Spin-Orbit Coupling in Iridates

by

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Abstract

Transition-metal oxides (TMOs) are a widely studied class of materials with fascinating electronic properties and a great potential for applications. Sr_2IrO_4 is such a TMO, with a partially filled $5d t_{2g}$ shell. Given the reduced Coulomb interactions in these extended 5d orbitals, the insulating state in Sr_2IrO_4 is quite unexpected. To explain this state, it has been proposed that spin-orbit coupling (SOC) entangles the t_{2g} states into a filled $j_{\text{eff}} = 3/2$ state and a half-filled $j_{\text{eff}} = 1/2$ state, in which a smaller Coulomb interaction can open a gap. This new scheme extends filling and bandwidth. the canonical control parameters for metal-insulator transitions, to the relativistic domain. Naturally the question arises whether in this case, SOC can in fact drive such a transition. In order to address this question, we have studied the behaviour of Sr_2IrO_4 when substituting Ir for Ru or Rh. Both of these elements change the electronic structure and drive the system into a metallic state. A careful analysis of filling, bandwidth, and SOC, demonstrates that only SOC can satisfactorily explain the transition. This establishes the importance of SOC in the description of metal-insulator transitions and stabilizing the insulating state in Sr_2IrO_4 .

It has furthermore been proposed that the $j_{\text{eff}} = 1/2$ model in $\text{Sr}_2 \text{IrO}_4$ is an analogue to the superconducting cuprates, realizing a two-dimensional pseudo-spin 1/2 model. We test this directly by measuring the spin-orbital entanglement using circularly polarized spin-ARPES. Our results indicate that there is a drastic change in the spin-orbital entanglement throughout the Brillouin zone, implying that $\text{Sr}_2 \text{IrO}_4$ can not simply be described as a pseudo-spin 1/2 insulator, casting doubt on direct comparisons to the cuprate superconductors. We thus find that the insulating ground state in Sr_2IrO_4 is mediated by SOC, however, SOC is not strong enough to fully disentangle the $j_{\text{eff}} = 1/2$ state, requiring that Sr_2IrO_4 is described as a multi-orbital relativistic Mott insulator.

Lay Summary

This thesis studies the behaviour of electrons in the crystalline compound Sr_2IrO_4 . Generally, crystals can subdivided into two classes; those that do conduct electricity (metals), and those that do not (insulators); Sr_2IrO_4 belongs to the latter of these two classes. In this work, we observe a transition into a metallic state, by changing the coupling between spin and momentum. This proves that the insulating properties in Sr_2IrO_4 derive from this coupling and is the first demonstration of a transition into a metallic state by changing this parameter. It has further been proposed that Sr_2IrO_4 is a system that models cuprate superconductors. A superconductor is a material that conducts electricity without any loss. Sr_2IrO_4 does not superconduct, but comparing to it can help identify requirements for superconductivity. The experiments in this work show that Sr_2IrO_4 is in fact different on two crucial aspects, highlighting their importance to superconductivity.

Preface

The work in this thesis is a representation of my scientific activity during my time as a graduate student at UBC. For all the work presented in this thesis I was the primary responsible investigator. However, the nature of experimental physics dictates that none of the work presented here was done alone, in particular there has been incidental involvement from all the members of our research group and technical staff. For the experimental chapters, I will detail the contributions I and others have made below.

Chapter 3 – Spin-orbit Controlled Metal-Insulator Transition in $\mathbf{Sr}_{2}\mathbf{IrO}_{4}$

This chapter investigates the metal-insulator transition in Sr_2IrO_4 upon substitution of Rh and Ru. The work is a combination of experimental work (ARPES) and theoretical modelling (DFT, TB, matrix element analysis). The experiment was conceived by A. Damascelli and me. Preliminary studies (that are not presented in this thesis) were done in the lab at UBC, for which all of our research group is responsible. The experimental work was done at multiple synchrotron radiation facilities. Planning and experiment design was done by me. A first set of data was taken at the Swiss Light Source in Villegen, Switzerland, together with E. Razzoli, M. Michiardi, with assistance from M.Shi and N. Xu. A second set of data was taken at the Advanced Light Source in Berkeley, California together with E. Razzoli with support from J. D. Denlinger. Sr_2IrO_4 samples were provided by the group of H. Takagi. The Rh doped samples were grown by K. Ueda and J. Bertinshaw. Ru doped samples were provided by S. Calder and G. Cao at Oakridge National Laboratory. Data analysis was done by me, with input from E. Razzoli, R. P. Day and A. Damascelli. The numerical modelling was done by me, where the DFT calculations were supervised by I.S. Elfimov, the TB calculations and matrix element analysis had extensive inputs from R. P. Day. The interpretation of the work has involved inputs from many people, but is mostly done by me, R. P. Day, I. S. Elfimov and A. Damascelli. Andrea Damascelli supervised the project. Andrea Damascelli was responsible for overall project direction, planning and management. Large parts of the chapter form the basis for a manuscript which was written by me, R. P. Day and A. Damascelli. This manuscript has been accepted for publication in *Nature Physics*.

Chapter 4 – Spin and k_z Resolved ARPES on Sr₂IrO₄

This chapter discusses the spin-orbital entanglement of the states in Sr_2IrO_4 . The work presented in this chapter is a combination of experimental (spin-ARPES) and numerical work. The experiment was conceived by A. Damascelli and me. The experiments were performed at the Elettra Syncrotrone in Trieste, Italy. These experiments were done over multiple beam times. While I was the primary responsible for the planning and schedule, the practical execution involved the help of R. P. Day, M. Michiardi, E. Razzoli, M. Schneider, S. Zhdanovic, M. X. Na, and G. Levy. Our experiments were supported by C. Bigi, J. Fuji and I. Vobornik. The samples for these experiments came from the group of H. Takagi. The data analysis and numerical simulations were done by me, with input from R. P. Day. Andrea Damascelli supervised the project. Andrea Damascelli was responsible for overall project direction, planning and management. These results are currently being prepared for publication.

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List of Abbreviations

ARPES	angle-resolved photoelectron spectroscopy
AFM	antiferromagnetic
BC	bandwidth controlled
ВСТ	body centred tetragonal
BZ	Brillouin zone
CE	constant energy
CLS	Canadian Light Source
CPSA	circularly polarized spin-ARPES
DFT	density functional theory
DOS	density of states
EDC	energy distribution curve
FC	filling controlled
GGA	generalized gradient approximation
нк	Hohenberg-Kohn
KS	Kohn-Sham
LAPW	linear augmented plane wave

- **LDA** local density approximation
- **MDC** momentum distribution curve
- **MIT** metal-insulator transition
- **QMSC** Quantum Materials Spectroscopy Center
- **REXS** resonant elastic x-ray scattering
- **RIXS** resonant inelastic x-ray scattering
- **SOC** spin-orbit coupling
- **STEM** scanning transmission electron microscopy
- **STM** scanning tunnelling microscopy
- **STS** scanning tunnelling microscopy
- **TB** tight binding
- **TM** transition metal
- **TMO** transition-metal oxide
- **UV** ultraviolet
- **VLEED** very low energy electron diffraction (used to describe a type of spin-detector)

List of Symbols

10Dq	the crystal field splitting
E_F	the Fermi energy
ε	impurity potential strength
e_g	subset of the <i>d</i> orbitals $(d_{z^2}, d_{x^2-y^2})$
Г	the high symmetry point $\mathbf{k} = (0, 0, 0)$
I^{π}	π -polarization, in the same plane as the slit $(\hat{x} + \hat{z})$
I^{σ}	$\sigma\text{-polarization},$ perpendicular to the slit direction (\hat{y})
$j_{ m eff}$	effective coupled angular momentum
λ	spin-orbit coupling strength
M	the high symmetry point $\mathbf{k} = (\pi/2a, \pi/2a, 0)$, see X
N	the high symmetry point $\mathbf{k} = (\pi/a, \pi/a, 0)$, see X
t	hopping strength (kinetic energy)
t_{2g}	subset of the <i>d</i> orbitals (d_{xy}, d_{xz}, d_{yz})
U	Coulomb repulsion
x	concentration of impurities
Х	the high symmetry point $\mathbf{k} = (\pi/a, 0, 0)$, with \hat{x} along the TM-O bond, and a the TM-TM spacing
Ζ	the high symmetry point $\mathbf{k} = (0, 0, \pi/c)$, see X

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Chapter 1

Introduction

1.1 Materials

The compounds studied in this thesis are most commonly referred to as transition-metal oxides (TMOs). The physics describing these materials arises from the interplay between the electronic states belonging to the transition-metal and oxygen ions. Transition-metal oxides are materials that have been studied intensively in contemporary physics for a multitude of reasons. This includes that their constituents are abundant in the earth's crust and therefore inexpensive and accessible. Furthermore, these materials have great potential for possible applications [1, 2], as they host a plethora of interesting physics such as magnetism [3], superconductivity [4, 5], Mott and charge transfer insulating behaviour [6, 7], charge and orbital ordering [8-10], and the colossal magnetoresistance effect [11-13]. Due to a combination of a partially filled d shell and strong electron-electron interactions, TMOs host a large variety of physical phases, in a class of compounds that appears similar based on their constituents and structure. However, the partially filled d shell and strong electron-electron interactions is also what makes these compounds incredibly challenging to understand. A key challenge in the field is the exploration of correlated insulating phases (referred to as "Mott-insulating" phases), where these electron-electron interactions cause the localization of charge carriers. More so, the transition from insulating



Figure 1.1: Overview of different kinds of insulators. A onedimensional material is schematically depicted as a series of lattice sites (black horizontal lines) with a spin occupying each site indicated as an arrow (a,b) Trivial corner cases of insulators, in (a) the lattice is empty, so no spins can be transported. In (b) the lattice is completely filled and the Pauli exclusion principle prevents movement of the spins. (c) In the case the system is half filled, charges can move if the transition probability t is high enough to overcome the Coulomb potential for double occupation U. If U outweighs the effects of t the system is a Mott insulator.

to metallic phase is an important topic, as the aforementioned phenomena often arise in close vicinity to these transitions. The mechanisms and control parameters describing these phases and transitions are therefore of great interest to the field.

