increases in electron-doped flakes relative to their charge-neutral counterparts, whereas it decreases in hole-doped flakes. A concomitant trend is observed in structural parameters, such as the Ru–O and Ru–Ru bond distances. Structural reconstruction at the Sr-terminated layer is pronounced and extends into the underlying Ru<sub>2</sub>O<sub>6</sub> sublayer, as illustrated in Figure 4.7 for nanosheets comprising three magnetic sublayers. As a result, nanosheets with and without the Sr termination exhibit equivalent thickness. For instance, trilayer nanosheets have a thickness of approximately 1.3 nm regardless of termination [Figure 4.7], which is in excellent agreement with experimental findings [60]. Moreover, charge carriers influence other structural parameters, including Sr–O distances, as well as

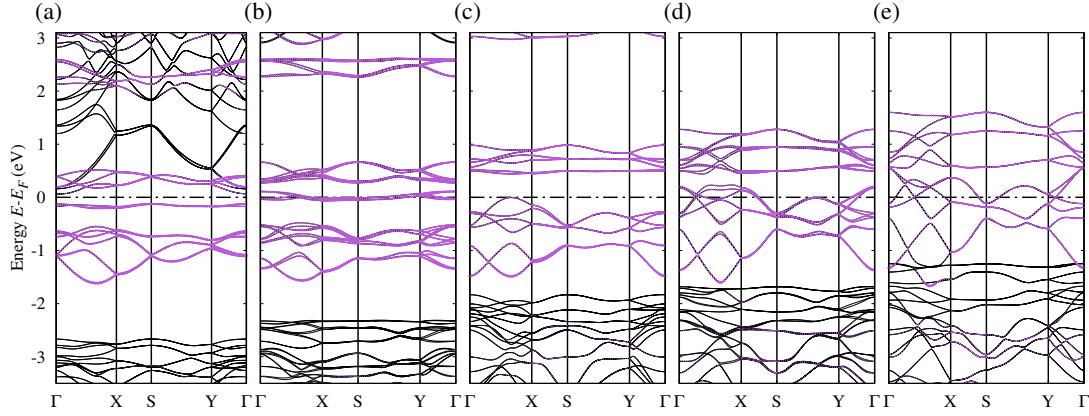


Figure 4.8: Band structures of monolayer flakes. (a) and (b) correspond to electron-doped monolayers with  $[\text{Sr}|\cdots|\text{Sr}]$  and  $[\text{H}-\text{Sr}|\cdots|\text{Sr}]$  configurations, respectively. (c) shows the charge-neutral monolayer. (d) and (e) represent hole-doped monolayers with  $[\text{H}-\text{Sr}|\cdots|\otimes]$  and  $[\otimes|\cdots|\otimes]$  configurations, respectively. Purple shading denotes the Ru-projected states, with  $t_{2g}$  orbitals dominating near  $E_F$ .

$\text{Ru}-\text{O}-\text{Ru}$  and  $\text{O}-\text{Ru}-\text{O}$  bond angles [Table 4.5, 4.7 and 4.8].

Carrier doping significantly alters the electronic structure, leading to an insulator-to-metal transition in the adjacent  $\text{Ru}_2\text{O}_6$  sublayer, irrespective of the termination [Figure 4.8 and 4.9]. While the fully passivated monolayer  $[\text{H}-\text{Sr}|\text{Ru}_2\text{O}_6|\text{Sr}-\text{H}]$  retains insulating behavior, hole-doped nanosheets  $[\text{H}-\text{Sr}|\text{Ru}_2\text{O}_6|\otimes]$ ,  $[\otimes|\text{Ru}_2\text{O}_6|\otimes]$  and electron-doped  $[\text{H}-\text{Sr}|\text{Ru}_2\text{O}_6|\text{Sr}]$  flakes exhibit metallic characteristics [Figure 4.8 and 4.9]. The sole exception arises when the monolayer is terminated with Sr layers on both sides,  $[\text{Sr}|\text{Ru}_2\text{O}_6|\text{Sr}]$ , which remains insulating with a band gap of 188 meV as the unoccupied  $a_{1g}$  band becomes completely filled. The insulator-to-metal transition persists in thicker flakes, where metallic and insulating  $\text{Ru}_2\text{O}_6$  sublayers coexist simultaneously [Figure 4.10 and 4.11]. For instance, in the trilayer  $[\otimes|\text{Ru}_2\text{O}_6|\cdots|\text{Ru}_2\text{O}_6|\text{Sr}]$ , both surface  $\text{Ru}_2\text{O}_6$  sublayers, irrespective of Sr-termination, exhibit metallic behavior, while the central  $\text{Ru}_2\text{O}_6$  sublayer remains insulating. Furthermore, the density of states analysis indicates that irrespective of the surface termination, the Sr-layers between the magnetic  $\text{Ru}_2\text{O}_6$  sublayers remain insulating, indicating 2D surface metallicity in these nanosheets.

Magnetism is retained in the atomically thin sheets even under charge dop-

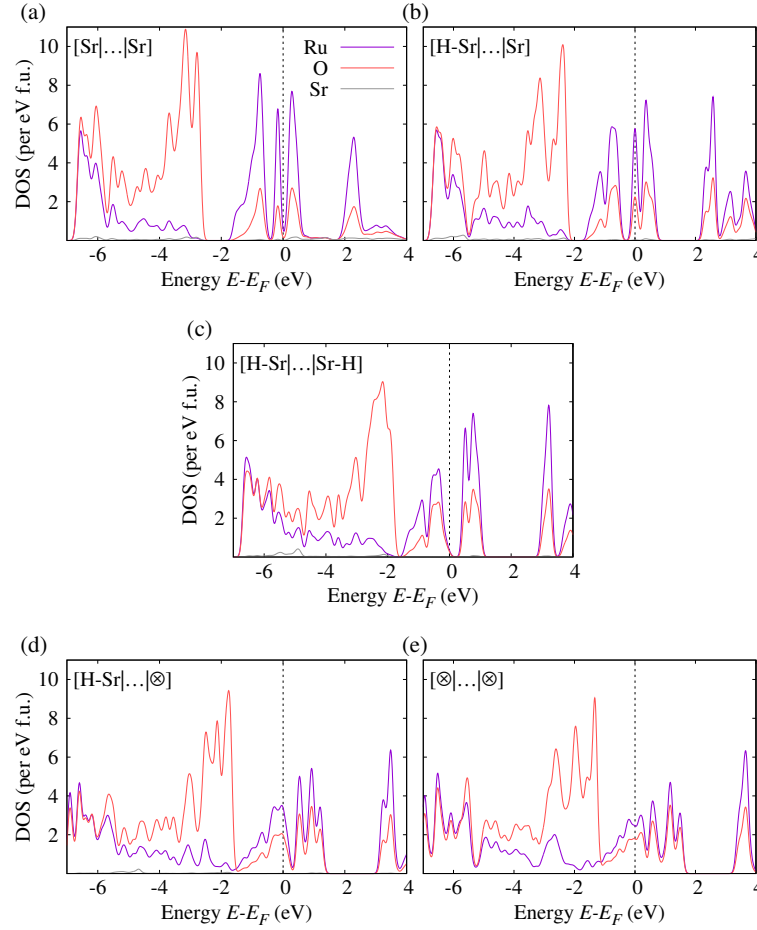


Figure 4.9: The corresponding density of states for monolayer nanosheets is shown. (a) and (b) depict  $[\text{Sr}] \cdots [\text{Sr}]$  and  $[\text{H-Sr}] \cdots [\text{Sr}]$  configurations, respectively. (c) represents the charge-neutral nanosheet, while (d) and (e) correspond to  $[\text{H-Sr}] \cdots [\otimes]$  and  $[\text{Sr}] \cdots [\text{Sr}]$  configurations, respectively.

ing [Table 4.6, 4.9 and 4.10]. Despite significant changes in structural and electronic properties, the  $\text{Ru}_2\text{O}_6$  sublayers maintain robust Néel AFM ordering. The interlayer exchange interaction remains antiferromagnetic in all cases, except in the bilayer with Sr termination on both sides, where the coupling becomes ferromagnetic between the two electron-doped metallic  $\text{Ru}_2\text{O}_6$  sublayers [Table 4.9 and 4.10]. Although magnetism persists, charge doping modifies the local Ru spin and orbital moments, SO coupling, magnetic anisotropy, and exchange interactions. Several general trends are observed depending on the type and density of doping [Table 4.6, 4.9 and 4.10].



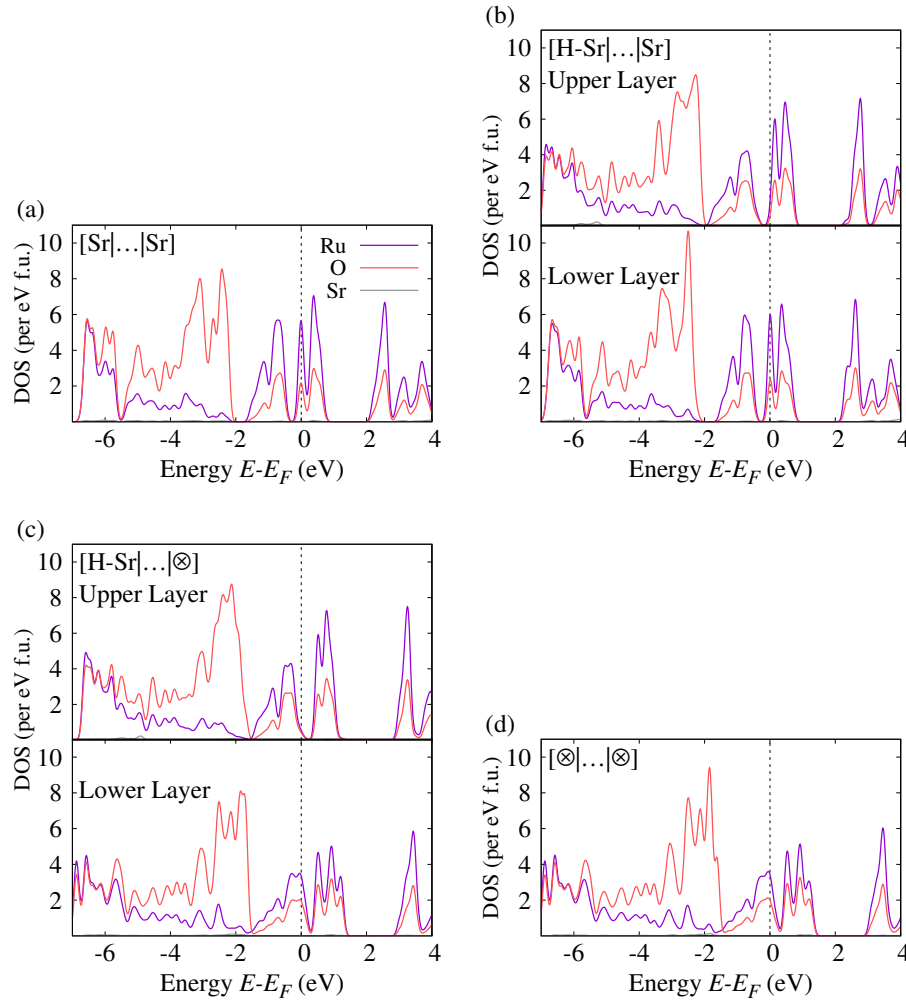


Figure 4.10: Layer-resolved density of states for bilayer nanosheets. Panels (a) and (b) correspond to electron-doped nanosheets with  $[\text{Sr}] \cdots [\text{Sr}]$  and  $[\text{H-Sr}] \cdots [\text{Sr}]$  configurations, respectively. Panels (c) and (d) depict hole-doped flakes with  $[\text{H-Sr}] \cdots [\otimes]$  and  $[\otimes] \cdots [\otimes]$  configurations, respectively.

First, charge carrier doping reduces the spin moment from  $1.36\mu_B$  in the charge-neutral state, with the reduction being significantly more pronounced in hole-doped  $\text{Ru}_2\text{O}_6$  sublayers ( $m_{\text{s}|\text{Ru}} \sim 0.3\mu_B$ ) compared to electron-doped ones ( $m_{\text{s}|\text{Ru}} \sim 1\mu_B$ ), despite identical carrier densities [Table 4.6, 4.9 and 4.10]. In electron-doped layers, the slightly elongated Ru–O bond indicates reduced covalency, while the filling of the minority-spin  $a_{1g}$  band accounts for a moderate reduction in the spin moment. In contrast, in hole-doped layers, increased Ru–O covalency, due to shorter bond

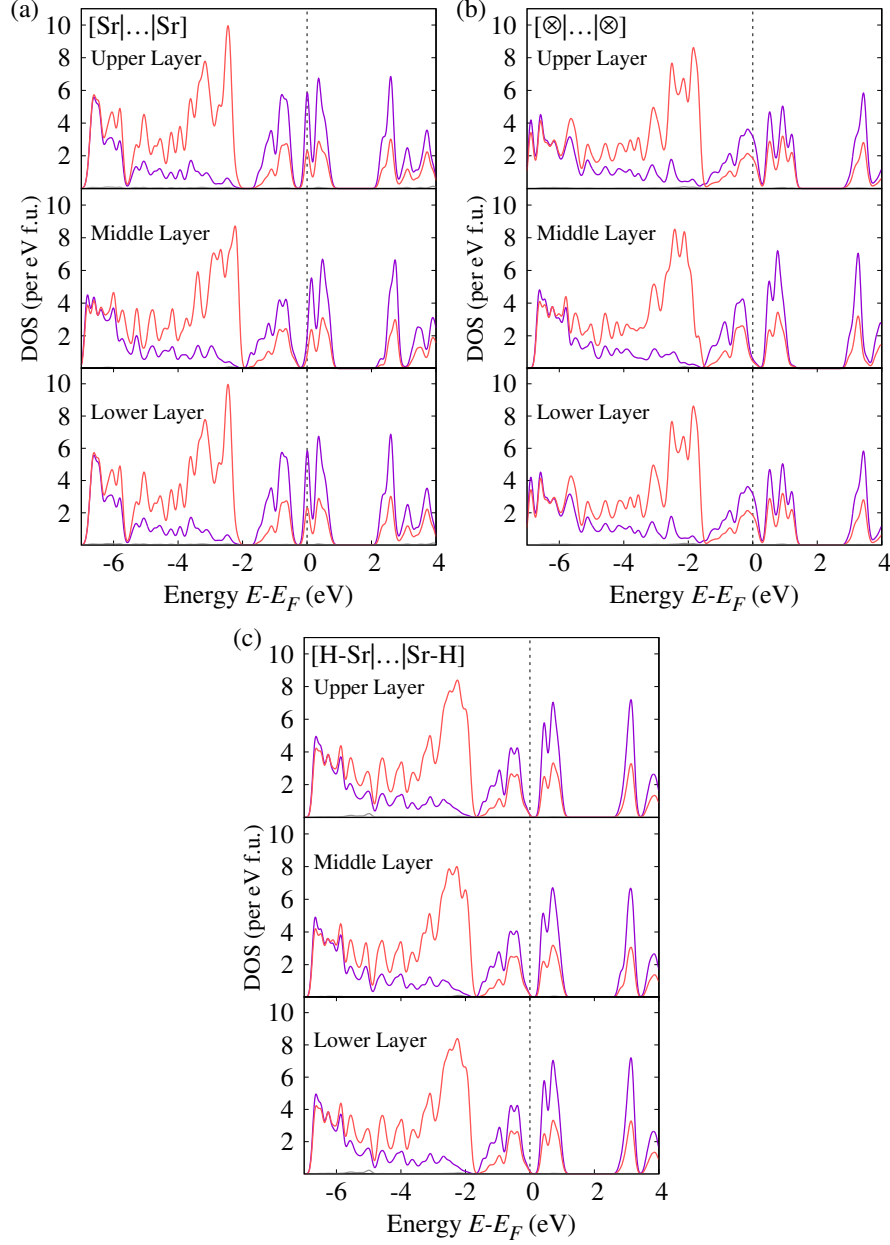


Figure 4.11: Layer-resolved density of states for trilayer nanosheets: Panel (a) depicts electron-doped nanosheets with the  $[\text{Sr}] \cdots [\text{Sr}]$  configuration, while panel (b) illustrates hole-doped flakes with the  $[\otimes] \cdots [\otimes]$  configuration. (c) Layer-projected DOS for charge-neutral trilayer,  $[\text{H}-\text{Sr}] \cdots [\text{Sr}-\text{H}]$ . Charge doping drives an insulator-to-metal transition, while the middle layer remains insulating.

distances, combined with depopulation of the majority-spin  $e'_g$  band, results in a significant reduction of the Ru spin moment.