A description of different insulating phase is depicted in Fig. 1.1. Two trivial corner cases of a completely empty and filled system are shown in Fig. 1.1a and b. In the former case no excitations can be made because no electrons are available, the latter case is insulating because such excitations are impossible due to the Pauli exclusion principle; both cases are insulating. In the intermediate case, where the system is exactly half filled, an interesting scenario arises. Electrons can move from one site to the next, as indicated by the hopping transition rate t, but whether or not the system is insulating depends on the Coulomb repulsion U related to two electrons occupying the same site. This system is referred to as the Hubbard model, and if the effect of U is large enough to suppress electron movement (U > t), the system is a Mott insulator.

The cuprate superconductors are believed to be well described by a half filled Hubbard model on a square, two-dimensional lattice. A great effort has therefore been made to discover new materials that can be described with the same basic Hamiltonian. This search has been primarily focussed on materials with 3d transition metals, although 4d and 5d compounds have also been studied. In these latter categories, the discovery of superconductivity in Sr_2RuO_4 was made [14], but also Sr_2RhO_4 [15] and Sr_2IrO_4 [16, 17] gained attention. Although these compounds are close to their 3d counterparts in the periodic table, properties of 4d and 5d materials are markedly different from those with 3d elements. The 4d and 5d orbitals are much more extended than 3d's, which has a few effects. Firstly, since the electrons are more spread out, the integrals determining the Coulomb and exchange interactions are significantly reduced. Secondly, the bandwidth is larger due to the increased orbital size, which increases hopping between orbitals [16, 17].

Because the itinerancy of the electrons increases and the Coulomb interaction decreases in the 4d and 5d orbitals, these systems are expected to show more metallic behaviour. A metallic state is indeed found for the 4d materials Sr_2RhO_4 and Sr_2RuO_4 [14, 15]. Sr_2IrO_4 on the other hand, was found to be insulating [16], which was an unexpected result [16, 17], as the electronic repulsion should not be sufficient to open a Mott gap.

1.1.1 The $j_{\text{eff}} = 1/2$ state

An explanation for the insulating state was ultimately found by considering the effects of spin-orbit coupling (SOC). This interaction is a further important deviation from the 3*d* properties as SOC is significantly increased in 4*d* and 5*d* compounds [18]. SOC strength (as derived more thoroughly in Section 1.3) is given by the gradient of the potential and therefore increases with atomic number Z. If this derivation is done including the effects of screening, one finds the magnitude scales as Z^2 [19]. This Z^2 behaviour gives a good agreement with experimental values found for materials in these groups of the periodic table: ~ 0.4 eV for Ir [20], ~ 0.19 eV for Rh and Ru [18, 21, 22], ~ 0.02 - 0.1 eV [23, 24] for Fe.

In their seminal work published in 2008 [25], B.J. Kim and colleagues pointed out that the insulating state in Sr_2IrO_4 could be interpreted by considering spin-orbit coupling. As stated, the insulating state in Sr_2IrO_4 had been somewhat of a puzzle, since the increased bandwidth and reduced Coulomb interactions associated with the 5d compounds could not explain why the partially filled d band could result in insulating behaviour. The electrons in Sr_2IrO_4 occupy the t_{2g} bands, a subset of the transition metal d bands. Their reasoning was that SOC is large enough to couple the t_{2g} orbitals into spin-orbitally entangled states. They suggest the bands couple into a so-called $j_{\text{eff}} = 1/2$ and 3/2 manifold (explained further in Section 1.4). This splits the bands, reducing the bandwidth, and creates a singly occupied $j_{\text{eff}} = 1/2$ orbital. This half-filled band gives the smaller U $(\sim 2 \text{ eV} [26])$ an opportunity to open a gap creating a " $j_{\text{eff}} = 1/2$ Mott insulator". A diagram for this process, schematically indicating the densities of states as a function of energy upon including the various energy terms, is presented in Fig. 1.2a.

Convincing evidence for the existence of this state was provided by resonant elastic x-ray scattering (REXS) measurements performed on the Ir edge [27]. In particular, the branching ratio of the L_2 and L_3 at a magnetic reflection is taken as indication that the ground state is well described by a $j_{\text{eff}} = 1/2$ state. This result was later questioned, however, when it was demonstrated that for a system with magnetic moments lying in the *ab* plane, as is the case for Sr_2IrO_4 , the branching ratio is identically zero, regardless of the amount of spin-orbital entanglement [28]. The authors of [27] later acknowledge this in [29], where they analyze the matrix elements for REXS in more detail. Moreover, it was demonstrated in [30], that the $j_{\text{eff}} = 1/2$ is quite close to a collapse. While spin-orbit coupling in Sr_2IrO_4 is undoubtedly very strong, it seems that a schematic of the density of states for Sr_2IrO_4 may in fact look more like Fig. 1.2b and therefore the precise



Figure 1.2: Schematic overview of the energy diagram of the j_{eff} states. (a) The idealized $j_{\text{eff}} = 1/2$ model, where the spin-orbit splitting is large enough that the $j_{\text{eff}} = 1/2$ and the $j_{\text{eff}} = 3/2$ manifold no longer overlap. (b) A situation in which the bandwidth is large enough to cause significant overlap between the $j_{\text{eff}} = 1/2$ and 3/2 states, which results in a ground state in which the $j_{\text{eff}} = 3/2$ cannot simply be projected out.

nature of the insulating state is still unknown.

Alternative scenarios could still hold true, for example a Slater insulator, in which the insulating state is mediated by a band folding causing antiferromagnetism has been suggested by Arita and coworkers [26]. This has been ruled out for Na₂IrO₃ [31] but the Néel temperature in Sr₂IrO₄ is too high to allow for a similar analysis. Other suggestions that still fit within current observations are a multi-orbital Mott system in the presence of strong spin orbit coupling, such as in Ca₂RuO₄ [32, 33], or a non- $j_{\text{eff}} = 1/2$ relativistic Mott insulator such as CaIrO₃ [34].

1.1.2 A pseudo-spin 1/2 model

While the true ground state may still be elusive, many consequences have been proposed if the $j_{\text{eff}} = 1/2$ state were to hold true. It was quickly realized that the system would have a large number of properties that are commonly found in cuprate superconductors [35]. The structure is identical to that of La_2CuO_4 . Moreover the compound is an anti-ferromagnetic (pseudo-) spin 1/2 model, in which the Coulomb interaction causes an insulating state in the parent compound. Resonant inelastic x-ray scattering (RIXS) data show a remarkable similarity to inelastic neutron scattering data taken on La_2CuO_4 [36]. This data is in good agreement with a Heisenberg model [37], which describes the ground state of the cuprates [38, 39]. More detailed analvses indeed predict a superconducting ground state [40, 41], with one key difference from the cuprates; since the model Hamiltonian for the iridates is equivalent to that of the cuprates with $t \to -t$, the superconductivity appears in the phase diagram on the electron doped side. Attempts were made to electron dope the system, using La $(Sr_{2-x}La_xIrO_4 [42])$ and oxygen [43]. Promising signs were observed on La doped compounds, which showed a pseudogap like state in angle-resolved photoelectron spectroscopy (ARPES) [44]. The spatial behaviour of the charge gap observed using STM, displays similarities to related cuprate compounds [45]. Moreover, using potassium to surface dope electrons, signatures of a *d*-wave gap were seen in both scanning tunnelling microscopy (STS) [46] and ARPES [47]. Unfortunately, so far no reports of bulk superconductivity have been made. It is possible that La is not able to dope enough electrons for the system to become bulk superconductive. However, the models presented in [40, 41] assume the spinorbit coupling is strong enough to cause full separation of the $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ states, an assumption which is explored in more detail in Chapter 4. If it turns out that electron doped Sr_2IrO_4 is in fact not superconductive, this may lead to an interesting perspective on necessary ingredients for superconductivity.

1.1.3 This work

To provide an overview of the field of relativistic correlated oxides, we can identify two important open questions. The first question is whether spinorbit-coupling should be considered as a parameter in the canonical phase diagram of Mott insulators and if Sr_2IrO_4 is a material that can be placed on and tuned along this axis. Secondly, whether the $j_{\text{eff}} = 1/2$ model is a valid description of the ground state of Sr_2IrO_4 and what that means for parallels identified with the superconducting cuprates. We will address both these points in detail, in Chapter 3 and Chapter 4 respectively. The body of this thesis thus considers and attends to key questions in the field of relativistic correlated materials. In the remainder of this chapter, some of the fundamental physics of these materials will be considered, in particular the crystal and electronic structure and the effects of spin-orbit coupling.

1.2 Structure

The basic building block for all TMOs is the TM-O₆ octahedron, depicted in Fig. 1.3a. This is a transition metal ion, surrounded by six oxygen atoms that can be corner-shared between octahedra. The oxygen atoms provide a potential background, referred to as the crystal field, that breaks the spherical symmetry of the transition metal ion and thereby lifts the degeneracy of the *d* band. Moreover, the oxygen atoms mediate the electron bonding between octahedra through hybridization.

A large fraction of these materials follow the basic formula of the Perovskite ABO₃, in which A is an alkali, earth-alkali, or lanthanoid ion and B is a transition metal. Another important element of the compounds studied here is they are layered. These layered materials are members of the Ruddlesden-Popper series [48] having alternating layers of AO and BO₂, following the series $A_{N+1}B_NO_{3N+1}$ (schematically shown in Fig. 1.3b). The A_2BO_4 (N = 1) series of oxides, studied in this thesis, has a repeating unit of a stack of AO - BO₂ - AO, isolating the BO₂ layers from each other, to form a mostly two-dimensional compound (Fig. 1.3c for Sr₂IrO₄). It should be clarified that these materials are not truly two-dimensional, but rather a layered three-dimensional structure. Two-dimensionality in this case is characterized by the fact that the electrons move mostly within one of the layers, and the interaction between layers is relatively small. The A-site ion (Sr in this thesis) can be safely ignored, since it has a full shell and its electrons are all strongly bound to the core. The focus with these compounds is thus on the transition metal (TM) ion seated on the B site of the perovskite structure (Ir, Rh or Ru in this thesis), which is octahedrally coordinated with oxygen atoms. While oxygen hybridizes with the TM ion, which is particularly true for the 4d and 5d compounds, the physics related to the TM ion can effectively be expressed in terms of TM-d O-p hybrids, which follow the symmetry of the original d orbitals.

The structure of these materials can be seen in Fig. 1.3c. While the crystallographic space group for Sr_2RuO_4 is I4/mmm, the structure of Sr_2RhO_4 and Sr_2IrO_4 is I4/acd. The key difference is that the TMO₆ octahedra are rotated in a checkerboard pattern in Sr_2RhO_4 and Sr_2IrO_4 throughout the crystal. A similar rotation occurs in Sr_2RuO_4 , but only on the surface [49].

1.2.1 Electronic structure

The degeneracy lifting, caused by the ligand oxygen atoms, induces well defined shifts to particular d orbitals. Representing these orbitals in the basis of cubic harmonics, it is the orbitals with lobes pointing towards the oxygen ions that gain energy $(d_{x^2-y^2} \text{ and } d_{z^2-r^2})$, also called the e_g orbitals. The orbitals with lobes pointing in-between the oxygens, the t_{2g} orbitals $(d_{xy}, d_{xz} \text{ and } d_{yz})$ are lowered in energy. The energy splitting related to the oxygen is referred to as 10Dq. A further degeneracy breaking can be induced by a tetragonal distortion, in which octahedra are stretched or compressed along one axis, further splitting the e_g and t_{2g} bands. In the case of a layered 3D material like Sr_2IrO_4 , this symmetry is already broken in the global structure and therefore, a degeneracy would be purely accidental. A schematic representation of the induced splitting is plotted in Fig. 1.3d. While a tetragonal splitting indeed exists for all compounds studied in this thesis, the splitting is much smaller than the bandwidth and therefore the t_{2g} manifold is, for practical purposes, often assumed to be degenerate.

We can gain some further insight into the electronic structure of Sr_2IrO_4 , Sr_2RhO_4 and Sr_2RuO_4 by counting electrons. We can make the assumption that O and Sr assume completely filled shells as O^{2-} and Sr^{2+} . This dictates that the charge on Ir, Ru and Rh should be 4+, which implies that Ir and



Figure 1.3: Overview of the structure and electronic basics of the transition metal oxides studied in this thesis. (a) A single oxygen octahedron, the building block that is the foundation for the physics of the materials in this thesis. (b) A schematic overview of the Ruddlesden-Popper series. Alternating units of AO (SrO for Sr₂IrO₄) and BO₂ (IrO₂ for Sr₂IrO₄) are stacked with varying layer thicknesses. The compound studied in this thesis is the compound with N = 1, consisting of only singly connected layers of IrO₂ between two layers of SrO. (c) The unit cell structure for Sr₂IrO₄. Alternating layers of SrO and IrO₂ can be seen stacked along the c-axis [50]. (d) Energy diagram explaining the effect of the crystal field on the *d* orbitals, that split into different subsets under influence of the octahedral field (10Dq) and the tetragonal splitting (δ_{tet}) .

Rh are d^5 , while Ru is d^4 .

For most 3*d* compounds Hund's first rule is valid (U - U' > 10Dq) and ions are high spin. However, 4*d* and 5*d* TMOs tend to have 10Dq > U - U'since the orbitals are further extended and the effect of the crystal field is large, and it is therefore more favourable for two electrons to occupy the same site in the t_{2g} manifold, in a low spin configuration [51]. Therefore, to the most basic extent, the physics of Sr₂IrO₄ can be considered as five electrons in the (spin-degenerate) t_{2g} manifold. This means a partially filled t_{2g} shell for all materials, implying a metallic ground state in the absence of electron-electron interactions. Spin-orbit coupling then proceeds to modify the structure of these (nominally) degenerate bands, as will be discussed in Section 1.3.

1.2.2 Mott insulators

The introduction of band theory has been very successful in the explanation of metallic and insulating properties. In the case of a partially filled band, gapless excitations are possible and the system is metallic. In the opposite case, where a band is empty (or completely filled), a finite amount of energy (the gap), has to be overcome for an excitation to be made, causing these systems to instead be insulating. Band theory has been successful for many materials and has helped shape the world by explaining the behaviour of silicon and aiding in the creation of the transistor. However, already in 1937, de Boer and Verwey pointed out that many transition-metal oxides had partially filled d-bands and were insulators [52]. Commenting on the paper of de Boer and Verwey, Peierls pointed out that this behaviour may be due to the electrostatic interaction of electrons [53]. It was Mott who later laid the ground-work for what is now known as a Mott insulator [54]; a system in which electrons are localized and excitations are gapped due to the strong electron-electron repulsion. Since then, an extensive amount of attention has been paid to these types of compounds. Not in the least because a Mott insulating phase is often found in close proximity to many of the exotic states mentioned in Section 1.1. Because the nature of the insulating states can be found in electron-electron interactions, Mott insulators are very challenging to study. As correlations require the exact treatment of an exponentially growing number of possible interactions in a many-body system, there remain many questions still unanswered.

1.2.3 The metal-insulator transition

In the case of Mott insulators, a frequently studied physical phenomenon is the transition into a metallic state, called a metal-insulator transition (MIT). An excellent in depth review of both theoretical and experimental aspects of this field of physics can be found in Ref. 6. A MIT can in general be driven through the tuning of two individual parameters; the filling, n, and the bandwidth, often denoted U/t. Tuning through the former of these parameters is called a filling controlled (FC) MIT, whereas the latter is referred to as a bandwidth controlled (BC) MIT. It is instructive to consider the physical mechanism behind these two. In the BC MIT, the kinetic energy terms t are modified, to an extent to which it can be found more favourable for electrons to be itinerant, regardless the cost of U that an electron pays to occupy the same site as another. Meanwhile, an FC MIT can be easily understood from a system at integer filling. While for a system exactly at half filling, excitations are energetically costly (U for one electron to hop to a site where another electron is already present), for a system that is not exactly half filled, sites that are already doubly occupied can hop at no additional cost, as that U was already expended.

Experimentally, there are various tuning knobs that control these parameters. For bandwidth control, pressure is effective, either applied chemically or externally. In the case of perovskite structures, changing the radius of the A site ion is an effective way to change the bandwidth and such MITs can be found for example in RNiO₃ with R is a rare-earth ion [55]. Another example is the substitution of Ca in Ca₂RuO₄ for Sr, which has a larger ionic radius and drives the system from insulating to metallic [56]. The advantage of substituting an A site ion is that they generally do not partake in the low-energy physics (as discussed in Section 1.2) and only provide sideline support such as adjusting charge and chemical pressure. For the case of filling control, modifications can be made chemically or by electronic gating. A classic example is to substitute an A site for one with a different valence, for example, substitute part of trivalent La in La_2CuO_4 for divalent Sr, to create $Sr_xLa_{2-x}CuO_4$, which changes n to n-x. This strategy has been successfully applied to Sr_2IrO_4 to electron dope it, by creating $La_x Sr_{2-x} IrO_4$ [42, 44]. Another possibility is to change the oxygen content, a strategy that has seen a large success in the field of the superconducting cuprates and has also been demonstrated in Sr_2IrO_4 [43]. Lastly, a type of transition that is mentioned here for completeness, is the control of dimensionality. For example, of the Ruddlesden-Popper series of manganites, the single layer compound $La_{1-x}Sr_{1+x}MnO_4$ is insulating, while the bi-layer compound, $La_{2-x}Sr_{1+x}Mn_2O_7$, is metallic. Since all the compounds studied in this thesis are single-layer compounds, dimensionality will not be considered here. In Chapter 3, we will study a new variety of MIT: the one that is controlled by spin-orbit coupling. While it may not be immediately obvious why spin-orbit coupling is fundamentally different from a FC MIT, the simulations in [57, 58] should provide a compelling answer: where U/t changes the itinerancy, λ/t changes the entanglement of the multi-orbital Mott system and the two control-parameters lead to surprisingly different phases. In this work, we will show for the first time an experimental demonstration of such a SOC controlled MIT, as is explained in Chapter 3.

1.3 Spin-orbit coupling

A central theme in this thesis is SOC, a term in the Hamiltonian that arises from relativistic corrections to the Schrödinger equation, which entangles spin and orbital angular momentum degrees of freedom. This entanglement causes a wavefunction in which spin and orbital angular momentum degrees of freedom can no longer be factored out. I will first describe spin-orbit coupling from the historical point of view, which is a treatment which is often presented in introductory textbooks. After this, a description derived from the relativistic Dirac equation will be given.