Secondly, the SO coupling is influenced by charge doping, primarily through

Table 4.9: Magnetic and electronic properties of charge-neutral and charge-doped bilayer nanosheets. Layer-resolved magnetic moments are reported, showing variations depending on the type and density of charge doping in the respective magnetic  $\text{Ru}_2\text{O}_6$  sublayers.

|                                                  | $[\text{Sr} \cdots \text{Sr}]$ | $[\text{H}-\text{Sr} \cdots \text{Sr}]$       | $[\text{H}-\text{Sr} \cdots \text{Sr}-\text{H}]$ | $[\text{H}-\text{Sr} \cdots \otimes]$           | $[\otimes \cdots \otimes]$ |
|--------------------------------------------------|--------------------------------|-----------------------------------------------|--------------------------------------------------|-------------------------------------------------|----------------------------|
| FM                                               | 453                            |                                               | 958                                              |                                                 | 37                         |
| Zigzag                                           | 172                            |                                               | 593                                              |                                                 | 62                         |
| Stripy                                           | 78                             |                                               | 352                                              |                                                 | 15                         |
| G-AFM <sub>z</sub>                               | 4                              | 2.1                                           | 0                                                | 0                                               | 0                          |
| G-AFM <sub>x</sub>                               | 0.5                            | 3.1                                           | 6.8                                              | 3.7                                             | 0.4                        |
| C-AFM                                            | 0                              | 0.9                                           | 0.5                                              | 0.4                                             | 2.1                        |
| Ground state                                     | $\text{AF}_x   \text{AF}_x$    | $\text{AF}_z   \text{AF}_x$                   | G-AFM <sub>z</sub>                               | G-AFM <sub>z</sub>                              | G-AFM <sub>z</sub>         |
| $\mu_s$ ( $\mu_B/\text{Ru}$ )                    | 1.02                           | (1.33   1.02)                                 | 1.36                                             | (1.31   0.33)                                   | 0.32                       |
| $\mu_o$ ( $\mu_B/\text{Ru}$ )                    | 0.04                           | (0.02   0.04)                                 | 0.02                                             | (0.02   0.01)                                   | 0.01                       |
| $\mu_o$ relative to $\mu_s$                      | $\uparrow\uparrow$             | ( $\uparrow\downarrow$   $\uparrow\uparrow$ ) | $\uparrow\downarrow$                             | ( $\uparrow\downarrow$   $\uparrow\downarrow$ ) | $\uparrow\uparrow$         |
| $J_1$ (meV)                                      | -131.6                         |                                               | -162.3                                           |                                                 | -200.1                     |
| $J_2$ (meV)                                      | -24.4                          |                                               | -0.9                                             |                                                 | 50.3                       |
| $J_3$ (meV)                                      | -13.9                          |                                               | -10.4                                            |                                                 | 86.8                       |
| $J_\perp$ (meV)                                  | 0.2                            |                                               | -0.1                                             |                                                 | -10.2                      |
| $A_z$ (meV)                                      | -3.8                           |                                               | 3.7                                              |                                                 | 3.7                        |
| $T_N$ (K)                                        | 91                             |                                               | 445                                              |                                                 | 29                         |
| Band Gap (meV)                                   | metallic                       | metallic                                      | 399                                              | metallic                                        | metallic                   |
| $\delta_{e^-/h^+}$ ( $10^{14} \text{ cm}^{-2}$ ) | -3.49                          | (neutral   -3.67)                             | neutral                                          | 3.22                                            | (neutral   3.27)           |

changes in the electronic structure. In electron-doped  $\text{Ru}_2\text{O}_6$  sublayers, SO coupling is enhanced, as evidenced by an increase in the orbital moment from  $m_{o|\text{Ru}} \sim 0.04$  to  $0.08\mu_B$  [Table 4.6, 4.9 and 4.10]. Conversely, a reduction in the orbital moment is observed in hole-doped sublayers. Furthermore, the spin and orbital moments align parallel in electron-doped cases as the  $t_{2g}$  band becomes more than half-filled.

Lastly, charge doping significantly alters the on-site magnetic anisotropy [Table 4.2, 4.9 and 4.10]. In neutral  $\text{SrRu}_2\text{O}_6$  nanosheets, magnetism is characterized by perpendicular anisotropy ( $\text{AFM}_\perp$ ,  $A_z > 0$ ) relative to the 2D honeycomb Ru lattice, as illustrated in Figure 4.12. However, electron doping induces a transition to in-plane anisotropy ( $\text{AFM}_\parallel$ ,  $A_z < 0$ ) in the  $\text{Ru}_2\text{O}_6$  sublayer. In contrast, hole-doped sublayers retain their easy-axis  $\text{AFM}_\perp$  magnetism, preserving the perpendicular alignment [Figure 4.12]. The transition in the direction of magnetic

Table 4.10: The magnetic and electronic properties of charge-neutral and charge-doped trilayer nanosheets are analyzed. The magnetic moments, resolved for individual layers, exhibit variations influenced by the type and concentration of charge doping in the corresponding magnetic  $\text{Ru}_2\text{O}_6$  sublayers. Band gap is in meV while  $\mu_s$  and  $\mu_o$  are in  $\mu_B/\text{Ru}$  and  $\delta_{e^-/h^+}$  is in  $10^{14} \text{ cm}^{-2}$

|                     | $[\text{Sr} \dots \text{Sr}]$                                | $[\text{H}-\text{Sr} \dots \text{Sr}]$                         | $[\text{H}-\text{Sr} \dots \text{Sr}-\text{H}]$                  | $[\text{H}-\text{Sr} \dots \otimes]$                             | $[\otimes \dots \otimes]$                                        |
|---------------------|--------------------------------------------------------------|----------------------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|
| Ground state        | $(\text{AF}_x \text{AF}_z \text{AF}_x)$                      | $(\text{AF}_z \text{AF}_z \text{AF}_x)$                        | G-AFM <sub>z</sub>                                               | $(\text{AF}_z \text{AF}_z \text{AF}_z)$                          | $(\text{AF}_z \text{AF}_z \text{AF}_z)$                          |
| $\mu_s$             | (1.01   1.29   1.01)                                         | (1.35   1.33   0.99)                                           | (1.37   1.36   1.37)                                             | (1.36   1.32   0.33)                                             | (0.32   1.28   0.32)                                             |
| $\mu_o$             | (0.04   0.02   0.04)                                         | (0.02   0.02   0.04)                                           | (0.02   0.02   0.02)                                             | (0.02   0.02   0.01)                                             | (0.01   0.02   0.01)                                             |
| $\mu_o$ wrt $\mu_s$ | $(\uparrow\uparrow   \uparrow\downarrow   \uparrow\uparrow)$ | $(\uparrow\uparrow   \uparrow\downarrow   \uparrow\downarrow)$ | $(\uparrow\downarrow   \uparrow\downarrow   \uparrow\downarrow)$ | $(\uparrow\downarrow   \uparrow\downarrow   \uparrow\downarrow)$ | $(\uparrow\downarrow   \uparrow\downarrow   \uparrow\downarrow)$ |
| Band Gap            | metallic                                                     | metallic                                                       | 380 meV                                                          | metallic                                                         | metallic                                                         |
| $\delta_{e^-/h^+}$  | (-3.54   N   -3.54)                                          | (N   N   -3.41)                                                | N: neutral                                                       | (N   N   3.15)                                                   | (3.34   N   3.34)                                                |

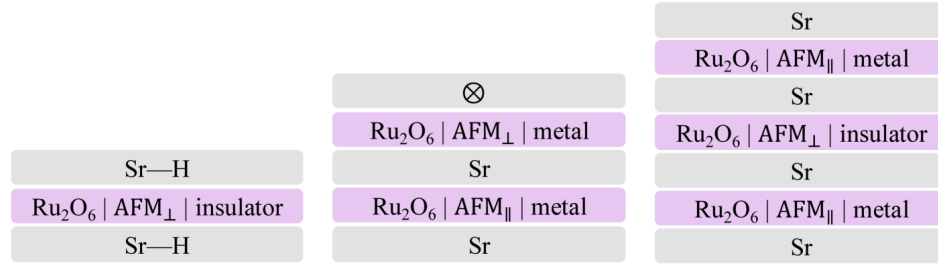


Figure 4.12: Schematic illustrations of electronic and magnetic states in selected nanosheets reveal that the magnetic  $\text{Ru}_2\text{O}_6$  sublayers consistently exhibit Néel AFM ordering, regardless of doping. However, the magnetic anisotropy switches from an out-of-plane direction ( $\text{AFM}_\perp$ ) to an in-plane direction ( $\text{AFM}_\parallel$ ) in electron-doped sublayers. Additionally, charge carrier doping induces an insulator-to-metal transition within the  $\text{Ru}_2\text{O}_6$  sublayers. These naturally grown nanosheets with intrinsic charge doping feature complex combinations of layered electronic and magnetic states that hold promising potential for spintronic applications.

anisotropy can be explained by treating SO coupling within the second-order perturbation theory [196]. First, the matrix element  $\langle d_{xy} | L_z | d_{x^2-y^2} \rangle$ , which promotes in-plane magnetic anisotropy, increases significantly in the electron-doped  $\text{Ru}_2\text{O}_6$  sublayer. Second, the orbital-projected contribution from  $\langle d_{z^2} | L_x | d_{yz} \rangle$ , typically favoring out-of-plane anisotropy, changes sign in the electron-doped sublayer, as both orbitals predominantly host minority spins. These changes collectively drive the observed transition from perpendicular to in-plane magnetic anisotropy.

The bilayer and trilayer flakes exhibit intricate combinations of electronic and magnetic states across adjacent  $\text{Ru}_2\text{O}_6$  sublayers, separated by atomically thin in-

ulating Sr layers [Figure 4.12 and Table 4.9, 4.10]. For example, the [Sr] · · · [Sr] trilayer demonstrates a [metal-AFM<sub>||</sub> | insulator-AFM<sub>⊥</sub> | metal-AFM<sub>||</sub>] configuration. The extreme misalignment of magnetic anisotropy between adjacent layers can be exploited to harness field-induced phenomena with promising applications [197]. In doped bilayer nanosheets [Figure 4.12], the Néel vectors in the 2D metallic Ru<sub>2</sub>O<sub>6</sub> layers are mutually orthogonal ( $\varphi = 90^\circ$ ), separated by an insulating Sr spacer layer. This configuration enables the bilayer nanosheets to act as antiferromagnetic tunnel junctions, [198] yielding a high-resistance state in the absence of an external magnetic field. Applying a magnetic field along the easy (hard) axis of the AFM<sub>⊥</sub> (AFM<sub>||</sub>) monolayer gradually reorients the Néel vector in one of the layers. At sufficiently high field strengths, the Néel vectors in both Ru<sub>2</sub>O<sub>6</sub> layers align parallel ( $\varphi = 0^\circ$ ), resulting in a low-resistance state. This tunability suggests that such exfoliated flakes could be integrated into magnetoresistive devices, similar to the behavior observed in orthogonally twisted ferromagnetic CrSBr monolayers [199–201]. Additionally, the ability to manipulate the magnetic field strength and direction offers opportunities to engineer complex spin textures, providing further avenues for functional magnetic applications. Alternatively, the Néel vectors can be tuned electrostatically by gating, which drives the magnetic layers from the electron-doped regime to the neutral or hole-doped regime.

To gain further microscopic insights into the magnetism of charge-doped flakes, we calculate the exchange interactions, which are significantly altered by the added electrons or holes to the Ru<sub>2</sub>O<sub>6</sub> sublayers [Table 4.6]. Electron doping leads to a monotonic reduction in  $J_1$  with increasing carrier density, accompanied by drastic changes in the second-neighbor interaction  $J_2$ . In [H–Sr|Ru<sub>2</sub>O<sub>6</sub>|Sr] flake, the AFM  $J_2$  significantly increases, with  $J_2/J_1 \sim 0.19$ , compared to the negligible  $J_2/J_1 \sim 0.01$  observed in the passivated monolayer. Upon further electron doping,  $J_2$  transitions to a ferromagnetic interaction in [Sr|Ru<sub>2</sub>O<sub>6</sub>|Sr] nanosheet. Fur-

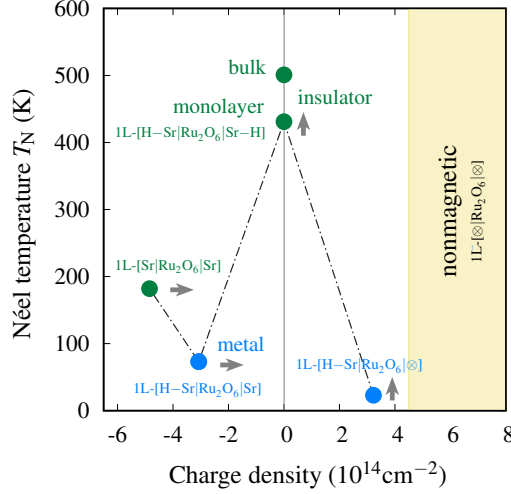


Figure 4.13: The calculated Néel temperature exhibits nonmonotonic behaviour with charge carrier density as shown for the monolayer. The Ru moment, exchange interactions, and magnetic anisotropy are altered in charge-doped nanosheets [Table 4.6]. The calculated bulk  $T_N$  aligns well with experimental results, [61, 62, 152, 153] while the ordering temperature is renormalized in the monolayer. Charge doping is found to be detrimental to magnetic ordering, with a pronounced effect observed in hole-doped samples. Furthermore, the magnetic anisotropy, indicated by the arrow, transitions to the in-plane direction ( $\rightarrow$ ), aligning parallel to the honeycomb Ru lattice.

thermore, SO coupling is enhanced with increasing electron density as the  $t_{2g}$  occupancy surpasses half-filling, leading to a pronounced increase in in-plane magnetic anisotropy. Using these exchange parameters, we compute the Néel temperatures via Heisenberg Monte Carlo simulations. Notably,  $T_N$  exhibits nonmonotonic behaviour [Figure 4.13], driven primarily by the changes in the nature of  $J_2$ . Since the Néel AFM configuration on the honeycomb lattice is stabilized by FM  $J_2$  and AFM  $J_3$ , variations in exchange interactions predominantly dictate the reduction in  $T_N$ . This effect is further compounded by a moderate quenching of the Ru spin moment, which decreases to  $1\mu_B$ . As expected, the exchange interactions in the electron-doped  $[\text{Sr}|\cdots|\text{Sr}]$  bilayer closely resemble those of the  $[\text{H-Sr}|\text{Ru}_2\text{O}_6|\text{Sr}]$  monolayer, resulting in a comparable ordering temperature.