1.3.1 A simple description of spin-orbit coupling

The initial description of spin-orbit coupling came after Goudsmit and Uhlenbeck suggested that a new quantum number, related to intrinsic angular momentum of the electron could better explain the spectral lines of Hydrogen [59, 60]. They proposed the existence of such a "spin", *ad hoc* and derived the associated energies following from electrostatics. Due to the effects of relativity, an electron moving in the presence of the potential of the nucleus will experience a magnetic field in its rest frame. This magnetic field is:

$$\mathbf{B}_{el} = \frac{\mathbf{v}}{c^2} \times \mathbf{E} = \frac{\mathbf{v}}{ec^2} \times \boldsymbol{\nabla} V.$$
(1.1)

The moment of the electron will align with this field, where the energy of the spin magnetic moment is given by:

$$V_{\mu s} = \boldsymbol{\mu}_{\boldsymbol{s}} \cdot \mathbf{B}_{el}. \tag{1.2}$$

Writing the electron magnetic moment as $\mu_s = -g_s \mu_B \frac{\mathbf{S}}{\hbar}$ and substituting $g_s = 2$ we arrive (up to a constant) at the energy for the spin-orbit coupling:

$$V_{\mu s} = -\frac{1}{m_e^2 c^2} \mathbf{S} \cdot \mathbf{p} \times \boldsymbol{\nabla} V.$$
(1.3)

In a spherically symmetric potential we can write the gradient of the potential as $\nabla V = -\frac{1}{r} \frac{dV}{dr} \mathbf{r}$ which leads to the more familiar form:

$$V_{\mu s} = \frac{1}{m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S}.$$
 (1.4)

This is the correct result up to a factor 2. The error arises from the fact that an electron in a spherical potential is not moving with a constant velocity but is continuously accelerated by the centripetal force. This was resolved by accounting for the appropriate Lorentz factor by Thomas [61], which leads to the correct expression. Although this derivation of spin-orbit coupling as some external perturbation is quite insightful, since it provides an intuitive origin for the term, it is not at all rigorous from a physics point of view. Although this description gives the correct result, it is a complicated mix of classical, quantum and relativistic physics. Most importantly, electron spin is added *ad hoc*, justified by intrinsic angular momentum. It was pointed out by Slater that the picture of a spinning electron would violate relativity as the periphery of the electron would spin significantly faster than the speed of light [62].

1.3.2 The Dirac equation

Shortly after the description by Uhlenbeck and Goudsmit with the correction from Thomas, the same solution was found more rigorously through the Dirac equation[63]:

$$\left(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta m_e c^2\right)\psi = E\psi. \tag{1.5}$$

Here, α and β are both 4×4 matrices, given by:

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}, \quad \boldsymbol{\beta} = \begin{pmatrix} \boldsymbol{I} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{I} \end{pmatrix}, \quad (1.6)$$

with all elements here being 2×2 matrices, $\boldsymbol{\sigma}$ are the Pauli spin-matrices and \boldsymbol{I} is the identity matrix. This derivation of spin-orbit coupling, mainly follows [64]. We start by writing the four-component wavefunction as two two-component vectors, $\psi = (\psi_A, \psi_B)$. In this representation, we get two coupled equations for ψ_A and ψ_B , from which we can eliminate ψ_B and we obtain for ψ_A (in the presence of an electronic potential V):

$$\mathbf{p} \cdot \boldsymbol{\sigma} \frac{c^2}{E - V + m_e c^2} \mathbf{p} \cdot \boldsymbol{\sigma} \psi_A = (E - V - m_e c^2) \psi_A.$$
(1.7)

We can substitute $E = m_e c^2 + \epsilon$ and in the non-relativistic limit, where $\epsilon - V \ll mc^2$, we can make an expansion in the energy around mc^2 to find for the middle term:

$$\frac{c^2}{E - V + m_e c^2} = \frac{1}{2m_e} \left(1 - \frac{\epsilon - V}{2m_e c^2} + \mathcal{O}\left(\left(\frac{\epsilon - V}{2m_e c^2}\right)^2 \right) \right).$$
(1.8)

Here, the zeroth order gives a term containing $(\mathbf{p} \cdot \boldsymbol{\sigma})^2 = p^2$,¹ which results in the ordinary, scalar Schrödinger equation, degenerate in the spin degree of freedom:

$$\left(\frac{p^2}{2m_e} + V\right)\psi = \epsilon\psi. \tag{1.9}$$

Taking the first order expansion, we get an additional set of terms, arising from the fact that $V = V(\mathbf{r})$ and that generally $[V(\mathbf{r}), \mathbf{p}] \neq 0$. The result as stated in [64] is:

$$\left(\frac{p^2}{2m_e} + V + \frac{p^4}{8m_e^3 c^2} + \frac{\hbar}{4m_e^2 c^2}\boldsymbol{\sigma} \cdot \boldsymbol{\nabla} V \times \mathbf{p} + \frac{\hbar^2}{8m_e^2 c^2} \boldsymbol{\nabla}^2 V\right)\psi = \epsilon\psi. \quad (1.10)$$

The first two terms describe the non-relativistic Hamiltonian from the zeroth order. The third term is the relativistic correction to the kinetic energy of the electron, the fourth term is the spin-orbit coupling, and the fifth term is the Darwin term. Setting $\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$, we can finally cast the spin-orbit coupling in its usual form:

$$H_{SOC} = -\frac{1}{2m_e^2 c^2} \mathbf{p} \times (\nabla V) \cdot \mathbf{S}.$$
 (1.11)

Or when the potential V is spherically symmetric:

$$H_{SOC} = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S}.$$
 (1.12)

This is the correct result including the factor of 2 that needed to be added to the electrostatic picture.

1.4 SOC and angular momentum in solids

All of the work in this thesis is focussed on coupling of spin and orbital angular momentum in solids. It therefore seems apt to give a thorough description of some of the generally used bases and coupling terms. This section serves to expand the well known textbook treatment of spin-orbit coupling and states of coupled angular momentum to the realm of solids in

¹This holds since all the squares of the Pauli matrices give the identity: $(\sigma_i)^2 = I$.

which the crystal field breaks certain symmetries.

1.4.1 SOC in atoms

The treatment of spin-orbit coupling here will deal with the inclusion of the Hamiltonian $\mathbf{L} \cdot \mathbf{S}$ as derived above. This is technically incorrect, as the substitution $\nabla V = -\frac{dV}{dr} \hat{\mathbf{r}}$ made to obtain this form is only valid for a spherically symmetric potential. However, the largest influence on every individual orbital comes mostly from the region very close to the nucleus. Therefore it is still a reasonable approximation to neglect the influence from neighbouring nuclei, as their contributions to the gradient are much smaller than that from the centre atom.

To start, we briefly revisit the states of coupled orbital angular momentum. Our challenge is to find an operator representation that commutes with the spin-orbit coupling Hamiltonian derived in Section 1.3.2. It turns out that while S_z and L_z no longer commute individually with the Hamiltonian, their sum does. The Hamiltonian can be written as a combination of the absolute value of the spin, orbital, and coupled angular momentum:

$$H_{SOC} = \lambda_{SOC} \mathbf{L} \cdot \mathbf{S} = \lambda_{SOC} \frac{1}{2} (\mathbf{J} \cdot \mathbf{J} - \mathbf{S} \cdot \mathbf{S} - \mathbf{L} \cdot \mathbf{L}).$$
(1.13)

The eigenstates for this Hamiltonian are given in Table A.2 and Table A.1 for $\ell = 1$ and $\ell = 2$ respectively, sorted by their angular momentum projection on the z-axis. The values for $\mathbf{L} \cdot \mathbf{S}$ and their components are given for each state. Note that in the absence of a term that breaks the symmetry and lifts the degeneracy between the different m_j states, the different values for $L_i S_i$ are artificial and arise from writing the states as separate m_j states. Rather, these expectation values should be taken as an average over the degenerate states, which gives a more satisfying result that the spin-angular momentum coupling is independent of direction, as one would expect for a spherically symmetric system. These considerations are important for later, where we use circularly polarized spin-ARPES (CPSA) to measure entanglement of spin and orbital momentum, this technique essentially directly probes $L_i S_i$ along a particular axis i.

1.4.2 SOC in the presence of a crystal field

We now turn to the effect of spin-orbit coupling in the presence of a crystal field potential. As mentioned, the effect the surrounding lattice has on an atom, in changing the gradient of the potential, is quite small. However, the crystal field imbues big changes on orbital energies. If it is comparable to or larger than the energy of spin-orbit coupling, it influences the ability of SOC to entangle spin and orbital degrees of freedom. The potential arising from the crystal field will break certain symmetries and lift degeneracies. If the energy splittings related to these degeneracy liftings are larger than spin-orbit coupling, that means the full ℓ manifold is no longer available and eigenstates of coupled orbital angular momentum like the ones in Table A.1 may no longer form. The energy scale associated with the crystal field is generally around $\sim 3 \, \text{eV}$, making it between one and two orders of magnitude larger than the relevant values for SOC (Section 1.1.1). This means that in a first approximation, we can simply project out the crystal field split states and transform the SOC Hamiltonian into the new reduced basis. We consider the basis of the cubic harmonics, which are the eigenstates of the Hamiltonian in an octahedral crystal field. These states all have quenched orbital angular momentum, making each individual state insensitive to SOC. Nevertheless, for higher symmetries (e.g. cubic rather than tetragonal), degeneracies persist and spin-orbit interaction can couple degenerate subsets of these states.

We consider here the d states, since they are most appropriate for this work. We first consider an octahedral crystal field, which splits the degenerate d band into a manifold of e_g and t_{2g} states. Although the e_g states are in general above the Fermi level for the compounds studied in this thesis, for completeness we discuss their spin-orbit coupling here. Since the e_g orbitals consist of spherical harmonics with $m_l = \{-2, 0, 2\}$, which the L^+ and $L^$ terms arising from $\mathbf{L} \cdot \mathbf{S}$ are unable to couple, the Hamiltonian reduces to zero:

$$H_{SOC,e_g} = B_{e_g}^{\dagger} H_{SOC} B_{e_g} = \mathbf{0}, \qquad (1.14)$$

where H_{SOC} is the Hamiltonian in Eq. 1.13 and B_{e_g} is the operator that
projects the e_g states onto the spherical harmonics, the basis of H_{SOC}

1.4.3 The $j_{\text{eff}} = 1/2$ State

The same is not true for the t_{2g} states, where the projected SOC Hamiltonian does entangle the states. Taking as a basis:

$$b_{t_{2g}} = \{ d_{xy,\uparrow}, d_{xz,\uparrow}, d_{yz,\uparrow}, d_{xy,\downarrow}, d_{xz,\downarrow}, d_{yz,\downarrow} \}, \qquad (1.15)$$

we get for the H_{SOC} :

$$H_{SOC,t_{2g}} = \frac{\lambda}{2} \begin{pmatrix} 0 & 0 & 0 & 0 & -i & 1 \\ 0 & 0 & -i & i & 0 & 0 \\ 0 & i & 0 & -1 & 0 & 0 \\ 0 & -i & -1 & 0 & 0 & 0 \\ i & 0 & 0 & 0 & 0 & i \\ 1 & 0 & 0 & 0 & -i & 0 \end{pmatrix}.$$
 (1.16)