The microscopic behavior in hole-doped nanosheets differs significantly [Table 4.6]. Analysis of the exchange interactions in both monolayer and bilayer

nanosheets reveals key insights into their ordering temperature. A moderate increase in AFM  $J_1$ , combined with a substantial FM  $J_2$  ( $J_2/J_1 \sim -0.25$ ), should theoretically stabilize the Néel AFM configuration. However, a large FM  $J_3$  ( $J_3/J_1 \sim -0.45$ ) and a significant quenching of the Ru spin moment to  $0.3\mu_B$  primarily drive the magnetic ordering to much lower temperatures. As a result, the hole-doped monolayer and bilayer exhibit magnetic ordering below 45 K [Figure 4.13], which is substantially lower than their charge-neutral counterparts. With further increases in hole density, the Ru spin moment is fully quenched, leading to a non-magnetic state.

## 4.4 Summary

We present a comprehensive investigation of two-dimensional magnetism in atomically thin, non-vdW oxide  $\text{SrRu}_2\text{O}_6$  sheets using first-principles calculations combined with classical Heisenberg Monte Carlo simulations. This study is further inspired by the recent successful synthesis of ultrathin  $\text{SrRu}_2\text{O}_6$  nanosheets, down to three layers, accompanied by detailed structural characterizations [60]. Within the adopted approach, the bulk properties are accurately reproduced, exhibiting G-type AFM ordering with a high Néel temperature. Charge neutral flakes exhibit magnetic ordering with  $T_N > 430$  K, positioning them as the highest known two-dimensional antiferromagnets [Figure 4.14]. Although the ordering temperature in the monolayer limit is reduced due to enhanced thermal spin fluctuations, the renormalization is minimal, with  $T_N^{\text{1L}} \sim 0.86T_N^{\text{bulk}}$ , significantly outperforming vdW magnets in retaining robust magnetic ordering at reduced dimensions.

Charge carrier doping profoundly influences the properties of  $\text{SrRu}_2\text{O}_6$  nanosheets by altering their electronic structure, spin and orbital moments, spin-orbit coupling, exchange interactions, and on-site anisotropy. A charge-induced insulator-

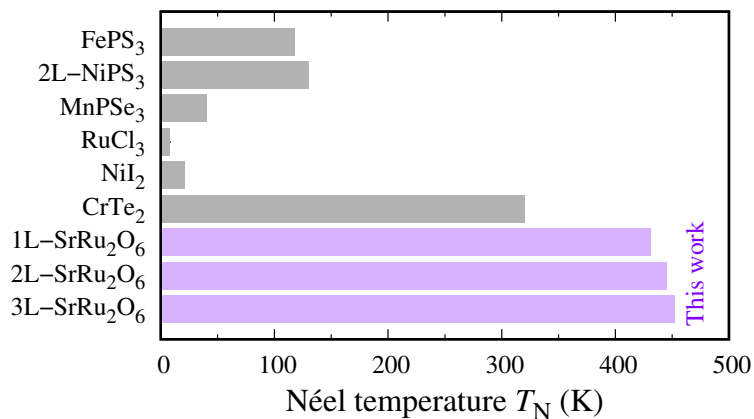


Figure 4.14: The high Néel temperature of passivated nanosheets is compared with experimentally exfoliated two-dimensional magnets exhibiting in-plane AFM ordering [130, 166, 193, 202–204]. Layered correlated oxide nanosheets could serve as a promising platform for realizing high-temperature two-dimensional antiferromagnets.

to-metal transition is observed, while robust antiferromagnetic ordering persists in these ultrathin sheets. This behavior contrasts with  $\text{Na}_2\text{IrO}_3$  nanosheets, where charge doping induces a magnetic phase transition [162]. The Néel temperature decreases with charge doping, with a more pronounced reduction in hole-doped nanosheets. A detailed microscopic model supports these observations, linking the changes in exchange interactions and spin moments to the observed reduction in  $T_N$ . The remarkable electronic and magnetic properties, including above-room-temperature magnetic ordering in the as-grown nanosheets, highlight their potential for antiferromagnetic spintronic applications. These findings warrant further theoretical and experimental exploration to unlock their full potential.





## CHAPTER 5

### UNDERSTANDING SPIN-FLIP TRANSITIONS IN $d^3$

#### LAYERED MAGNETS

Magnetic anisotropy is fundamental to 2D magnetism and plays a crucial role in enabling advanced technologies such as spintronic devices and quantum computing. This chapter explores the mechanisms driving magnetic anisotropy in  $d^3$  compounds, specifically  $\text{CrI}_3$ ,  $\text{CrTe}_2$ , and  $\text{SrRu}_2\text{O}_6$ , focusing on honeycomb and triangular lattices in both ferromagnetic (FM) and antiferromagnetic (AFM) phases. First-principles calculations demonstrate that spin-orbit coupling (SOC) and the orbital geometry near the Fermi level play pivotal roles in defining magnetic anisotropy. We observe that beyond a critical level of electron doping, the magnetic anisotropy transitions from an easy-axis to an easy-plane orientation, a behavior that can also be tuned via strain and dimensional reduction. The spin orientation is significantly influenced by the presence or absence of  $p_z$  and  $d_{z^2}$  orbitals near the Fermi level. These insights have the potential to contribute to the design of materials with controlled magnetic anisotropy.

### 5.1 Introduction

The magnetism and magnetic properties of components in a plethora of vital technologies such as magnetic storage, magnetic random access memories (MRAM), hybrid complementary metal oxide semiconductor (CMOS), RF components and sensors are heavily influenced by their magnetic anisotropy [205]. In order to advance these technologies, scientists have turned to two dimensional magnets.

2D materials possess mechanical flexibility, easy tunability in multiphysical fields, integratability on arbitrary heterostructures and respond well to defect engineering [1, 2]. At finite temperatures, Hohenberg-Mermin-Wagner theorem [3, 4] prohibits magnetic order in 1D and 2D lattices. However, magnetic anisotropy plays a crucial role in overcoming this limitation, leading to the discovery of the first 2D magnets [9, 10]. Massive gapless magnon excitations are prevented when an additional component in the form of uniaxial magnetic anisotropy under spin-orbit coupling or shape/stress anisotropy is present.

Owing to their insensitivity to stray/disturbing magnetic fields and high frequency dynamics, antiferromagnets are increasingly favored for spin-transfer devices, such as spin valves and spin-current pumps, which operate based on the spin-transfer torque effect [163, 164, 206]. However, tunneling anisotropic magnetoresistance (TAMR) devices, which leverage the spin-orbit torque effect, exhibit even larger effects [207]. Therefore, an understanding of magnetic anisotropy is crucial in these systems.

Magnetic anisotropy tuning can also be used to switch the magnetic field direction between in-plane and out-of-plane in a ferromagnetic substrate, thereby controlling the magnetic field applied to an active material on top of it. Such architectures are particularly valuable in experiments that require very high magnetic fields [208]. For instance, producing fault-tolerant quantum computing machines would involve topological majorana excitations present in the quantum spin liquid (QSL) phase. A QSL candidate can be switched from a normal magnetic state to QSL state on the application of a magnetic field [209]. Many intriguing topological phase transitions such as - from a trivial insulator to a Chern insulator or inducing a zero-field quantum anomalous Hall effect, can be driven by manipulating the magnetic substrate [208, 210, 211]. Magnetic anisotropy switching can also be accompanied by an enhancement of transition temperature [212]. Engi-

neering an in-plane magnetization can help us realize second order topological phases [213, 214].

There are various strategies for transforming magnetic anisotropy: 1) straining the in-plane lattice parameters [215–217], 2) changing the stacking of the magnetic layers, for example in MXenes [218] and orthogonally twisted CrSBr [219], 3) heavy-metal ion-adsorption in 2D magnets [220, 221], 4) tuning electronic-correlations of the transition metal [222], 5) substitutional doping [221], 6) changing the dimensionality from bulk to 2D, for example in CrTe<sub>2</sub> and RuCl<sub>3</sub> [130, 223], 7) subjecting to interfacial effects by fabricating a heterostructure with a heavy-metal or a heavy-metal compound [224–226], 8) applying external electric field [221, 226–228], 9) inducing optical excitations [221] and 10) electron/hole-doping via gating [221, 223]. Among these, the most practically viable techniques for flipping magnetic anisotropy are the application of an electric field and carrier gating.

We now delve into the origin of magnetic anisotropy, specifically, the magnetocrystalline anisotropy, as shape anisotropy in heteronuclear compounds is typically several orders of magnitude weaker [229]. In 1989, Bruno proposed that bonding anisotropy in a lattice, arising from interactions between the ligands and the magnetic center, locks the orbital moment in a preferred direction. This, in turn, aligns the spin moment along the same axis through spin-orbit coupling (SOC) [230]. The spin-orbit coupling (SOC) is significantly smaller in magnitude compared to other crystalline energy terms in the Hamiltonian, making Bruno's use of a perturbative approach appropriate. Later, Freeman and co-workers gave a more explicit form of the expression for magnetocrystalline-anisotropy energy (MAE) [196]. The spin-orbit expectation energy within the second-order perturbation theory is:

$$E^{sl} = - \sum_{o,u} \frac{|\langle o | H^{sl} | u \rangle|^2}{\delta \epsilon_{uo}} \quad (5.1)$$

where  $o, u$  represent the occupied and unoccupied orbitals which interact with

Table 5.1: Nonvanishing angular momentum matrix elements. We skip  $L_y$  operator because they are symmetrically complementary to  $L_x$  and are not included in this study.

| Element                                 | $ \langle i L j\rangle $ value |
|-----------------------------------------|--------------------------------|
| $\langle d_{xz} L_z d_{yz}\rangle$      | 1                              |
| $\langle d_{x^2-y^2} L_z d_{xy}\rangle$ | 2                              |
| $\langle d_{z^2} L_x d_{yz}\rangle$     | $\sqrt{3}$                     |
| $\langle d_{xy} L_x d_{xz}\rangle$      | 1                              |
| $\langle d_{x^2-y^2} L_x d_{yz}\rangle$ | 1                              |
| $\langle p_y L_z p_x\rangle$            | 1                              |
| $\langle p_z L_x p_y\rangle$            | 1                              |

each other and  $\delta\epsilon_{uo}$  is their energy difference. The magnetocrystalline anisotropy energy was derived as:

$$\begin{aligned}\Delta E^{ud} &= E^{ud}(x) - E^{ud}(z) \\ \Delta E^{ud} &= \zeta^2 \left[ \frac{|\langle o^+|L_x|u^- \rangle|^2 - |\langle o^+|L_z|u^- \rangle|^2}{\epsilon_{u^-} - \epsilon_{o^+}} \right]\end{aligned}\quad (5.2)$$

$$\begin{aligned}\Delta E^{dd} &= E^{dd}(x) - E^{dd}(z) \\ \Delta E^{dd} &= \zeta^2 \left[ \frac{|\langle o^-|L_z|u^- \rangle|^2 - |\langle o^-|L_x|u^- \rangle|^2}{\epsilon_{u^-} - \epsilon_{o^-}} \right]\end{aligned}\quad (5.3)$$

Here superscripts  $ud$  and  $dd$  represent interactions between up-down bands and down-down bands respectively.  $o^+(u^+)$  and  $o^-(u^-)$  represent occupied (empty) spin-up and spin-down states.  $\epsilon$  is the corresponding energy of the orbitals. It should be noted that the sign of anisotropy energies are opposite for  $ud$  and  $dd$  band interactions. Due to symmetry, most of the angular momentum matrix elements are zero, with the nonzero elements provided in Table 5.1.

Using the diatomic-pair model and the state-tracking method, it was demonstrated that the bonding character between the atoms, band broadening and geom-

etry are the key factors in determining MAE [231]. Advanced techniques, such as the torque method combined with the rigid-band model, yield similar results while also providing additional insights into spin-polarization-resolved MAE [232].

In this chapter we study the properties of selected  $d^3$  layered magnets and explore how magnetic anisotropy evolves with carrier doping, strain and dimensionality through first-principles calculations. From the equations above, it is evident that the strength of interaction between two specific orbitals depends on their geometry, nature of polarisations i.e.  $uu$  ( $dd$ ) or  $ud$  ( $du$ ), the energy difference between their band-centers and the magnitude of integrated densities. We use the terms orbital resolved magnetic anisotropy energy and SOC matrix elements (energy difference between easy-plane and easy-axis directions) interchangeably.