This gives rise to coupling of these degenerate substates as was the case for SOC without a crystal field. The t_{2g} states have the special property that they mimic the behaviour of p states as has been noted in [25]. To show the derivation of these states, we start by writing down a new basis (the naming of which will become clear after the derivation), $b_{\ell_{\text{eff}}}$:

$$\left|1_{\text{eff}}\right\rangle = \frac{1}{\sqrt{2}} \left(\left|d_{yz}\right\rangle + i \left|d_{xz}\right\rangle\right) = i \left|Y_2^{-1}\right\rangle, \qquad (1.17)$$

$$|0_{\text{eff}}\rangle = -|d_{xy}\rangle = -\frac{i}{\sqrt{2}}\left(\left|Y_2^{-2}\rangle - \left|Y_2^{2}\right\rangle\right),\tag{1.18}$$

$$|-1_{\text{eff}}\rangle = \frac{1}{\sqrt{2}} \left(-|d_{yz}\rangle + i |d_{xz}\rangle \right) = -i \left| Y_2^1 \right\rangle.$$
 (1.19)

Note that this basis transformation reintroduces orbital angular momentum, having $m_l = \{-1, 0, 1\}$. Within this basis, the L^+ and L_z operators become:

$$L_{l_{\text{eff}}}^{+} = B_{l_{\text{eff}}}^{-1} L^{+} B_{l_{\text{eff}}} = \sqrt{2} \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix}, \qquad (1.20)$$

$$L_{z,l_{\text{eff}}} = B_{l_{\text{eff}}}^{-1} L^+ B_{l_{\text{eff}}} = \begin{pmatrix} -1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 1 \end{pmatrix}.$$
 (1.21)

These are identical to the respective matrices for the p orbitals, except with $\ell \to -1$. We can now construct coupled states of angular momentum in a similar way as was done for Eq. 1.13, which are given in Table A.3 and constructed explicitly from t_{2g} orbitals in Table A.4. Spin-orbit coupling thus entangles the manifold of t_{2g} states into the so-called j_{eff} states, called "effective" because their expectations are inconsistent with ordinary j values. Instead, following the observation that the ℓ_{eff} states behave like states with $\ell = -1$, the expectation values of $\mathbf{L} \cdot \mathbf{S}$ and their components are precisely negative that of what the equivalent j state using CPSA later. The basis of j_{eff} diagonalizes the SOC Hamiltonian:

$$H_{SOC,j_{\text{eff}}} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}.$$
 (1.22)

1.4.4 Tetragonal splitting

In Sr_2IrO_4 , more than just the spherical symmetry is broken. An expansion or compression along the z-axis or even the dimensionality of the solid may give rise to a tetragonal splitting, in which the e_g and t_{2g} orbitals split into non-degenerate $d_{x^2-y^2}$, $d_{z^2-r^2}$, d_{xy} and degenerate d_{xz} and d_{yz} states. This splitting is smaller than the spin-orbit coupling for Sr₂IrO₄ [65], but plays an important role in 4d materials with strong structural distortions, such as Ca₂RuO₄ [66, 67] and 3d systems such as Fe superconductors [23]. Moreover, spin-orbit coupling only couples states at one particular k-point. This implies that the bandwidth plays an important role in determining how spinorbit coupling is able to entangle certain states. For example in materials like Sr₂IrO₄, Sr₂RuO₄ and Sr₂RhO₄, the d_{xy} orbital has a two-dimensional character, while the d_{xz} and d_{yz} bands are one-dimensional. This means that the d_{xy} has approximately double the bandwidth compared to the others, creating a k-dependent effective tetragonal splitting on the order of the bandwidth, which is in turn much larger than SOC. It is therefore of interest, to also study the states that form upon coupling only the d_{xz} and d_{yz} . The Hamiltonian in the reduced basis ($\{d_{xz,\uparrow}, d_{yz,\uparrow}, d_{xz,\downarrow}, d_{yz,\downarrow}\}$) becomes:

$$L_{z,l_{\text{eff}}} = B_{l_{\text{eff}}}^{-1} L^+ B_{l_{\text{eff}}} = \begin{pmatrix} 0 & -\frac{i}{2} & 0 & 0\\ \frac{i}{2} & 0 & 0 & 0\\ 0 & 0 & 0 & \frac{i}{2}\\ 0 & 0 & -\frac{i}{2} & 0 \end{pmatrix}.$$
 (1.23)

This gives rise to a basis of two Kramers degenerate states, parallel and anti parallel, labelled here as $|j^+\rangle$ and $|j^-\rangle$, the relevant expectation values for which are given in Table A.5. The tetragonal splitting thus causes a different splitting of the states and hence a different expectation value for each component of $\mathbf{L} \cdot \mathbf{S}$. The remaining states are all singly degenerate and therefore do not couple under spin-orbit coupling.

Fig. 1.4 shows the splitting of states as a function of the discussed parameters, with the colour encoding for the expectation value of L_iS_i . The diagram shows that these expectation values can change significantly through the Brillouin zone, if a k-dependent energy splitting between the d_{xy} and d_{xz}/d_{yz} is taken into account. Furthermore it shows that although spin-orbit coupling itself does not change, its effects on the band-structure change sig-



Figure 1.4: Expectation values of the *d* bands subject to the introduction of various of splittings $(\lambda_{SOC}, 10Dq, \delta_{tet})$ for $\mathbf{L} \cdot \mathbf{S}$ operator (a) and its components $L_x S_x$ (b) and $L_z S_z$ (c). Due to the fourfold rotational symmetry that is conserved, the expectation value for $L_y S_y$ is identical to $L_x S_x$ and therefore not shown.

nificantly depending on other crystal parameters.

Chapter 2

Methods

The work in this thesis makes use of a combination of *ab initio*, numerical, and experimental methods. A combination of these two approaches can be an extremely useful tool in understanding real-world systems. This chapter is meant to provide the reader with information about the frameworks and models used in later chapters.

2.1 Ab initio calculations

The description of many-body electron systems, such as transition-metal oxides (TMOs), is highly complex and requires the use of appropriate approximations to avoid exponential scaling of computational resources. This is particularly true for a system like Sr_2IrO_4 , in which the system is not easily described simply by a reduced effective model. In general there is no silver bullet, and this work makes use of a combination of techniques to describe the systems studied.

2.1.1 Density functional theory

A very successful approach in dealing with the many-particle problem has come from density functional theory (DFT), a technique that relies on the fact that a system can be uniquely described by its charge density, which can itself be described as a function of just three variables $n(\mathbf{r})$, rather than 3N variables $\Psi(\mathbf{r}_i)$. To give an introduction to DFT, it is instructive to start by considering the Hohenberg-Kohn (HK) theorems [68], the first of which states:

Theorem 1 The ground state particle density of a system with a potential V, uniquely determines the potential of that system up to a constant.

The consequence of this is that the ground state particle density must contain all the relevant physical properties of the system, as it uniquely describes the potential of the system. This means any physical quantity should be able to be expressed in terms of the particle density $n(\mathbf{r})$ alone. The second theorem states that:

Theorem 2 There exists a functional F[n], that is independent of the external potential V_{ext} , that has the property that when $E_0[n] = F[n] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r})$ has a minimum E_0 which is the ground state energy of the system, and n_0 , the ground state particle density, is the functional that minimizes it.

This implies that the system is completely described by $E_0[n]$, since it describes n_0 . Meanwhile, F[n] is the functional that contains a description of all kinetic and interaction energy terms in the system which is, remarkably, completely independent of the external potential. Unfortunately, there is no known form for F[n], meaning that we cannot use this result directly. However, Kohn and Sham later developed a strategy [69] that maps this problem onto a problem which we can solve using some assumptions. We start by writing the particle density as a sum over occupied single particle states:

$$n(\mathbf{r}) = \sum_{i} |\psi_{i}^{*}\psi_{i}|^{2}.$$
 (2.1)

We then write the equation from the second HK theorem, adding a Lagrange multiplier to conserve particle number:

$$\delta \left\{ F[n] + \int \mathrm{d}\mathbf{r} n(\mathbf{r}) V_{ext} \mathbf{r} - \mu \left(\int \mathrm{d}\mathbf{r} n(\mathbf{r}) - N \right) \right\}.$$
 (2.2)

This yields the equation:

$$\frac{\delta T_s[n]}{\delta n} + V_{KS} = \mu, \qquad (2.3)$$

where $T_s[n]$ is the kinetic energy functional, and V_{KS} is a potential, which not only includes the external potential but also the exchange and correlation potentials. It is equal to:

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}), \qquad (2.4)$$

where $V_{xc}(\mathbf{r})$ is the exchange correlation term and the integral is the Hartree term, both arising from F[n]. This equation can now be solved by considering the set of N coupled equations:

$$\ddot{H}_{KS}\psi_i = \varepsilon_i\psi_i,\tag{2.5}$$

with $\hat{H}_{KS} = \sum_{i} \frac{\hbar}{2m} \nabla_i^2 + V_{KX}(\mathbf{r})$. Although the problem is now much more tractable, there is unfortunately, no simple description of what V_{xc} should be. There have been many approximations to this problem. Among the most famous of these are the so-called local density approximation (LDA) and the generalized gradient approximation (GGA). The former only considers the local density, and treats the exchange potential like that of a homogeneous electron gas, for which the exchange potential was calculated by Dirac [70]. The correlation potential can be fit to Monte-Carlo simulations [71]. The GGA also considers gradient terms, as implemented in Ref. 72 for example. Throughout this work, we rely mostly on the GGA exchange correlation potential described by Perdew, Burke and Ernzerhof [73].

Since V_{KS} depends on the particle density, this equation has to be solved self-consistently. The way this is done in practice is by making an assumption about the particle density, from which the potential is calculated and the Kohn-Sham (KS) equations are solved, which leads to a new particle density. This is repeated until a convergence criterion is reached. This can be taken to be the total energy or charge density differing by less than a user-set amount from one iteration to the next.

There are various sets of basis functions one can choose for the ψ_i . An obvious choice is the atomic orbitals (Gaussian or Slater type orbitals), which is a basis set often used for molecular calculations. For periodic systems, an appropriate choice is a set of plane waves on a k-point grid. A practical problem that arises in that case is that the 1/r like potentials of nuclei cause a very sharply spiked wave function at the centre of the nuclei, for which a very large number of small wavelength plane waves is needed to accurately describe the charge density. This means that the basis set becomes large, causing larger computational times for the matrix diagonalization step in solving the set of coupled equations in Eq. 2.5. These scale as $\mathcal{O}(S^3)$, with S the size of the basis, so it is advantageous to reduce the number of basis functions as much as possible, without losing accuracy. A solution to this problem is to change the atomic potentials with so-called pseudopotentials, which give wavefunctions that are equal to the ones found from real potentials at $r > r_A$. An example of a code that uses this scheme is Quantum Espresso [74]. Another solution to this problem is the linear augmented plane wave (LAPW) basis set, in which the basis functions are defined to be atomic orbitals within a sphere around each atom, augmented with plane waves in the interstitial region. An example of a code that uses this scheme is Wien2k [75], which is the program that has been primarily used for this work.

Although the KS approach allows us to find the ground state density of the system, and therefore find its energy, there is no guarantee that the KS eigenenergies ε_i carry any physical meaning. Hartree Fock theory has Koopmans' theorem that states the ionization energy of the system is equal to the energy of the highest occupied molecular orbital [76]. This description would in principle map onto the Kohn-Sham equations, however this turns out to be difficult in practice and is very dependent on the form of the functional [77–79]. Unfortunately, this still does not give any meaning to other ε_i , and direct comparison to techniques that measure the one-particle spectral function, like angle-resolved photoelectron spectroscopy (ARPES), should only be done with this caveat in mind. Nevertheless, the comparison is frequently made and we can find some comfort in symmetry considerations that constrain a large part of the problem. On a more intuitive level, the Kohn-Sham equations appear to describe exactly the problem of a single electron moving through the background of all other electrons and the external potential of the system. This justifies the interpretation of the ε_i as the single particle energies but does not guarantee the same interpretation for many-body systems.

Although band structure comparisons only hold in the single particle limit, there are other properties that DFT is able to capture more robustly. This includes, for example, ion valencies and charge densities, as well as atomic forces and the derived results using structure optimization. Recognizing the weaknesses and strengths of DFT makes it an incredibly powerful and useful tool for modelling and understanding experimental data. DFT is used throughout this thesis as the basis of many models and calculations.

2.1.2 Wannier functions

Wannier functions are the real space counterpart of Bloch functions and can be useful if an interpretation in real space is appropriate. In a simple description, Wannier functions are a non-unique set of functions that form the building blocks for the periodic $u_{n,\mathbf{k}}(\mathbf{r})$ part of the Bloch waves. Conversely, the Fourier transform of a Bloch function should yield a Wannier function centred at all real-space lattice sites. Wannier defined a set of real-space functions as the building blocks for Bloch functions as[80–82]:

$$\left|\mathbf{R}n\right\rangle = \frac{V}{2\pi} \int_{BZ} \mathrm{d}\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} \left|\psi_{n\mathbf{k}}\right\rangle,\tag{2.6}$$

where $|\mathbf{R}n\rangle$ is the Wannier function with label n at lattice position \mathbf{R} , $|\psi_{n\mathbf{k}}\rangle$ is the Bloch state with label n at \mathbf{k} , and the integral is over the entire Brillouin zone. In the case of a discrete \mathbf{k} grid, as is often the case in electronic structure calculations, this integral would be replaced by a sum



Figure 2.1: The relationship between a Bloch wave and a Wannier function. (a) A Bloch wave consisting of a phase changing with wavevector k, that multiply the repeating Wannier function depicted in (b).

over all **k**-points. The inverse of the transformation is given by:

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\mathbf{R}n\rangle. \qquad (2.7)$$

From this equation it can easily be seen that Wannier functions form building blocks of Bloch waves, which are modulated only by a phase factor throughout a crystal. Fig. 2.1a shows a Bloch wave, consisting of Wannier functions in Fig. 2.1b. Both form a complete orthonormal basis set, and the Fourier transform is the relation between the two.

There is, however, one difficulty arising from the calculation of Wannier functions, which is that Bloch waves have a gauge freedom that propagates into the shape of the Wannier functions. In other words, the Wannier functions belonging to a set of Bloch waves are not unique. The gauge invariance is [82]:

$$\tilde{\psi}_{n\mathbf{k}} \rangle = e^{i\phi(\mathbf{k})} |\psi_{n\mathbf{k}}\rangle, \qquad (2.8)$$

with $\phi(\mathbf{k})$ being any smooth function that follows the periodicity of the lattice in k-space. Both $|\tilde{\psi}_{n\mathbf{k}}\rangle$ and $|\psi_{n\mathbf{k}}\rangle$ give physically accurate descriptions of the system in question, but their calculated Wannier functions differ. The case gets more complex in the multi band case, as any unitary transformation applied to the set of Bloch waves results in the same physical description of the system:

$$\left|\tilde{\psi}_{m\mathbf{k}}\right\rangle = \sum_{m} U_{nm}\left(\mathbf{k}\right) \left|\psi_{n\mathbf{k}}\right\rangle,$$
(2.9)

where $U_{nm}(\mathbf{k})$ is now an arbitrary unitary transformation that is periodic and smooth in \mathbf{k} .

To fix the gauge and set the matrix of phases, a widely used criterion is the one of maximal localization, the gauge that yields Wannier functions that are the most localized. The method for calculating maximally localized Wannier functions (MLWFs) was developed by Marzari and Vanderbilt [83], and relies on minimizing the functional that describes the spread in the home unit cell:

$$\Omega = \sum_{n} \left(\langle \mathbf{0}n | r^2 | \mathbf{0}n \rangle - \langle \mathbf{0}n | \mathbf{r} | \mathbf{0}n \rangle^2 \right).$$
(2.10)

The minimization happens with respect to $U_{nm}(\mathbf{k})$, to find the correct gauge that describes a set of Wannier functions that are maximally localized within the home cell.

An example of a Wannier calculation performed on Sr_2IrO_4 is presented in Fig. 2.2. The calculated DFT band structure is plotted in black with the corresponding Wannier band structure displayed in red. The real space shape of the Wannier orbitals is plotted too as an iso-surface for each individual orbital. The shapes of the Wannier orbitals reflect a previously mentioned point (Section 1.2.1): the physics that is often only discussed in terms of Ir *d* orbitals should rather be seen as Ir-O hybrids, here visible in the Wannier functions as additional lobes to the t_{2g} orbitals. Note that these hybrids still follow the symmetry of the original Ir orbitals.

Wannier functions in this work are mainly used to derive a model Hamiltonian from first principles calculations, which is more versatile for further calculations than the results from DFT. In particular, when the right choice for $U_{nm}(\mathbf{k})$ is found, this defines a transformation from k-space into real space that can be applied to the KS Hamiltonian $H_{\mathbf{k}}$. We obtain the real



Figure 2.2: An example of a Wannier calculation: the black thin lines represent a DFT calculation of Sr_2IrO_4 , with the red curve a Wannier band structure generated from the t_{2g} orbitals. The inferred Wannier model projects onto the low energy physics and is more compact and interpretable than the original DFT calculation. Iso-surface plots of the generated orbitals are shown, with red and blue colours representing positive and negative amplitudes. The iso-surface for each orbital is taken at 10% of the maximum value of the wavefunction. space Hamiltonian by applying the transformation:

$$H_{\mathbf{R}-\mathbf{R}'} = \int_{BZ} \mathrm{d}\mathbf{k} e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} U_{nm}^{\dagger}(\mathbf{k}) H_{\mathbf{k}} U_{nm}(\mathbf{k}), \qquad (2.11)$$

which can be interpreted as a tight-binding Hamiltonian with the obtained Wannier functions as an orbital basis. This can now be used as a strategy to extract a tight-binding like Hamiltonian from *ab initio* calculations for orbitals with particularly chosen symmetries, for example, the $\text{Ir-}t_{2g}$ orbitals in Fig. 2.2. A projected tight binding Hamiltonian, in which only orbitals of particular character are kept, is often preferable to an electron density obtained from an *ab initio* code for two reasons. Firstly, simplifying the Hamiltonian makes the physics that is relevant to the problem much more interpretable. Secondly, because calculations are simpler and therefore faster. This makes it easier to define relevant quantities and calculate expectation values.

2.1.3 The tight binding approach

The tight binding approach has been used extensively throughout this thesis. The following section briefly highlights important aspects of the technique, its strengths, and why it is convenient and appropriate to use for this work. The rudimentary idea is that we treat the electrons as independent particles which move independently in the crystal potential. If we use a basis set $\{|i\rangle\}$, the Hamiltonian can be expressed in terms of its matrix elements:

$$H_{ij} = \langle i|H|j\rangle, \qquad (2.12)$$

where $\{|i\rangle\}$ are some set of localized atomic like wavefunctions, limited to a particular set of orbital angular momenta. In the case of this thesis, this is often the iridium *d*-orbitals. The Hamiltonian matrix elements can in principle be calculated from the chosen basis and the Hamiltonian by direct integration. In practice they can be derived from Wannier calculations or fitting a model with orbitals of interest to either *ab initio* calculations or experimental data. When fitting such models, symmetry restricts many of the possible matrix elements to particular values. After collecting all matrix elements, the wavefunctions can be simply found by diagonalizing H_{ij} :

$$H\mathbf{v}_n = \varepsilon_n \mathbf{v}_n. \tag{2.13}$$

These wavefunctions include phases, which means we can easily calculate expectation values of operators, band projections, (partial) densities of states, as well as more complex quantities like the photoemission matrix element. The approach is computationally cheap, the calculation time required is the diagonalization of an $N \times N$ matrix, where N is the size of the basis. This allows us to study large clusters of atoms (up to 12×12 with 10 basis states per site for this work), without computational time becoming a limitation. Moreover, for a system like Sr_2IrO_4 , in which all *d*-orbitals on two separate Ir sites are important, it becomes computationally very costly to treat electron-electron interactions fully. Furthermore, the generated models are quite interpretable and therefore aid in explaining the underlying physics of the problem.