## 5.2 Computational Details

First principles based density functional theory (DFT) [25, 26] calculations were performed within the generalized gradient approximation (GGA). The plane-waves based projector augmented wave (PAW) method [107] implemented in the VASP code [106, 173, 174] was used along with a Perdew-Burk-Ernzerhof [68] type exchange-correlation functional. A range of Hubbard corrections,  $U_{Cr} = 0.5$  eV for  $CrI_3$ ,  $U_{Cr} = 1.0$  eV for  $CrBr_3$ ,  $U_{Cr} = 2.0$  eV for  $CrTe_2$  on the correlated  $3d$  electrons were considered under the Dudarev approach [70] after considering their agreement with experimental results. The inherent correlations of  $4d$  electrons in Ru-atoms were sufficient to describe  $SrRu_2O_6$ . The lattice parameters and ionic positions were optimized until all force components are reduced below a threshold of  $0.01$  eV/Å. The lattice constants were kept fixed for monolayer  $CrTe_2$ . The SOC matrix elements were computed by subtracting the corresponding elements of relativistic calculations for spins aligned along the  $z$  and  $x$  axes. The density of states were

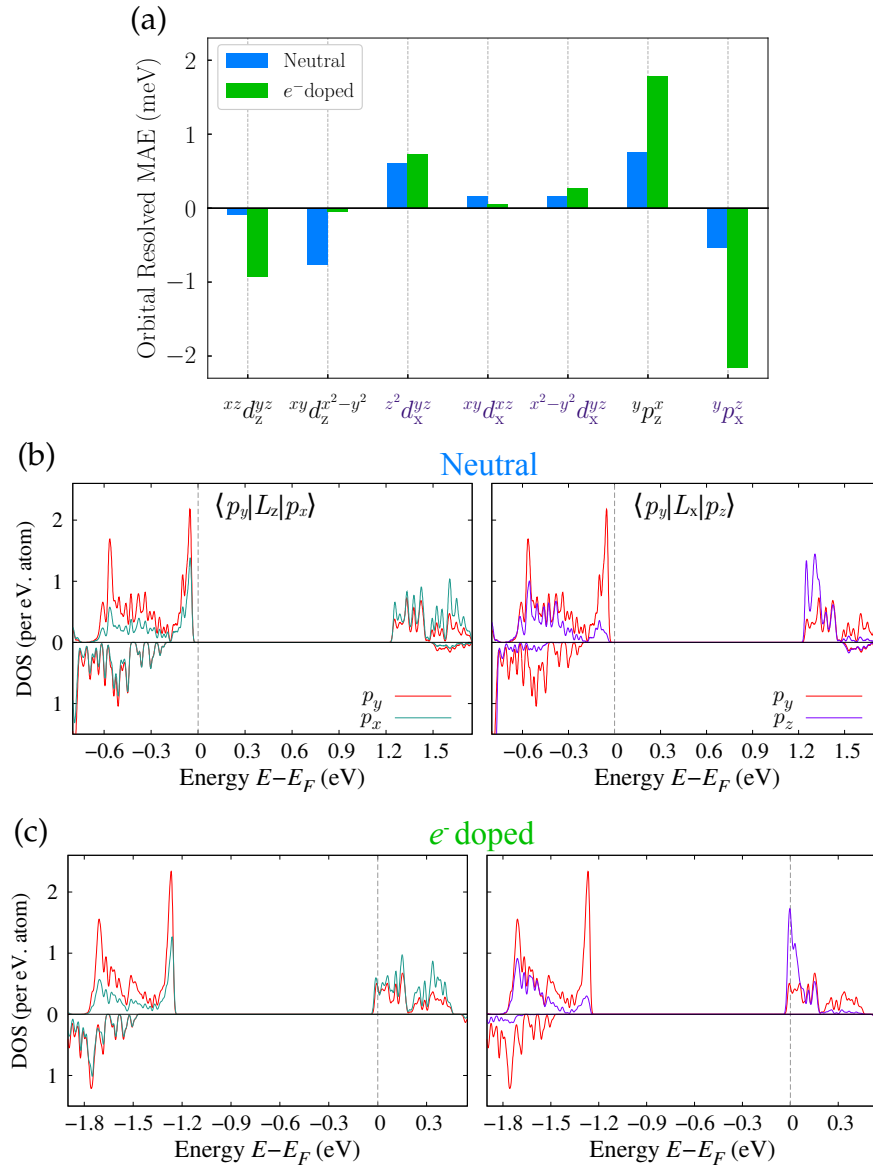


Figure 5.1: (a) The orbital resolved magnetic anisotropy energy (SOC matrix elements) of neutral and electron doped  $\text{CrI}_3$  monolayer.  $^a d_C^b$  on x-axis are the elements, where  $a$  and  $b$  are the geometries of the  $d/p$  orbitals involved and  $C$  indicates the component of angular momentum operator through which they interact. Clearly, the primary contributions stem from the  $p$ - $p$  orbital interactions of the ligands, i.e. the iodine atoms. We try to understand the major SOC matrix elements through density of states (DOS). (b) and (c) DOS of neutral and  $e^-$ -doped monolayer. The first plot shows DOS of  $p_y$  and  $p_x$  orbitals corresponding to  $\langle p_y | L_z | p_x \rangle$  term whereas the second plot shows DOS of  $p_y$  and  $p_z$  orbitals corresponding to  $\langle p_y | L_x | p_z \rangle$  term.

derived from the spin-polarized ground state solutions.

To understand the microscopic mechanism of carrier-doped spin-flip transitions we explore  $\text{CrI}_3$  and  $\text{CrBr}_3$  monolayers, as well as neutralized and self-doped

non-layered flakes of  $\text{SrRu}_2\text{O}_6$ . Additionally, we investigate how strain and dimensionality govern spin-flip transitions in  $\text{CrTe}_2$ .

### 5.2.1 $\text{CrI}_3$ monolayer

Monolayer  $\text{CrI}_3$  and  $\text{CrGeTe}_3$  were the first materials discovered to exhibit true two-dimensional magnetism [9, 10].  $\text{CrI}_3$  is a well known van der Waals magnet, with  $\text{Cr}^{3+}$  ions arranged in honeycomb layers. The magnetic atom is in the  $t_{2g}^3 e_g^0$  electronic state which implies an  $S = 3/2$  state and a completely quenched orbital moment. However, the ligand atoms - in this case, iodine (I) - are relatively heavy and contribute to the magnetic anisotropy. The single-ion-anisotropy is expectedly low, on the order of  $A_z \sim 0.3$  meV [78, 171]. The extended Heisenberg model was deemed appropriate for capturing the essential physics and predicting a Curie temperature ( $T_C$ ) consistent with experimental observations [171]. According to Goodenough-Kanomori rules, magnetism is governed by the occupancy of the  $d$  orbitals of the magnetic ions and the angle extended by the magnetic ions over the ligands ( $\angle \text{Cr-I-Cr}$ ). Thus, the nature of magnetism can be modified using strain or gating/doping carriers. In the pristine structure, experiments and calculations reveal a ferromagnetic (FM) state and an out-of-plane easy axis anisotropy [233]. However, hole-doping enhances  $T_C$  and beyond densities  $\delta_h = 0.6$   $h/\text{CrI}_3$ , the magnetic anisotropy reverses to in-plane [171, 233]. Whereas, electron-doping decreases  $T_C$  and the magnetic anisotropy flips at a cut-off density of only  $\delta_e = 0.2$   $e^-/\text{CrI}_3$ . The Kugel-Khomskii mechanism explains the variation in the transition temperature through the  $t_{2g}^3$ - $t_{2g}^3$  interaction, which is antiferromagnetic (AFM), and the  $t_{2g}^3$ - $e_g^0$  interaction, which is FM [234]. We compare the anisotropy mechanism in neutral and  $\delta_e = 0.25$   $e^-/\text{CrI}_3$  doped monolayers. The mechanism in  $h$ -doped flakes are complementary to that of  $e^-$ -doped flakes.

In Figure 5.1a, we plot the orbital resolved magnetic anisotropy energies. The



$p$ - $p$  orbital interactions of the ligands dominate the anisotropy structure, which is expected given iodine's higher spin-orbit coupling (SOC) energy. Since the spin-down states are farther below the Fermi-level than the spin-up states, the  $uu$  interactions play a more significant role, as shown in Figure 5.1(b) and (c). The  $\langle p_y | L_z | p_x \rangle$  and  $\langle p_y | L_x | p_z \rangle$  terms have an opposing effect. The  $p_y \uparrow - p_x \uparrow$  term contributes to the out-of-plane interaction whereas the  $p_y \uparrow - p_z \uparrow$  term contributes to the in-plane interaction. Both interactions are enhanced by  $e^-$  doping, as the emergence of bands within the Fermi-level reduces the effective energy difference (denominator in Eq.(2)). However, the  $p_y \uparrow - p_z \uparrow$  term prevails because of higher density of  $p_z$  orbital near the Fermi-level, eventually leading to an in-plane magnetic anisotropy observed for the  $e^-$  doped monolayer. The aggregate SOC matrix elements yield  $\Delta E_n(\text{CrI}_3) = 0.70 \text{ meV/formula unit (f.u.)}$  for the neutral layer and  $\Delta E_{e^-}(\text{CrI}_3) = -1.08 \text{ meV/f.u.}$  for the  $e^-$ -doped layer. Therefore we conclude, in this material, the presence of the  $p_z$  orbital near the Fermi level is the key determinant of the sign of the magnetic anisotropy.

### 5.2.2 CrBr<sub>3</sub> monolayer

CrBr<sub>3</sub> is a sibling compound of CrI<sub>3</sub>, differing by the presence of bromine as a ligand, which has a weaker SOC compared to iodine. Similar to CrI<sub>3</sub>, CrBr<sub>3</sub> has a honeycomb lattice and orders in an FM state near 30 K [235, 236]. The Mott insulating state with the electronic configuration  $t_{2g}^3 e_g^0$ , suggests that, in this case as well, the Kugel-Khomskii superexchange mechanism governs the ferromagnetic (FM) state, driven by the dominance of the  $t_{2g}^3 - e_g^0$  interaction over the  $t_{2g}^3 - t_{2g}^3$  interaction [78, 234]. The single-ion anisotropy ( $A_z \sim 0.1 \text{ meV}$ , easy-axis) is approximately three times lower than that of CrI<sub>3</sub>, as anticipated due to the smaller SOC [172]. Hole doping significantly enhances the Curie temperature, peaking above room temperature near  $\delta_h = 0.56 \text{ h/CrBr}_3$ , before transitioning to an easy-plane

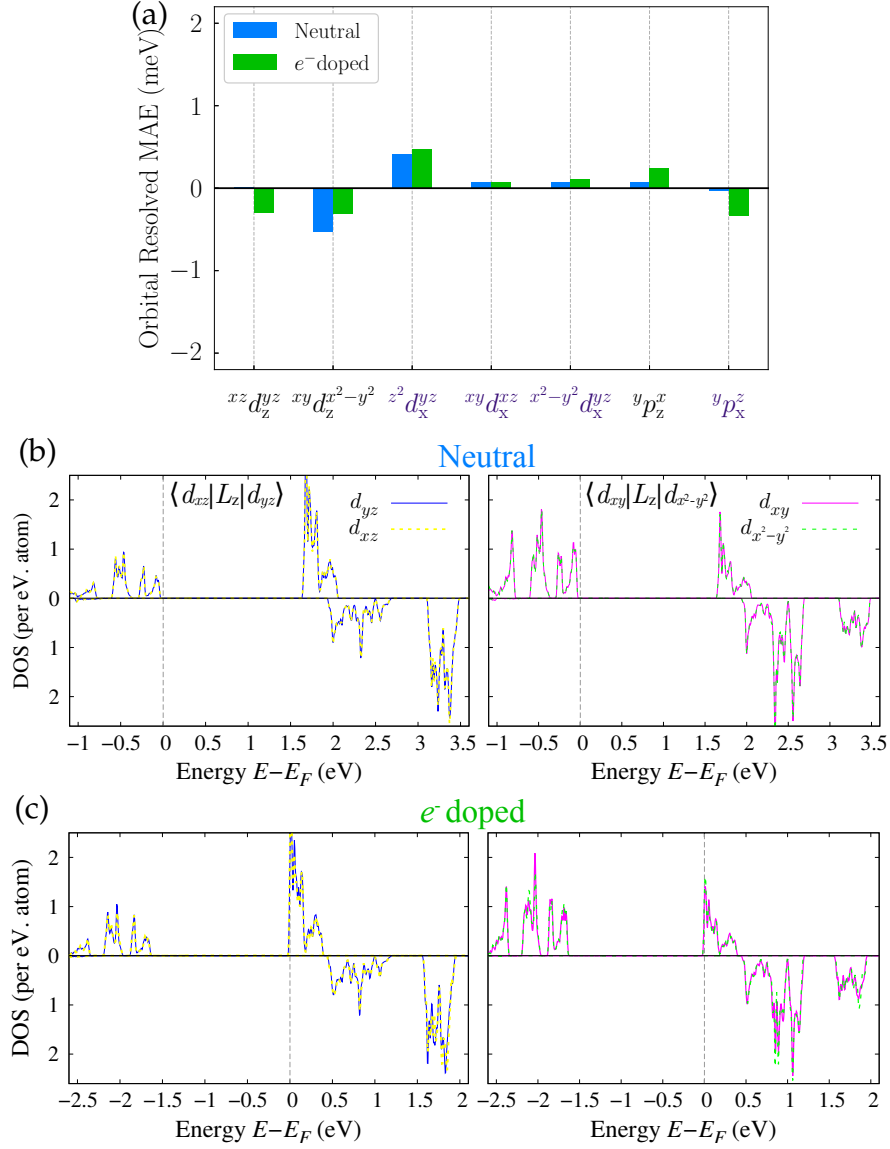


Figure 5.2: (a) The orbital resolved magnetic anisotropy energy of neutral and electron doped  $\text{CrBr}_3$  monolayer. (b) and (c) DOS of neutral and  $e^-$ -doped monolayer. The first plot shows DOS of  $d_{xz}$  and  $d_{yz}$  orbitals corresponding to the  $\langle d_{xz} | L_z | d_{yz} \rangle$  term whereas the second plot shows DOS of  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals corresponding to the  $\langle d_{xy} | L_z | d_{x^2-y^2} \rangle$  term.

anisotropy at higher doping levels [172]. On the other hand, electron doping was found to be detrimental to magnetic ordering, and the anisotropy flips beyond a small threshold density of  $\delta_e = 0.02 e^-/\text{CrBr}_3$ . Here we contrast, the undoped and  $\delta_e = 0.125 e^-/\text{CrBr}_3$  doped monolayers.