The downside of this is that the only way electronic interactions are included is as a background potential term arising from the original KS equations. Hence, this method cannot make accurate predictions about correlated physics, like the existence of a Mott gap. Nevertheless, the prevalence of orbital symmetry in solid state physics makes this a very predictive technique, particularly when it comes to calculating dipole matrix elements, on which both experimental chapters put a significant amount of emphasis. Therefore, tight binding built on *ab intio* calculations is one of the preferred methods for calculating quantities in this thesis.

2.2 Band unfolding

In physical systems, one of the useful control parameters is often chemical doping or substitution. To describe systems with impurities or dopants, the most accurate approach would be to work in the position basis, studying large clusters of atoms. However, this has the disadvantage that the basis set becomes very large and secondly, because of working in the position basis, calculations lose their interpretation with regards to k-dependence. A workaround to this problem is to take a combined approach and to make supercells of atoms. This consists of repeating the unit cell (N_x, N_y, N_z) times and adding impurities, vacancies, or making substitutions in the original lattice. A new synthetic periodic system is hereby effectively created, which no longer has the periodicity of the original crystal but models a regular distribution of impurities. Although this can, at best, be an approximation to the real system, the advantage is that it fits within the previously discussed models and momentum is kept as a good quantum number. A complication that arises, is that since the unit cell becomes larger, the reciprocal lattice vectors become N_i times shorter, with N_i times more bands in the first Brillouin zone. One can easily plot this band structure in the unfolded zone but that still leaves $N_x N_y N_z$ folded replica's that hinder a direct comparison to the original band structure. To interpret the folded band structure, we make use of band unfolding, a technique that attempts to recover the character of bands in the original Brillouin zone. A projection onto the Bloch waves that follow the periodicity of the original unit cell can be made, a technique discussed in [84, 85].

2.2.1 A simple example

We first consider a simple example, the case of a 1D chain of atoms with a single s orbital, with nearest neighbour hopping t. We will then consider a supercell consisting of two atoms, that makes up a new representation of an identical chain (see Fig. 2.4(a)). Before considering these band structures, it is insightful to highlight that the units of this supercell chain can be considered as diatomic molecules. The energy spectrum and wavefunctions for each of these molecules can be easily calculated. When two atoms are allowed to interact via some kinetic term 2t, we can write the Hamiltonian:

$$H = \begin{pmatrix} 0 & 2t \\ 2t & 0 \end{pmatrix}.$$
 (2.14)



Figure 2.3: The energy levels and wavefunctions of a diatomic molecule. The separate atoms are depicted on the outside of the figure, with the symmetric and anti-symmetric wavefunctions and energies in the centre.

This Hamiltonian has eigen-energies $E = \pm 2t$, with corresponding wavefunctions $\frac{1}{\sqrt{2}}(1,\pm 1)$. The wavefunctions and energies are also plotted in Fig. 2.3, for the uncoupled (a) and coupled case (b). The coupling of these states causes a symmetric (low energy) and anti-symmetric state (often referred to as a bonding and anti-bonding orbital). We now construct a chain of these atoms and compare it to a chain of molecules. Since these systems are physically identical (they only differ in their description), they should present the same observable results. A schematic of the comparison is sketched in Fig. 2.4a, with the description of the same system in terms of a size a and 2a unit cell. We start by considering the chain of single atoms, with unit cell size a. The dispersion for this system is shown in Fig. 2.4b, in black, from $\Gamma(k=0)$ to $X(k=\pi/a)$ (with a the spacing between two single atoms). To obtain the wavefunction at the Γ and X points, we use Bloch's theorem, which dictates that the wavefunction is only allowed to change up to a phase from unit cell and that phase should progress as e^{ikr} . We fix the phase of the first atom to one and plot the wavefunction for both the Γ $(|\psi_{\Gamma}(r)\rangle)$ and the X $(|\psi_X(r)\rangle)$ point, in Fig. 2.4(c) and (d) respectively.



Figure 2.4: Band unfolding in a chain of diatomic molecules. (a) Schematic overview of the model. The atoms are spaced aapart, and a supercell of two atoms (sized 2a) is considered. (b) Dispersion relation for a 1D chain of atoms (blue) and a 1D chain of diatomic molecules with the same hopping parameters (red). (c) The wavefunction for the 1D chain of atoms (black) and the progression of the phase (blue) at Γ . (d) The same at X. (e). Wavefunction from the symmetric state for the chain of molecules (black) with the phase indicated at Γ (blue) and Γ' (red). (f) The same as (e) for the anti-symmetric state. In this case the phase at Γ is indicated in red, while Γ' is in blue. The blue coloured phase lines correspond to the correct phase for the original unfolded cell.

Now we turn to the band structure of the two atom unit cell, indicated with the red dashed lines in Fig. 2.4a, which adds the folded replica of the original band structure plotted in red in panel (b). Note that these folded bands are effectively plotted in the first and second Brillouin zone, since the unit cell size doubled and the Brilluoin zone halved in size. The two folded bands have a simple interpretation at the Γ (and $\Gamma' = \pi/a$) point: they are the band structure of the symmetric (low energy) and anti-symmetric (high energy) hybrids that form in the previously discussed diatomic molecule. To identify which of these bands holds physical meaning at which k-points, we look at the phase progression of the wavefunction and require the same progression as in the single-atom case. Using the hybrid wavefunctions as the basis for the Bloch wave, we plot the wavefunctions $(|\psi_{sum}(r)\rangle)$ and $|\psi_{asym}(r)\rangle)$ of the folded band structure at the Γ point (identical to Γ'), including their phase progression for both Γ and Γ' in Fig. 2.4 (e) and (f). In this supercell model, the states displayed in (c) and (e) are reproduced as expected. However, the wavefunction that occurs at $\Gamma'(X)$ can now be found at Γ and similarly for the wavefunction at Γ can now also be found at $\Gamma'(X)$. As stated, since these models are identical, they should yield the same observable results. Comparing the wavefunctions in (e) and (f) to the plotted Bloch phases of the unreconstructed cell, it is clear which wavefunction is the correct one for which k-point. The wavefunction in (e) belongs to Γ while the wavefunction in (f) belongs to Γ' . We therefore find that both models yield the same results as expected, as long as we enforce the correct progression of Bloch phases.

For this example, it is easy to see which state belongs to the original cell. However, for unit cells with more than two atoms, this quickly gets rather complex. We can extend the requirement of a physically correct band beyond our simple model; we need to require that the phases of the wavefunction in the supercell follow the phase progression of the Bloch waves in the primitive cell. Quantitatively, we project the supercell wavefunction onto the Bloch phases of the original cell. By doing this, it is easy to see that $|\psi_{sym}(r)\rangle$ in Fig. 2.4 has the correct phase for Γ and would project to unity but for X it would project to zero. This method implicitly assumes that the impurities are similar to the original species, as it enforces the symmetries of the original crystal onto the supercell. Practically, it also requires that the number and type of orbitals are the same.

2.2.2 Projecting Bloch phases

A more rigorous derivation calculates the weight of the spectral function for Bloch functions in the original primitive cell from the spectral function in the supercell. This is demonstrated in Ref. 85, we present that derivation here, including some intermediate steps. The spectral function for a Wannier function $|kn\rangle$ reads:

$$A_{kn}(\omega) = \sum_{K,J} |\langle kn | KJ \rangle|^2 A_{KJ}(\omega), \qquad (2.15)$$

where $|kn\rangle = \frac{1}{\sqrt{N_{\mathbf{r}}}} \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} |rn\rangle$, with n an index that labels the Wannier orbital. $|KJ\rangle$ are the eigenstates of the supercell, with K the momentum in the folded Brillouin zone, and J a band index. We can express $|KJ\rangle$ in terms of its Wannier constituents as:

$$|\mathbf{K}J\rangle = \sum_{N} \langle \mathbf{K}N | \mathbf{K}J \rangle | \mathbf{K}N \rangle .$$
 (2.16)

Where $|\mathbf{K}N\rangle$ is a Bloch wave constructed of Wannier functions in the same way the $|kn\rangle$ was defined:

$$|KN\rangle = \sum_{\mathbf{R}} e^{i\mathbf{K}\cdot\mathbf{R}} |\mathbf{K},\mathbf{R}\rangle.$$
 (2.17)

We can then write the projection as:

$$\langle kn|KJ \rangle = \sum_{\mathbf{R},N} \langle kn|\mathbf{R}N \rangle \langle \mathbf{R}|KN \rangle \langle KN|KJ \rangle$$

$$= \sum_{\mathbf{R},\mathbf{R}',N,\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle \mathbf{r}n|\mathbf{R}N \rangle e^{i\mathbf{K}\cdot\mathbf{R}'} \langle \mathbf{R}N|\mathbf{R}'N \rangle \langle \mathbf{K}N|\mathbf{K}J \rangle.$$
(2.18)

To evaluate $\langle \mathbf{r}n | \mathbf{R}N \rangle$, we write the normal cell position in terms of the supercell position and set $\mathbf{r} = \mathbf{R} + \boldsymbol{\rho}(N)$, a sum of the supercell position, and a vector within the supercell pointing to the particular atom $\boldsymbol{\rho}(N)$. We can now eliminate most projections and write the expression as:

$$\langle \mathbf{k}n | \mathbf{K}J \rangle = \sum_{\mathbf{R},N} e^{i(\mathbf{K}-\mathbf{k})\cdot\mathbf{R}} e^{-i\mathbf{k}\cdot\boldsymbol{\rho}N} \delta_{n,n'(N)} \langle \mathbf{K}N | \mathbf{K}J \rangle$$
$$= \sum_{N} e^{-i\mathbf{k}\cdot\boldsymbol{\rho}N} \delta_{n,n'(N)} \delta_{\mathbf{K}'(\mathbf{k}),\mathbf{K}} \langle \mathbf{K}N | \mathbf{K}J \rangle.$$
(2.19)

Here, n'(N) is the function that recovers the band index in the original cell. This means that the sum should only run over orbitals that are identical in the primitive cell. Meanwhile, $\mathbf{K}'(\mathbf{k})$ describes the momentum of \mathbf{k} in the folded unit cell. In the case when the supercell model is constructed as a tight binding model from Wannier orbitals, the terms $\langle \mathbf{K}N | \mathbf{K}J \rangle$ are simply the coefficients of the eigenvectors $c_{J,N}(\mathbf{K})$, we recover the expected result for our weighted spectral function:

$$A_{\mathbf{k},n}^{J}(\omega) = \sum_{N \text{ in SC}} \left| e^{-i\mathbf{k}\cdot\boldsymbol{\rho}(N)} c_{J,N}(\mathbf{k}) \right|^{2} A_{\mathbf{k},J}^{N}(\omega).$$
(2.20)

This shows the intuition from the two-atom unit cell was correct. We need to require the phase within the supercell to progress the same way that the state in the original cell would. This is mathematically enforced by the product of coefficient and exponential; any solution that does not have the right phase relation will interfere out.