In  $\text{CrBr}_3$ , the  $d$ -orbital spin-orbit coupling (SOC) matrix elements of Cr-atoms contribute significantly, alongside the  $p$ -orbital elements of the ligands [Figure 5.2

a]. The  $\langle p_y | L_z | p_x \rangle$  and  $\langle p_y | L_x | p_z \rangle$  terms display behavior similar to those in  $\text{CrI}_3$ , leading to a significant easy-plane energy in the doped case and an opposite trend in the neutral case. We discuss the key  $d$ -orbital terms - **1)**  $\langle d_{xz} | L_z | d_{yz} \rangle$  : The valence band (VB) near Fermi-level composed of spin-up states remain same for all the projections [Figure 5.2 b,c]. In the neutral conduction band (CB) the  $d_{xz} \uparrow$  and  $d_{yz} \uparrow$  states are nearer to the VB but the  $d_{xz} \downarrow$  and  $d_{yz} \downarrow$  states have a higher integrated density which leads to cancellation of  $uu$  and  $ud$  energies. However, in the  $e^-$ -doped case, the  $d_{xz} \uparrow$  ( $d_{yz} \uparrow$ ) states get filled, reducing the  $\uparrow$  conduction band (CB) density, while the  $d_{xz} \downarrow$  and  $d_{yz} \downarrow$  densities remain unchanged. This results in the  $ud$  in-plane ( $\parallel$ ) interaction dominating over the  $uu$  out-of-plane ( $\perp$ ) interaction. **2)**  $\langle d_{xy} | L_z | d_{x^2-y^2} \rangle$  : The CB  $d_{x^2-y^2} \uparrow$  and  $d_{xy} \uparrow$  integrated densities are lower and the  $d_{x^2-y^2} \downarrow$  and  $d_{xy} \downarrow$  integrated densities are higher in the neutral state compared to the orbitals involved in term 1). Thus, the  $ud \parallel$ -interactions are dominant. In the  $e^-$ -doped flake, the  $d_{x^2-y^2} \uparrow$  and  $d_{xy} \uparrow$  states get filled which reduces the effective energy difference for the  $uu \perp$ -interaction, thereby slightly reducing the overall  $\parallel$ -interaction. **3)**  $\langle d_{z^2} | L_x | d_{yz} \rangle$  : This term interacts with a different angular momentum operator ( $L_x$ ) which leads to opposite effects. The  $d_{z^2}$  densities overlap with those of other orbitals, except for the absence of  $\uparrow$  conduction band (CB) density (not shown here). Thus, this term has an overall  $ud \perp$ -interaction. However, the difference compared to the  $e^-$ -doped layer is minimal. Therefore, the ligand SOC elements and the Cr-based  $\langle d_{xz} | L_z | d_{yz} \rangle$  and  $\langle d_{xy} | L_z | d_{x^2-y^2} \rangle$  terms ensure that the neutral monolayer has an easy-axis anisotropy ( $\Delta E_n(\text{CrBr}_3) = 0.17 \text{ meV/f.u.}$ ) whereas the  $e^-$ -doped monolayer has an easy-plane anisotropy ( $\Delta E_{e^-}(\text{CrBr}_3) = -0.27 \text{ meV/f.u.}$ ).

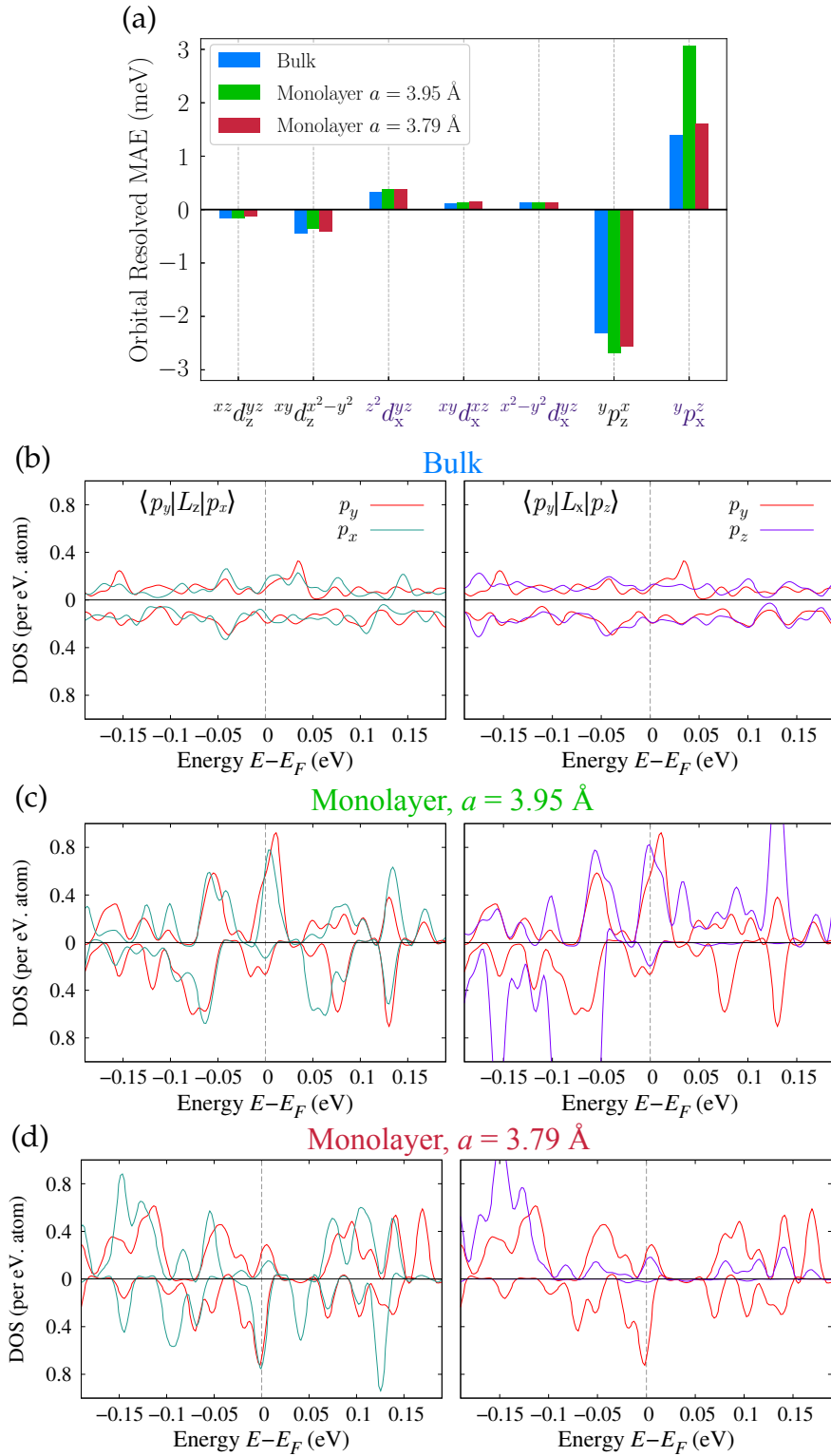


Figure 5.3: (a) The orbital resolved magnetic anisotropy energy of bulk and monolayer  $\text{CrTe}_2$ . DOS of (b) bulk, (c) and (d) Monolayers with lattice constants  $a = 3.95 \text{ \AA}$  and  $a = 3.79 \text{ \AA}$ . The first plot shows DOS of  $p_y$  and  $p_x$  orbitals corresponding to  $\langle p_y | L_z | p_x \rangle$  term whereas the second plot shows DOS of  $p_y$  and  $p_z$  orbitals corresponding to  $\langle p_y | L_x | p_z \rangle$  term.

### 5.2.3 CrTe<sub>2</sub> : Bulk and monolayers

We investigate 1T-CrTe<sub>2</sub>, which crystallizes in a triangular lattice with Cr atoms enclosed in a Te-octahedral field [237]. The Cr atoms adopt a quasi- $t_{2g}^3 e_g^0$  electronic configuration, resulting in a negligible orbital moment. In this compound, the SOC of the heavy ligand Te drives the magnetic anisotropy. The bulk phase orders in the FM state above room temperature ( $T_C = 310$  K), with the Cr-spins experiencing an in-plane single-ion anisotropy of  $A_z \sim -0.61$  meV [237–240]. Despite its metallic band structure, the localized moments ( $3.3 \mu_B/\text{Cr}$ ) remain nearly ideal, aligning closely with the  $S = 3/2$  state [194]. The ultrathin 1T-CrTe<sub>2</sub> is one of the few high temperature ( $T_C = 200$  K) 2D magnets [194, 241]. However, conflicting reports exist regarding the nature of its magnetic anisotropy, with some studies suggesting out-of-plane anisotropy [194, 241], while others propose in-plane anisotropy [239, 242, 243]. It turns out that this compound exhibits a high spin-lattice coupling, where strain from an external substrate can trigger a magnetic phase transition and/or reverse the magnetic anisotropy [216, 217, 244]. It was observed that the spin flip transition from easy-axis to easy-plane, occurs when the lattice parameter exceeds  $a < 3.87$  Å [244] in the monolayer. Although the monolayer CrTe<sub>2</sub> has a rich magnetic phase diagram, we limit our discussion to the FM phase to simplify the analysis.

We observe switching in magnetic anisotropy with dimensionality (bulk  $\rightarrow$  monolayer  $a = 3.95$  Å) and with strain (monolayer  $a = 3.95$  Å  $\rightarrow$  3.79 Å) [Figure 5.3 a]. Similar to CrI<sub>3</sub>, the sum of SOC elements in this compound is dictated by the ligand atom (Te), while the Cr- $d$  orbital SOC elements are almost negligible by comparison. The density of states reveal a highly dispersive electronic structure. We focus on a narrow energy range near the Fermi-level ( $\sim -0.10$  to 0.05 eV) [Figure 5.3 b-d]. In bulk, the density of  $p_y \downarrow$  ( $p_x \downarrow$ ) states near  $-0.042$  eV in VB strongly

interacts with  $p_x \uparrow$  ( $p_y \uparrow$ ) states near 0.025 eV of the CB, contributing to the in-plane anisotropy. It is weakened by the  $uu \perp$ -interaction of the  $p_x \uparrow$  and  $p_y \uparrow$  states in VB with their complementary  $\uparrow$  states in CB. However, only a single major  $p_z \downarrow$ - $p_y \uparrow$  ( $du$ ) interaction originates from the  $\langle p_y | L_x | p_z \rangle$  term due to the absence of a  $p_z \uparrow$  peak in the CB which leads to a weakened out-of-plane energy. Therefore, the overall magnetic anisotropy energy in bulk is  $\Delta E_b(\text{CrBr}_3) = -1.86 \text{ meV/f.u.}$

The density becomes sharper as we thin down from the bulk to the monolayer. The monolayer with lattice constant  $a = 3.95 \text{ \AA}$ , has large  $p_z \downarrow$  and  $p_z \uparrow$  peaks in the VB and CB respectively. Thus, the  $du \perp$ -interaction from the  $\langle p_y | L_x | p_z \rangle$  term increases drastically. The other terms remain comparable to those of the bulk. The sum of SOC elements in this structure is  $\Delta E_{m3.95}(\text{CrBr}_3) = 0.88 \text{ meV/f.u.}$  In the biaxially compressed monolayer with lattice constant  $a = 3.79 \text{ \AA}$ , the electronic structure evolves such that the bands become relatively dispersed. The  $p_z$  densities are pushed below the Fermi-level, with only the  $p_z \uparrow$ - $p_y \downarrow \perp$ -interaction coming from the  $\langle p_y | L_x | p_z \rangle$  term. The new densities  $p_x \uparrow$  and  $p_y \uparrow$  below the Fermi-level interacts with the  $p_y \downarrow$  and  $p_x \downarrow$  densities right above it, which is the major  $\parallel$ -interaction from the  $\langle p_y | L_z | p_x \rangle$  term. The sum of anisotropy energy terms in the strained monolayer is  $\Delta E_{m3.79}(\text{CrBr}_3) = -1.76 \text{ meV/f.u.}$  Thus, the out-of-plane magnetic anisotropy in the unstrained monolayer ( $a = 3.95 \text{ \AA}$ ) arises from the presence of  $p_z$  densities, while their suppression in the compressed monolayer, akin to  $e^-$  doping, induces in-plane magnetism.

#### 5.2.4 $\text{SrRu}_2\text{O}_6$ : Passivated and self-doped monolayers

We examine the 2D flakes of  $\text{SrRu}_2\text{O}_6$ , a high-temperature non-layered antiferromagnet ( $T_N \sim 560 \text{ K}$ ) [61, 62]. The Ru atoms are arranged in a honeycomb lattice composed of edge-sharing  $\text{RuO}_6$  octahedra. Despite of a  $t_{2g}^3$  electronic configuration, the magnetic moment is unexpectedly quenched to a mere  $1.4 \mu_B/\text{Ru}$  [61, 62].

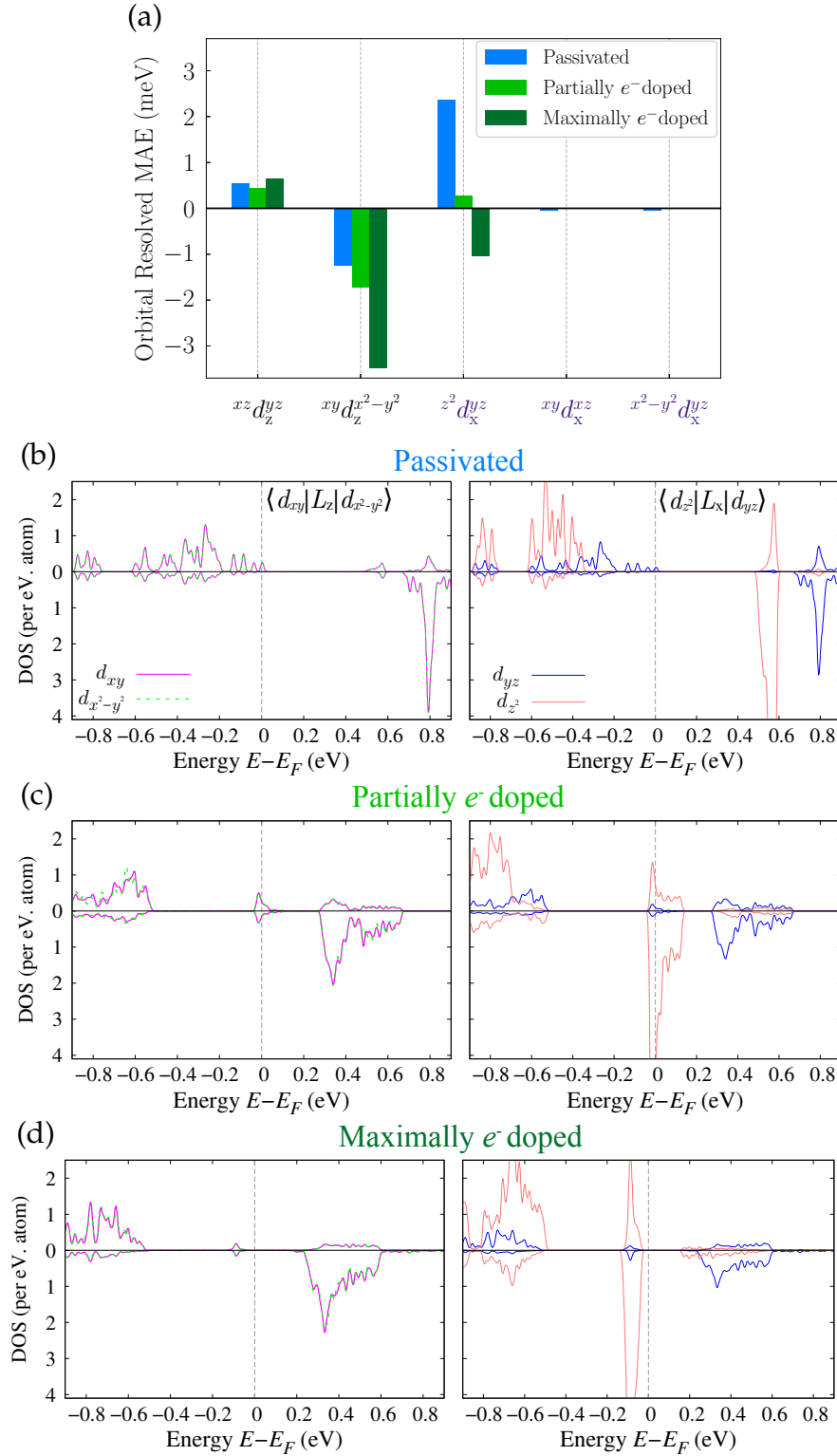


Figure 5.4: (a) The orbital resolved magnetic anisotropy energy of passivated and self-doped monolayers of  $\text{SrRu}_2\text{O}_6$ . DOS of (b) passivated, (c) partially  $e^-$ -doped and (d) maximally  $e^-$ -doped monolayers. The first plot shows DOS of  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals corresponding to the  $\langle d_{xy} | L_z | d_{x^2-y^2} \rangle$  term whereas the second plot shows DOS of  $d_{z^2}$  and  $d_{yz}$  orbitals corresponding to the  $\langle d_{z^2} | L_x | d_{yz} \rangle$  term.

The  $4d$  electrons of Ru atoms manifest intermediate electronic correlations and SOC, yet the material is classified as a band insulator [157–161]. As a result, the Ru-orbital moments are small but finite ( $m_{\text{o|Ru}} \sim 0.02 \mu_B$ ). Synthesizing 2D flakes of non van-der-Waals materials is quite challenging [56]. However, scientists successfully cleaved the weaker Sr-O bonds using a liquid exfoliation method [60]. The ultrathin flakes are terminated with or without Sr-layer with equal probability. Termination with Sr-layers on both sides of the monolayer maximally  $e^-$  dopes the system, while passivation on single side partially  $e^-$  dopes it [245]. Passivation on both sides mimics the bulk phase, and the absence of Sr-layer results in hole doping. The magnetic anisotropy stays out-of-plane for the passivated and hole-doped structures, but reverses to an in-plane axis in the  $e^-$ -doped structures [245].

We consider the orbital resolved magnetic anisotropy energies and find that it is controlled by  $d$ -orbital elements of Ru, owing to its intermediate SOC [Figure 5.4 a]. We discuss the primary elements: **1)**  $\langle d_{xy} | L_z | d_{x^2-y^2} \rangle$ : The  $uu$  interaction is out-of-plane and the  $ud$  interaction is in-plane. In the passivated case, very few  $d_{xy} \uparrow$  and  $d_{x^2-y^2} \uparrow$  states exist in the CB whereas the  $d_{xy} \downarrow$  and  $d_{x^2-y^2} \downarrow$  states have a high integrated density [Figure 5.4 b]. Thus, the  $d_{xy} \uparrow$ - $d_{x^2-y^2} \downarrow$  ( $d_{x^2-y^2} \uparrow$ - $d_{xy} \downarrow$ ) interaction between the VB and CB dominates, leading to an in-plane anisotropy energy. For the  $e^-$  doped structures, the  $d_{xy} \uparrow$  and  $d_{x^2-y^2} \uparrow$  states are vanishing which eliminates the  $uu \perp$ -interaction [Figure 5.4 c-d]. The  $d_{xy} \downarrow$  and  $d_{x^2-y^2} \downarrow$  states become more dispersive and the effective energy difference between the VB and CB states decreases. Both these factors give rise to a higher in-plane energy for the doped monolayers. **2)**  $\langle d_{z^2} | L_x | d_{yz} \rangle$ : In this case, the  $uu$  interaction is in-plane, while the  $ud$  interaction is out-of-plane, driven by the  $L_x$  operator. The conduction band (CB) of the passivated monolayer consists of a few  $d_{z^2} \uparrow$  and  $d_{yz} \uparrow$  states, in contrast to a significantly higher density of  $\downarrow$  states. Thus, the  $ud$  interactions prevail over the  $uu$  interactions between the VB and CB, resulting in an out-of-plane anisotropy energy.



In the  $e^-$  doped monolayers, the  $d_{z^2}$  states (both  $\uparrow$  and  $\downarrow$ ) get partly or fully filled for the partially  $e^-$  doped and maximally  $e^-$  doped monolayers, respectively. This virtually annihilates the  $d_{yz} \uparrow$ - $d_{z^2} \downarrow$  interaction between the VB and CB, thereby reducing the out-of-plane energy. Moreover, a new  $dd$  interaction between the filled  $d_{z^2} \downarrow$  state in VB and  $d_{yz} \downarrow$  state in CB emerges, which enhances the in-plane energy in this term. Adding the SOC matrix elements yields  $\Delta E_{neutral}(\text{SrRu}_2\text{O}_6) = 3.14$  meV/f.u. for the passivated monolayer,  $\Delta E_{partial-e^-}(\text{SrRu}_2\text{O}_6) = -2.00$  meV/f.u. for the partially doped monolayer and  $\Delta E_{max-e^-}(\text{SrRu}_2\text{O}_6) = -7.75$  meV/f.u. for the maximally doped monolayer. Therefore, the occupation of the  $d_{z^2}$  orbital is the primary factor driving the spin reorientation in monolayer  $\text{SrRu}_2\text{O}_6$ .

### 5.3 Summary

We investigated the mechanisms driving magnetic anisotropy in  $d^3$  compounds, focusing on honeycomb lattices in the FM phase ( $\text{CrI}_3$ ,  $\text{CrBr}_3$ ) and in the AFM phase ( $\text{SrRu}_2\text{O}_6$ ) and a triangular lattice in the FM phase ( $\text{CrTe}_2$ ). Expectedly, the dominant SOC elements originate from atoms with higher spin-orbit coupling. It was observed that, in general,  $e^-$  doping beyond a certain threshold induces easy-plane anisotropy. Decreased dispersion with decreasing dimensionality (bulk and monolayer  $a = 3.95$  Å  $\text{CrTe}_2$ ) and enhanced strain (monolayer  $a = 3.79$  Å  $\text{CrTe}_2$ ) also promotes in-plane spin alignment. In  $\text{CrI}_3$ ,  $\text{CrTe}_2$  and  $\text{SrRu}_2\text{O}_6$ , the key factor determining the magnetic anisotropy was the presence or absence of orbitals with lobes along the  $z$ -direction i.e.  $p_z$  and  $d_{z^2}$ , near the Fermi-level. However, the anisotropy mechanism in  $\text{CrBr}_3$  is more complex. We hope this study provides insights to both experimentalists and theorists for designing materials with a specific magnetic anisotropy orientation.

## CHAPTER 6

### SUMMARY AND FUTURE OUTLOOK

Two-dimensional magnetism has emerged as a dynamic frontier in condensed matter physics, driven by the isolation of intrinsic magnetic order in atomically thin materials such as  $\text{CrI}_3$  and  $\text{Cr}_2\text{Ge}_2\text{Te}_6$  [9, 10]. These materials exhibit long-range magnetic order at finite temperatures due to significant magnetic anisotropy, circumventing the Mermin-Wagner theorem and enabling the exploration of spin interactions in reduced dimensions. This breakthrough has allowed researchers to probe low-dimensional magnetism, including quantum spin fluctuations, Ising and XY-type interactions, and topological spin textures such as skyrmions and merons [202, 233, 246, 247].

On the materials side, the field has moved beyond conventional van der Waals (vdW) magnets to include non-vdW systems like  $\text{CrSe}$  [248] and  $\text{Mn}_3\text{N}_2$  [249], although much of the current research still revolves around  $3d$  transition-metal compounds. Remarkably, few-layer  $\text{Fe}_3\text{GeTe}_2$  has exhibited ferromagnetism near room temperature [170], pushing the boundaries of magnetic ordering temperatures in 2D systems. Similarly,  $\text{CrBr}_3$  has shown promising room-temperature magnetic signatures in bilayer structures [172].

Technological progress has paralleled these material discoveries. Chemical vapor deposition, molecular beam epitaxy, and liquid-phase exfoliation have significantly improved the synthesis of high-quality 2D magnets [60, 239, 248, 250–255]. These advancements have facilitated the development of vdW heterostructures where 2D magnets are coupled with other functional layers - leading to devices

such as magnetic tunnel junctions (MTJs) and gate-tunable magnetic transistors [256]. The integration of 2D magnets with topological insulators (e.g.,  $\text{CrI}_3/\text{Bi}_2\text{Te}_3$ ) has resulted in proximity-induced quantum phenomena, including the observation of the quantum anomalous Hall effect at elevated temperatures [208]. In parallel, coherent magnon excitation and manipulation in 2D-magnet-based hybrid systems have opened new possibilities for magnonic and spintronic devices, offering pathways for energy-efficient information storage and processing [257, 258]. Advanced imaging techniques like spin-polarized scanning tunneling microscopy and Lorentz transmission electron microscopy have revealed topological spin textures such as skyrmions and merons in 2D magnetic systems [247, 258–261].

However, the field continues to face key challenges. Many 2D magnets, such as  $\text{CrI}_3$  and  $\text{Fe}_3\text{GeTe}_2$ , are air-sensitive and degrade upon exposure to ambient conditions, requiring encapsulation with materials like hexagonal boron nitride [10, 262, 263]. Scalable synthesis of large-area, defect-free monolayers remains a bottleneck, as most existing techniques yield micron-sized flakes or introduce lattice imperfections that suppress intrinsic magnetic properties [1]. Device integration also presents hurdles: interface issues such as lattice mismatch, strain, and interfacial defects often impair the performance of magneto-electronic devices, particularly in MTJs where high tunneling magnetoresistance is critical [264].

Achieving robust, room-temperature magnetism in monolayers remains an open challenge. While materials such as  $\text{Fe}_3\text{GeTe}_2$ ,  $\text{CrBr}_3$ ,  $\text{Fe}_5\text{GeTe}_2$  and  $\text{CrTe}_2$  have demonstrated magnetic ordering above 300 K in few-layer configurations, [170, 172, 194, 265] their stability and tunability are still under active investigation. Furthermore, most research to date has concentrated on ferromagnets, while 2D antiferromagnets with their zero net magnetization, ultrafast spin dynamics, and resilience to external magnetic fields hold substantial promise for spintronic and quantum computing applications [163, 266, 267].

Theoretical studies of two-dimensional magnets increasingly rely on effective spin Hamiltonian models, with parameters such as exchange couplings and anisotropies extracted from first principles calculations. This approach enables the exploration of finite-temperature magnetic behavior, phase transitions, and anisotropy driven phenomena beyond the ground state.

In this context, the present thesis addresses several critical and timely aspects in the field of 2D magnetism. While much of the existing research has focused on *3d*-based vdW materials, this work pioneers the exploration of layered *4d* and *5d* transition metal oxide nanosheets as a new and compelling platform for 2D magnetism. These systems offer a fundamentally different landscape, where the balance among electron correlation, spin-orbit coupling, and itinerant behavior leads to rich and tunable magnetic phenomena [31]. Building upon the recent experimental realization of such nanosheets via chemical exfoliation, the thesis investigates their magnetic ground states and emergent properties, thus expanding the scope of low-dimensional magnetism into new material classes. This direction not only complements existing studies but also opens pathways to uncover unconventional magnetic behavior in non-vdW systems.

$\text{Na}_2\text{IrO}_3$ , a proximate Kitaev spin-liquid candidate in its bulk form, evolves when thinned down to the 2D limit [42]. How do the competing Kitaev interactions, which promote a disordered quantum spin-liquid state, and Heisenberg interactions, which drive magnetic order, evolve in  $\text{Na}_2\text{IrO}_3$ ? The critical question is whether, in the 2D limit, nanosheets of  $\text{Na}_2\text{IrO}_3$  shift toward the Kitaev spin-liquid state or deviate further from it. The second question addressed in this thesis is the potential discovery of a room-temperature antiferromagnet in 2D systems. While 2D ferromagnetic materials have garnered significant attention, antiferromagnetic materials in two dimensions have received comparatively less focus, despite their potential for robust spintronic applications and high stability against

external perturbations [163]. Furthermore, regardless of their magnetic state, the ordering of these materials has been restricted to cryogenic temperatures due to enhanced thermal spin fluctuations and weaker spin-orbit coupling [30]. This limitation raises a natural question: can we discover 2D materials with higher transition temperatures, enabling their use in future technologies? In this context, we explore  $\text{SrRu}_2\text{O}_6$  nanosheets as a candidate to overcome these limitations and investigate their intricate electronic and magnetic phase transitions [61, 62]. Results are obtained by combining the first-principles calculations with Hamiltonian modelling and Monte Carlo simulations. For both systems, first rigorous comparisons are drawn for the available experimental results for the bulk, before venturing into the unknown territory of 2D nanosheets. Building on these two broad contexts, we investigate the intricate electronic and magnetic phase transitions in  $\text{Na}_2\text{IrO}_3$  and  $\text{SrRu}_2\text{O}_6$  oxide nanosheets.

We conduct a thorough investigation of magnetism in ultrathin flakes of the correlated oxide  $\text{Na}_2\text{IrO}_3$ , which is known for its proximity to a quantum spin liquid state in the bulk form [42]. In a surprising result, magnetism persists even at the monolayer limit, with enhanced Heisenberg and off-diagonal exchange interactions that significantly strengthen the zigzag antiferromagnetic ordering [162]. In other words, the  $\text{Na}_2\text{IrO}_3$  nanosheets move further away from the quantum spin-liquid state. This heightened magnetic behavior in the 2D limit contrasts sharply with the typical trend seen in van der Waals magnets, where magnetism often weakens in reduced dimensions. We find that passivated flakes maintain their Mott insulator properties, while flakes with naturally induced carrier doping exhibit an insulator-to-metal transition. This electronic transition is accompanied by a shift from an antiferromagnetic to a ferromagnetic state. Consequently, multilayer flakes of  $\text{Na}_2\text{IrO}_3$  show promise for use in low-temperature spintronic devices.

The investigation of  $\text{SrRu}_2\text{O}_6$  nanosheets has unveiled intriguing electronic and magnetic properties that hold promise for advanced spintronic applications [60]. Ultrathin flakes of  $\text{SrRu}_2\text{O}_6$  exhibited remarkably robust antiferromagnetic ordering, with Néel temperatures surpassing 430 K, even at the monolayer limit - an environment where spin fluctuations typically dominate and destabilize magnetic ordering [245]. The remarkable retention of high magnetic ordering temperatures, despite the reduced dimensionality, is particularly noteworthy. In addition, the ability to modulate both the electronic and magnetic properties of these nanosheets through charge carrier doping offers a versatile platform for fine-tuning their behavior. These combined characteristics position  $\text{SrRu}_2\text{O}_6$  as a promising candidate for future room-temperature antiferromagnetic spintronic applications, where both stability and tunability of magnetic properties are crucial.

In addition to investigating the electronic and magnetic transitions, the thesis also explores the underlying mechanisms that govern magnetic anisotropy in two-dimensional magnets, which is crucial to their long-range ordering [196]. Focusing on  $d^3$  compounds such as  $\text{CrI}_3$  [171],  $\text{CrBr}_3$  [172],  $\text{CrTe}_2$  [194], and  $\text{SrRu}_2\text{O}_6$  [245], we identified key factors that significantly influence the preferential spin alignment, particularly spin-orbit coupling and the orbital geometry near the Fermi level. Our analysis revealed that the interplay between doping, strain, and dimensionality can systematically induce a transition from out-of-plane to in-plane spin alignment, highlighting the tunability of magnetic properties in these materials. Crucially, the presence or absence of orbitals with lobes along the  $z$ -direction - specifically  $p_z$  and  $d_{z^2}$  orbitals, emerged as a central factor in determining the magnetic anisotropy. These findings underscore the importance of orbital configurations in controlling magnetic behavior and provide new insights into the design of materials with tailored anisotropic properties.

While these findings significantly deepen our understanding of 2D magnetism

in non-vdW correlated oxides, they remain subject to experimental validation. Although both oxides have been chemically exfoliated, improved control over the synthesis process is necessary to achieve nanosheets with the desired thickness and large area [55]. Currently, experimental efforts have successfully synthesized nanosheets consisting of three to five monolayers [60]. Moving forward, it will be intriguing to achieve the synthesis of individual monolayers. While structural characterizations can be performed experimentally, electrical and magnetic characterizations are still pending. In this regard, experimental techniques such as magneto-optic Kerr effect and nitrogen-vacancy magnetometry will prove valuable for investigating the magnetic properties [20, 21]. As emphasized in the thesis, chemically exfoliated oxide nanosheets can be naturally charge-doped depending on their surface termination, which can significantly impact their electronic and magnetic properties. Therefore, greater experimental control over their surface chemistry is necessary. In particular, the volatility of Na-ions in  $\text{Na}_2\text{IrO}_3$  demands careful consideration during synthesis and handling [127].

This research opens several promising avenues for future investigation. One particularly compelling direction is the study of other layered transition metal oxides, such as ruthenates and iridates, where the interplay of spin-orbit coupling and electronic correlations can give rise to exotic ground states [268]. The added effect of electron confinement in the two-dimensional limit introduces a new tuning parameter, potentially leading to emergent phenomena beyond those observed in the bulk. Magneto-transport measurements will be instrumental in probing the electronic and magnetic ground states of these systems across different thickness regimes [2, 11, 24]. Furthermore, examining the response of these nanosheets to externally induced strain, especially when transferred onto various substrates offers another rich area of exploration, though this aspect lies beyond the scope of the present thesis.

This work marks a promising beginning for oxide nanosheets in the realm of two-dimensional magnetism, highlighting their potential as a versatile platform for future technologies. It is anticipated that these findings will motivate continued experimental and theoretical investigations into their fundamental properties and stimulate efforts toward their integration into device architectures, ultimately paving the way for novel applications in spintronics and beyond.





## BIBLIOGRAPHY

- [1] C. Gong and X. Zhang, *Science* **363**, (2019).
- [2] V. P. Ningrum *et al.*, *Research* **2020**, 1768918 (2020).
- [3] N. D. Mermin and H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966).
- [4] P. C. Hohenberg, *Phys. Rev.* **158**, 383 (1967).
- [5] V. L. Berezinsky, *Sov. Phys. JETP* **32**, 493 (1971).
- [6] J. M. Kosterlitz and D. J. Thouless, *Journal of Physics C: Solid State Physics* **6**, 1181 (1973).
- [7] L. Onsager, *Phys. Rev.* **65**, 117 (1944).
- [8] C. A. F. Vaz, J. A. C. Bland, and G. Lauhoff, *Reports on Progress in Physics* **71**, 056501 (2008).
- [9] C. Gong *et al.*, *Nature* **546**, 265 (2017).
- [10] B. Huang *et al.*, *Nature* **546**, 270 (2017).
- [11] P. Liu *et al.*, *iScience* **26**, 107584 (2023).
- [12] S. Y. Park *et al.*, *Nano Letters* **20**, 95 (2020), pMID: 31752490.
- [13] H. L. Zhuang, P. R. C. Kent, and R. G. Hennig, *Phys. Rev. B* **93**, 134407 (2016).
- [14] M. Zubair *et al.*, *Phys. Rev. Mater.* **8**, 054604 (2024).
- [15] J. Guo, J. Zhang, Y. Di, and Z. Gan, *Nanomaterials* **14**, (2024).

- [16] B. Dieny *et al.*, Journal of Magnetism and Magnetic Materials **93**, 101 (1991).
- [17] J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, Phys. Rev. Lett. **74**, 3273 (1995).
- [18] E. C. Ahn, npj 2D Materials and Applications **4**, 17 (2020).
- [19] B. Dieny and M. Chshiev, Rev. Mod. Phys. **89**, 025008 (2017).
- [20] J. Kerr, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science **3**, 321 (1877).
- [21] L. Thiel *et al.*, Science **364**, 973 (2019).
- [22] K. Kim, J.-U. Lee, and H. Cheong, Nanotechnology **30**, 452001 (2019).
- [23] Q. Li *et al.*, Nano Letters **18**, 5974 (2018), pMID: 30114354.
- [24] M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, Nature Nanotechnology **14**, 408 (2019).
- [25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [26] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [27] H. Xiang *et al.*, Dalton Trans. **42**, 823 (2013).
- [28] H. J. Xiang *et al.*, Phys. Rev. B **84**, 224429 (2011).
- [29] G. Pizzi *et al.*, Journal of Physics: Condensed Matter **32**, 165902 (2020).
- [30] M. Och *et al.*, Nanoscale **13**, 2157 (2021).
- [31] W. Witczak-Krempa, G. Chen, Y. B. Kim, and L. Balents, Annual Review of Condensed Matter Physics **5**, 57 (2014).
- [32] H. Takagi *et al.*, Nature Reviews Physics **1**, 264 (2019).

- [33] L. Balents, *Nature* **464**, 199 (2010).
- [34] Y. Zhou, K. Kanoda, and T.-K. Ng, *Rev. Mod. Phys.* **89**, 025003 (2017).
- [35] J. Knolle and R. Moessner, *Annual Review of Condensed Matter Physics* **10**, 451 (2019).
- [36] C. Broholm *et al.*, *Science* **367**, eaay0668 (2020).
- [37] P. Anderson, *Materials Research Bulletin* **8**, 153 (1973).
- [38] C. Lhuillier and P. Sindzingre, (2002).
- [39] B. S. Shastry and B. Sutherland, *Phys. Rev. Lett.* **47**, 964 (1981).
- [40] S. E. Palmer and J. T. Chalker, *Phys. Rev. B* **62**, 488 (2000).
- [41] A. Kitaev, *Annals of Physics* **321**, 2 (2006), january Special Issue.
- [42] A. Banerjee *et al.*, *Nat. Mater.* **15**, 733 (2016).
- [43] A. Banerjee *et al.*, *Science* **356**, 1055 (2017).
- [44] S. Hwan Chun *et al.*, *Nat. Phys.* **11**, 462 (2015).
- [45] K. Kitagawa *et al.*, *Nature* **554**, 341 (2018).
- [46] G. Khaliullin, *Prog. Theor. Phys. Suppl.* **160**, 155 (2005).
- [47] G. Jackeli and G. Khaliullin, *Phys. Rev. Lett.* **102**, 017205 (2009).
- [48] J. G. Rau, E. K.-H. Lee, and H.-Y. Kee, *Phys. Rev. Lett.* **112**, 077204 (2014).
- [49] J. G. Rau and H.-Y. Kee, arXiv:1408.4811 (2014).
- [50] H. B. Cao *et al.*, *Phys. Rev. B* **93**, 134423 (2016).
- [51] S. K. Choi *et al.*, *Phys. Rev. Lett.* **108**, 127204 (2012).

- [52] R. Akhter and S. S. Maktedar, *Journal of Materiomics* **9**, 1196 (2023).
- [53] M. Khazaei *et al.*, *Phys. Chem. Chem. Phys.* **20**, 8579 (2018).
- [54] G. Li *et al.*, *Langmuir* **33**, 9000 (2017), pMID: 28805394.
- [55] H. Xie *et al.*, *iScience* **25**, 103598 (2022).
- [56] F. Wang *et al.*, *Advanced Functional Materials* **27**, 1603254 (2017).
- [57] A. Puthirath Balan *et al.*, *Nature Nanotechnology* **13**, 602 (2018).
- [58] T. P. Yadav *et al.*, *Advanced Materials Interfaces* **5**, 1800549 (2018).
- [59] A. Puthirath Balan *et al.*, *Chemistry of Materials* **30**, 5923 (2018).
- [60] S. Homkar *et al.*, *ACS Applied Nano Materials* **4**, 9313 (2021).
- [61] C. I. Hiley *et al.*, *Phys. Rev. B* **92**, 104413 (2015).
- [62] W. Tian *et al.*, *Phys. Rev. B* **92**, 100404 (2015).
- [63] M. Born and R. Oppenheimer, *Annalen der Physik* **389**, 457 (1927).
- [64] D. R. Hartree, *Mathematical Proceedings of the Cambridge Philosophical Society* **24**, 89–110 (1928).
- [65] V. Fock, *Zeitschrift für Physik* **61**, 126 .
- [66] L. Hedin and B. I. Lundqvist, *Journal of Physics C: Solid State Physics* **4**, 2064 (1971).
- [67] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [68] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [69] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B* **52**, R5467 (1995).

- [70] S. L. Dudarev *et al.*, Phys. Rev. B **57**, 1505 (1998).
- [71] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
- [72] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
- [73] J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015).
- [74] A. P. Bartók and J. R. Yates, The Journal of Chemical Physics **150**, 161101 (2019).
- [75] Y. Yamamoto *et al.*, arXiv **2004.13393**, (2020).
- [76] J. W. Furness *et al.*, J. Phys. Chem. Lett. **11**, 8208 (2020).
- [77] D. C. Johnston *et al.*, Phys. Rev. B **84**, 094445 (2011).
- [78] J. L. Lado and J. Fernández-Rossier, 2D Materials **4**, 035002 (2017).
- [79] Y. S. Hou, J. H. Yang, H. J. Xiang, and X. G. Gong, Phys. Rev. B **98**, 094401 (2018).
- [80] C. Xu, J. Feng, H. Xiang, and L. Bellaiche, npj Computational Materials **4**, 57 (2018).
- [81] N. Metropolis and S. Ulam, Journal of the American Statistical Association **44**, 335 (1949), pMID: 18139350.
- [82] K. Binder and D. W. Heermann, *Monte Carlo simulation in statistical physics, Graduate texts in physics*, 5 ed. (Springer, Berlin, Germany, 2010).
- [83] N. Metropolis *et al.*, The Journal of Chemical Physics **21**, 1087 (1953).
- [84] G. Marsaglia, Journal of Statistical Software **1**, 1 (1972).

- [85] M. Matsumoto and T. Nishimura, *ACM Transactions on Modeling and Computer Simulation* **8**, 3 (1998).
- [86] Y. Shimizu *et al.*, *Phys. Rev. Lett.* **91**, 107001 (2003).
- [87] T. Itou *et al.*, *Phys. Rev. B* **77**, 104413 (2008).
- [88] A. Olariu *et al.*, *Phys. Rev. Lett.* **100**, 087202 (2008).
- [89] M. Yamashita *et al.*, *Science* **328**, 1246 (2010).
- [90] T.-H. Han *et al.*, *Nature* **492**, 406 (2012).
- [91] M. Fu, T. Imai, T.-H. Han, and Y. S. Lee, *Science* **350**, 655 (2015).
- [92] J. Chaloupka, G. Jackeli, and G. Khaliullin, *Phys. Rev. Lett.* **105**, 027204 (2010).
- [93] J. c. v. Chaloupka, G. Jackeli, and G. Khaliullin, *Phys. Rev. Lett.* **110**, 097204 (2013).
- [94] Y. Singh and P. Gegenwart, *Phys. Rev. B* **82**, 064412 (2010).
- [95] Y. Singh *et al.*, *Phys. Rev. Lett.* **108**, 127203 (2012).
- [96] R. D. Johnson *et al.*, *Phys. Rev. B* **92**, 235119 (2015).
- [97] R. Comin *et al.*, *Phys. Rev. Lett.* **109**, 266406 (2012).
- [98] B. H. Kim, T. Shirakawa, and S. Yunoki, *Phys. Rev. Lett.* **117**, 187201 (2016).
- [99] X. Xi *et al.*, *Phys. Rev. B* **98**, 125117 (2018).
- [100] B. J. Kim *et al.*, *Phys. Rev. Lett.* **101**, 076402 (2008).
- [101] B. J. Kim *et al.*, *Science* **323**, 1329 (2009).

- [102] S. M. Winter *et al.*, Journal of Physics: Condensed Matter **29**, 493002 (2017).
- [103] F. Ye *et al.*, Phys. Rev. B **85**, 180403 (2012).
- [104] X. Liu *et al.*, Phys. Rev. B **83**, 220403 (2011).
- [105] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- [106] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- [107] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- [108] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- [109] A. Togo and I. Tanaka, Scripta Materialia **108**, 1 (2015).
- [110] F. Eriksson, E. Fransson, and P. Erhart, Adv. Theor. Simul. **2**, 1800184 (2019).
- [111] S. Toth and B. Lake, J. Phys.: Condens. Matter **27**, 166002 (2015).
- [112] H. Gretarsson *et al.*, Phys. Rev. Lett. **110**, 076402 (2013).
- [113] C. H. Sohn *et al.*, Phys. Rev. B **88**, 085125 (2013).
- [114] M. Kim, B. H. Kim, and B. I. Min, Phys. Rev. B **93**, 195135 (2016).
- [115] Y. Li, K. Foyevtsova, H. O. Jeschke, and R. Valentí, Phys. Rev. B **91**, 161101 (2015).
- [116] V. M. Katukuri *et al.*, New Journal of Physics **16**, 013056 (2014).
- [117] M. Ge *et al.*, Phys. Rev. B **84**, 100402 (2011).
- [118] M. A. Laguna-Marco *et al.*, Phys. Rev. Lett. **105**, 216407 (2010).
- [119] A. Ruiz *et al.*, Nat. Commun. **8**, 961 (2017).
- [120] K. Hu, F. Wang, and J. Feng, Phys. Rev. Lett. **115**, 167204 (2015).



- [121] F. Lüpke *et al.*, Phys. Rev. B **91**, 041405 (2015).
- [122] L. Moreschini *et al.*, Phys. Rev. B **96**, 161116 (2017).
- [123] M. Naguib *et al.*, ACS Nano **6**, 1322 (2012).
- [124] M. Naguib *et al.*, J. Am. Chem. Soc. **135**, 15966 (2013).
- [125] B. Anasori *et al.*, ACS Nano **9**, 9507 (2015).
- [126] M. A. Tovar-Olvera, P. Ruiz-Díaz, and M. Saubanère, Phys. Rev. B **105**, 094413 (2022).
- [127] A. Vasdev *et al.*, J. Appl. Phys. **124**, 055102 (2018).
- [128] S. M. Winter, Y. Li, H. O. Jeschke, and R. Valentí, Phys. Rev. B **93**, 214431 (2016).
- [129] L. Janssen, E. C. Andrade, and M. Vojta, Phys. Rev. B **96**, 064430 (2017).
- [130] B. Yang *et al.*, Nat. Mater. **22**, 50 (2023).
- [131] S. G. Ovchinnikov, Physics-Uspekhi **46**, 21 (2003).
- [132] G. Cao *et al.*, Mater. Sci. Eng. B **63**, 76 (1999).
- [133] Y. Maeno *et al.*, Nature **372**, 532 (1994).
- [134] F. Lichtenberg, A. Catana, J. Mannhart, and D. G. Schlom, Appl. Phys. Lett. **60**, 1138 (1992).
- [135] Z. Mao, Y. Maenoab, and H. Fukazawa, Mater. Res. Bull. **35**, 1813 (2000).
- [136] A. Pustogow *et al.*, Nature **574**, 72 (2019).
- [137] R. S. Perry *et al.*, Phys. Rev. Lett. **86**, 2661 (2001).

- [138] C. H. Mousatov, E. Berg, and S. A. Hartnoll, Proc. Natl. Acad. Sci. U. S. A. **117**, 2852 (2020).
- [139] D. J. Singh and I. I. Mazin, Phys. Rev. B **63**, 165101 (2001).
- [140] G. Cao, S. McCall, J. E. Crow, and R. P. Guertin, Phys. Rev. Lett. **78**, 1751 (1997).
- [141] X. Ke *et al.*, Phys. Rev. B **84**, 014422 (2011).
- [142] D. A. Sokolov *et al.*, Nat. Phys. **15**, 671 (2019).
- [143] L. Capogna *et al.*, J. Magn. Magn. Mater. **493**, 165698 (2020).
- [144] H. Zheng *et al.*, Phys. Rev. B **98**, 064418 (2018).
- [145] J. M. Longo, P. M. Raccah, and J. B. Goodenough, J. Appl. Phys. **39**, 1327 (1968).
- [146] G. Koster *et al.*, Rev. Mod. Phys. **84**, 253 (2012).
- [147] H. Boschker *et al.*, Phys. Rev. X **9**, 011027 (2019).
- [148] J. A. Sears *et al.*, Phys. Rev. B **91**, 144420 (2015).
- [149] S.-H. Do *et al.*, Nat. Phys. **13**, 1079 (2017).
- [150] N. Janša *et al.*, Nat. Phys. **14**, 786 (2018).
- [151] S. Widmann *et al.*, Phys. Rev. B **99**, 094415 (2019).
- [152] C. I. Hiley *et al.*, Angew. Chem. Int. Ed. **53**, 4423 (2014).
- [153] T. Marchandier *et al.*, Chem. Mater. **32**, 8471 (2020).
- [154] E. E. Rodriguez *et al.*, Phys. Rev. Lett. **106**, 067201 (2011).

- [155] M. Avdeev *et al.*, J. Am. Chem. Soc. **133**, 1654 (2011).
- [156] Y. G. Shi *et al.*, Phys. Rev. B **80**, 161104 (2009).
- [157] H. Suzuki *et al.*, Nat. Mater. **18**, 563 (2019).
- [158] S. Streltsov, I. I. Mazin, and K. Foyevtsova, Phys. Rev. B **92**, 134408 (2015).
- [159] A. Hariki, A. Hausoel, G. Sangiovanni, and J. Kuneš, Phys. Rev. B **96**, 155135 (2017).
- [160] S. Okamoto *et al.*, Sci. Rep. **7**, 11742 (2017).
- [161] D. Csontosová *et al.*, Phys. Rev. B **108**, 195137 (2023).
- [162] D. K. Roy and M. Kabir, Phys. Rev. B **110**, L020403 (2024).
- [163] T. Jungwirth, X. Marti, P. Wadley, and J. Wunderlich, Nat. Nanotechnol. **11**, 231 (2016).
- [164] V. Baltz *et al.*, Rev. Mod. Phys. **90**, 015005 (2018).
- [165] J. Han *et al.*, Nat. Mater. **22**, 684 (2023).
- [166] J.-U. Lee *et al.*, Nano Lett. **16**, 7433 (2016).
- [167] S. Rahman, J. F. Torres, A. R. Khan, and Y. Lu, ACS Nano **15**, 17175 (2021).
- [168] Q. H. Wang *et al.*, ACS Nano **16**, 6960 (2022).
- [169] T. Olsen, 2D Mater. **11**, 033005 (2024).
- [170] Y. Deng *et al.*, Nature **563**, 94 (2018).
- [171] C. K. Singh and M. Kabir, Phys. Rev. B **103**, 214411 (2021).
- [172] C. K. Singh and M. Kabir, Phys. Rev. Mater. **6**, 084407 (2022).

- [173] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993).
- [174] J. Paier *et al.*, The Journal of Chemical Physics **124**, 154709 (2006).
- [175] R. F. L. Evans *et al.*, J. Phys. Condens. Matter **26**, 103202 (2014).
- [176] D. J. Singh, Phys. Rev. B **91**, 214420 (2015).
- [177] D. I. Khomskii, *Transition Metal Compounds* (Cambridge University Press, Cambridge, 2014).
- [178] J. Mravlje, M. Aichhorn, and A. Georges, Phys. Rev. Lett. **108**, 197202 (2012).
- [179] D. Wang, W.-S. Wang, and Q.-H. Wang, Phys. Rev. B **92**, 075112 (2015).
- [180] J. Goodenough, *Magnetism and the chemical bond, Interscience monographs on chemistry: Inorganic chemistry section* (Interscience Publishers, New York, 1963).
- [181] T. Takeda and S. Ohara, J. Phys. Soc. Jpn. **37**, 275 (1974).
- [182] S. Calder *et al.*, Phys. Rev. Lett. **108**, 257209 (2012).
- [183] P. Manuel *et al.*, Phys. Rev. B **84**, 174430 (2011).
- [184] P. Battle and W. Macklin, J. Solid State Chem. **52**, 138 (1984).
- [185] J. Darriet, F. Grasset, and P. D. Battle, Mater. Res. Bull. **32**, 139 (1997).
- [186] Y. Gogotsi and B. Anasori, ACS Nano **13**, 8491 (2019).
- [187] K. R. G. Lim *et al.*, Nat. Synth. **1**, 601 (2022).
- [188] Y. An *et al.*, Phys. Rev. B **101**, 075416 (2020).
- [189] V. Zólyomi, N. D. Drummond, and V. I. Fal'ko, Phys. Rev. B **89**, 205416 (2014).

- [190] S. Radescu, D. Machon, and P. Mélinon, *Phys. Rev. Mater.* **3**, 074002 (2019).
- [191] W. Tang, E. Sanville, and G. Henkelman, *Journal of Physics: Condensed Matter* **21**, 084204 (2009).
- [192] M. Wang *et al.*, *npj 2D Mater. Appl.* **8**, 22 (2024).
- [193] Z. Ni *et al.*, *Nat. Nanotechnol.* **16**, 782 (2021).
- [194] X. Zhang *et al.*, *Nat. Commun.* **12**, 2492 (2021).
- [195] G. Long *et al.*, *Nano Lett.* **20**, 2452 (2020).
- [196] D.-s. Wang, R. Wu, and A. J. Freeman, *Phys. Rev. B* **47**, 14932 (1993).
- [197] R. A. Duine, K.-J. Lee, S. S. P. Parkin, and M. D. Stiles, *Nat. Phys.* **14**, 217 (2018).
- [198] A. S. Núñez, R. A. Duine, P. Haney, and A. H. MacDonald, *Phys. Rev. B* **73**, 214426 (2006).
- [199] C. Boix-Constant *et al.*, *Nat. Mater.* **23**, 212 (2024).
- [200] Y. Chen *et al.*, *Nature* **632**, 1045 (2024).
- [201] A. J. Healey *et al.*, Imaging magnetic switching in orthogonally twisted stacks of a van der Waals antiferromagnet, 2024.
- [202] K. Kim *et al.*, *Nat. Commun.* **10**, 345 (2019).
- [203] Q. Song *et al.*, *Nature* **602**, 601 (2022).
- [204] J.-J. Xian *et al.*, *Nature Communications* **13**, 257 (2022).
- [205] B. Dieny and M. Chshiev, *Rev. Mod. Phys.* **89**, 025008 (2017).
- [206] J. Železný *et al.*, *Nature Physics* **14**, 220 (2018).

- [207] B. G. Park *et al.*, Nature Materials **10**, 347 (2011).
- [208] Y. Hou, J. Kim, and R. Wu, Science Advances **5**, eaaw1874 (2019).
- [209] J. Wen *et al.*, npj Quantum Materials **4**, 12 (2019).
- [210] J. Li *et al.*, Phys. Rev. B **100**, 121103 (2019).
- [211] H. Fu, C.-X. Liu, and B. Yan, Science Advances **6**, eaaz0948 (2020).
- [212] W. Zhuo *et al.*, Advanced Materials **33**, 2008586 (2021).
- [213] C. Chen *et al.*, Phys. Rev. Lett. **125**, 056402 (2020).
- [214] Y. Ren, Z. Qiao, and Q. Niu, Phys. Rev. Lett. **124**, 166804 (2020).
- [215] L. Webster and J.-A. Yan, Phys. Rev. B **98**, 144411 (2018).
- [216] Z. Lei *et al.*, The Journal of Physical Chemistry C **127**, 17179 (2023).
- [217] D. Feng *et al.*, Nanoscale **15**, 1561 (2023).
- [218] H. S. Sarmah and S. Ghosh, Journal of Physics D: Applied Physics **56**, 345002 (2023).
- [219] A. J. Healey *et al.*, (2024).
- [220] P. Gao *et al.*, Journal of Physics: Condensed Matter **35**, 405801 (2023).
- [221] J. Kim *et al.*, Nano Letters **20**, 929 (2020), pMID: 31885277.
- [222] W. Pan, Phys. Rev. B **106**, 125122 (2022).
- [223] S. Ji *et al.*, Phys. Rev. B **107**, 035438 (2023).
- [224] Z. Li, B. Chen, S. Shan, and Y. Zhang, RSC Adv. **13**, 9924 (2023).
- [225] J.-J. Liao *et al.*, Phys. Rev. B **107**, 184403 (2023).

- [226] S. B. Song, Z. Wang, and R. Q. Wu, Phys. Rev. B **107**, 184436 (2023).
- [227] M. Tang *et al.*, Nature Electronics **6**, 28 (2023).
- [228] J. Hu and R. Wu, Phys. Rev. Lett. **110**, 097202 (2013).
- [229] J. Stöhr and H. Siegmann, *Magnetism: From Fundamentals to Nanoscale Dynamics*, Springer Series in Solid-State Sciences (Springer, ADDRESS, 2006).
- [230] P. Bruno, Phys. Rev. B **39**, 865 (1989).
- [231] D.-s. Wang, R. Wu, and A. J. Freeman, Phys. Rev. Lett. **70**, 869 (1993).
- [232] X. Wang, R. Wu, D.-s. Wang, and A. J. Freeman, Phys. Rev. B **54**, 61 (1996).
- [233] S. Jiang *et al.*, Nature Nanotechnology **13**, 549 (2018).
- [234] K. I. Kugel' and D. I. Khomskii, Soviet Physics Uspekhi **25**, 231 (1982).
- [235] H. H. Kim *et al.*, Proceedings of the National Academy of Sciences **116**, 11131 (2019).
- [236] M. Kim *et al.*, Nature Electronics **2**, 457 (2019).
- [237] D. C. Freitas *et al.*, Journal of Physics: Condensed Matter **27**, 176002 (2015).
- [238] X. Sun *et al.*, Nano Research **13**, 3358 (2020).
- [239] L. Meng *et al.*, Nature Communications **12**, 809 (2021).
- [240] A. Otero Fumega, J. Phillips, and V. Pardo, The Journal of Physical Chemistry C **124**, 21047 (2020).
- [241] Y. Ou *et al.*, Nature Communications **13**, 2972 (2022).
- [242] F. Fabre *et al.*, Phys. Rev. Mater. **5**, 034008 (2021).

- [243] A. Purbawati *et al.*, ACS Applied Materials & Interfaces **12**, 30702 (2020), pMID: 32515190.
- [244] A. S. D. Roy, and M. Kabir, Unpublished (2025).
- [245] D. K. Roy and M. Kabir, Phys. Rev. B **111**, 134409 (2025).
- [246] M.-G. Han *et al.*, Nano Letters **19**, 7859 (2019), pMID: 31661617.
- [247] M. Augustin *et al.*, Nature Communications **12**, 185 (2021).
- [248] Y. Zhang *et al.*, Advanced Materials **31**, 1900056 (2019).
- [249] X. Xiao *et al.*, Advanced Functional Materials **29**, 1809001 (2019).
- [250] B. Tang *et al.*, ACS Applied Electronic Materials **4**, 3303 (2022).
- [251] B. Li *et al.*, Nature Materials **20**, 818 (2021).
- [252] M. Bonilla *et al.*, Nature Nanotechnology **13**, 289 (2018).
- [253] Q.-Q. Yuan *et al.*, Chinese Physics Letters **37**, 077502 (2020).
- [254] K. Lasek *et al.*, ACS Nano **14**, 8473 (2020), pMID: 32584543.
- [255] S. Ma *et al.*, ACS Nano **16**, 19439 (2022), pMID: 36288432.
- [256] T. Song *et al.*, Science **360**, 1214 (2018).
- [257] S. Qi *et al.*, Nature Communications **14**, 2526 (2023).
- [258] G. Chen *et al.*, Nature Communications **12**, 6279 (2021).
- [259] B. Ding *et al.*, Nano Letters **20**, 868 (2020), pMID: 31869236.
- [260] T.-E. Park *et al.*, Phys. Rev. B **103**, 104410 (2021).
- [261] B. W. Casas *et al.*, Advanced Materials **35**, 2212087 (2023).



- 
- [262] W. Xie *et al.*, APL Materials **12**, 031102 (2024).
- [263] Z. Wang *et al.*, Nature Communications **9**, 2516 (2018).
- [264] W. Zhu *et al.*, Nature Communications **14**, 5371 (2023).
- [265] J. Seo *et al.*, Science Advances **6**, eaay8912 (2020).
- [266] K. Olejník *et al.*, Science Advances **4**, eaar3566 (2018).
- [267] A. Dal Din, O. J. Amin, P. Wadley, and K. W. Edmonds, npj Spintronics **2**, 25 (2024).
- [268] B. Yang *et al.*, Nature Materials **22**, 50 (2023).