As an example, we extend the chain diatomic molecules presented in Fig. 2.4a to a supercell size of 20 atoms. The band structure for this system is plotted in thin black lines in Fig. 2.5a. To illustrate the unfolded bands, the band structure is also plotted in blue markers, with their transparency set by the unfolded weight. We see that this method effectively recovers the original expected band (red curve) from the many folds of bands. As an example of a way in which this technique can be used for a non-trivial calculation, we show the calculated unfolded band structure for the same system, where one atom

has an added impurity potential of 0.4t in Fig. 2.5b. The unfolded bands are shown in green and it can be seen that the single impurity introduces disorder into the band structure, in the form of intensity on the other folded bands, particularly around the Γ point. The interpretation of results that are obtained using this technique will be discussed in more detail in Chapter 3, in particular sections Section 3.3 and Section 3.3.2.

2.2.3 Impurity distributions

To represent a real substituted system and model a material that properly captures the observations as seen by ARPES, the system size would need to be on the order of the probe size (150 μ m) and the computation would be intractable (~ 10¹¹ atoms). Therefore, simulations are limited to smaller system sizes, in the case of this thesis up to 12 × 12. To reflect the different possibilities of distributions of impurities, many configurations are averaged until no further change is seen in the resulting spectrum.

A point to note here is the amount of impurities; the number of impurities for a given doping follows a binomial distribution. For a system with size nand doping p, the probability that we find k impurities is:

$$P(n, p, k) = {\binom{n}{k}} p^k \left(1 - p\right)^{n-k}.$$
 (2.21)

The binomial distribution has the property that its width increases as $\sigma_k \propto \sqrt{n}$. Since the actual observed doping can be calculated as $\bar{p} = \frac{k}{n}$, the spread in concentrations follows $\sigma_{\bar{p}} \propto \frac{1}{\sqrt{n}}$ and thus reduces as the modelled system size increases. This effect can be clearly seen in Fig. 2.6, where the distribution of impurities, $P_n(\bar{p})$, is plotted for various system sizes at a fixed p. To circumvent this issue, we find that more sensible results are obtained if the number of dopants for a particular configuration is fixed to a set number, obtained by rounding $\langle k \rangle = pn$ to the nearest integer. We then average over different configurations of impurities to simulate a system that reflects the impurity distribution of a large system size. This makes the results independent of the modelled system size. The approach equates to artificially setting the width of the distribution to zero, which is reflective



Figure 2.5: 20-site supercell model for a one-dimensional chain of atoms with a single s-orbital. (a). The band structure for the 20-site supercell (thin black curves) and the unfolded band structure (blue markers, transparency set by unfolded weight).
(b) Band structure for the same model where one atom has an impurity potential of 0.4t added (green markers, transparency encodes for the unfolded weight).



Figure 2.6: Probability to find a number of impurities as a function of the system size. While the number of impurities that are observed k grows linearly with system size n, the width of the distribution only grows as \sqrt{n} . This implies that the effective range of concentrations (k/n) reduces as the system size goes up.

of a very large system size as $\frac{1}{\sqrt{n}} \to 0$.

2.3 Angle-resolved photoelectron spectroscopy

Angle resolved photoelectron spectroscopy (ARPES) is a powerful technique used for studying the electronic structure of electrons in solids experimentally. It is a direct probe for both electron momentum and energy, and moreover provides a direct measure of the interactions between electrons and other particles. The information overlaid in this section mostly follows Ref. [86].

2.3.1 Theory of photoemission

The technique is based on the photoelectric effect, which is the liberation of an electron from a material after excitation by a photon. If the energy of the incident photon is known by using a monochromatized source of light, the kinetic energy E_k of the emitted photoelectron can be measured and the binding energy E_b can be calculated. We start by invoking conservation of energy:

$$E_b = h\nu - E_k - \Phi. \tag{2.22}$$

Here, $h\nu$ is the photon energy and Φ is the work-function, a sample dependent potential that describes the energy difference between the Fermi energy and the vacuum energy. If the photoelectron is emitted into vacuum, the kinetic energy also gives the absolute value of the momentum of the emitted electron, through the dispersion relation of a free particle:

$$\hbar k = \sqrt{2m_e E_k}.\tag{2.23}$$

By using conservation of momentum and the take-off angles of the photoelectron, we can extract the in-plane momentum of the electron before it was emitted:

$$\mathbf{k}_{\parallel} = k \sin \theta \left(\cos \left(\phi \right) \hat{\mathbf{x}} + \sin \left(\phi \right) \hat{\mathbf{y}} \right).$$
(2.24)

Unfortunately such a simple form does not exist for k_{\perp} . Since translational symmetry perpendicular to the surface is broken, this momentum is not conserved. The perpendicular momentum can however often be approximated by:

$$\hbar k_{\perp} = \sqrt{2m_e \left(E_k \cos^2 \theta + V_0\right)},\tag{2.25}$$

where V_0 is the inner potential, describing the bottom of the valence band. The inner potential, a parameter on the order of 10 eV is often inferred from experiment. The perpendicular momentum is only of importance for three-dimensional materials however. In general the preferred materials for an ARPES experiment are (quasi-) two-dimensional, in part because here k_z is irrelevant, but also because two-dimensional materials often have a natural cleavage plane, which is important for sample preparation. The definition of "two-dimensional" in this case means the electron dispersion is fully (or mostly) in a plane, embedded as a stack of layers in a threedimensional material. A useful criterion for determining two-dimensionality is the requirement that no bands cross, and no electron or hole pockets close as a function of k_z .

We consider the theory behind photoemission, by treating the interaction

with light perturbatively. We make the canonical substitution $\mathbf{p} \to \mathbf{p} - \frac{e\mathbf{A}}{c}$ to account for the light. Dropping the quadratic term in \mathbf{A} , we obtain for H_{int} :

$$H_{int} = -\frac{e}{2mc} \left(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} \right)$$
(2.26)

Using the commutator $[\mathbf{p}, \mathbf{A}] = -i\hbar \nabla \cdot \mathbf{A}$ and the fact that the wavelength of ultraviolet (UV) light is large enough that we can set $\nabla \cdot \mathbf{A} = 0$, we get for H_{int} :

$$H_{int} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \tag{2.27}$$

With the interaction Hamiltonian, we can describe the transition probability from the many body grounds state Ψ_i^N into a particular final state Ψ_f^N using Fermi's golden rule:

$$w_{f,i} = \frac{2\pi}{\hbar} \left| \left\langle \Psi_f^N \middle| H_{int} \middle| \Psi_i^N \right\rangle \right|^2 \delta \left(E_f^N - E_i^N - h\nu \right).$$
(2.28)

Here, E_f^N and E_i^N are the energies of the initial and final state many body electron wavefunctions.

To calculate this, one would need full knowledge of the many body wavefunction, properly taking into account the sample surface and related effects. This method is therefore quite cumbersome and often the process of photoemission is modelled by the so-called three-step model. In this case, the photoemission process is phenomenologically split up into separate processes: excitation into the bulk, travel to the surface, and emission from the surface. This allows one to approximate the photoemission intensity by transition probabilities that ignore the effect of the surface on the Hamiltonian. Another assumption that is made is the so-called sudden approximation, which considers the process of photoemission instantaneous and makes it possible to neglect any interactions between the photoelectron and core hole that is left by the photoemission process. The many body final state can then be written as a product of a single particle ψ_f and an N-1 particle many body state Ψ_f^{N-1} :

$$\Psi_f^N = \mathcal{A}\phi_f \Psi_f^{N-1}, \qquad (2.29)$$

where \mathcal{A} is an operator that anti-symmetrizes the wavefunction. If we assume that the initial state can be written as a single Slater determinant, we can write a similar factorization:

$$\Psi_i^N = \mathcal{A}\phi_i \Psi_i^{N-1}, \qquad (2.30)$$

where the subscript *i* now denotes the initial state wavefunction. As a convenient choice for the possible final states, we can take the eigenstates of the N-1 electron Hamiltonian, labelled by *m* as Ψ_m^{N-1} with energies E_m^{N-1} . The matrix element for the scattering amplitude in to one such eigenstate then becomes:

$$\left\langle \Psi_{f,m}^{N} \middle| H_{int} \middle| \Psi_{i}^{N} \right\rangle = \left\langle \phi_{f} \middle| H_{int} \middle| \phi_{i} \right\rangle \left\langle \Psi_{m}^{N-1} \middle| \Psi_{i}^{N-1} \right\rangle, \tag{2.31}$$

in which the first term is the dipole matrix element and the second term describes the many-body spectrum. To gain insight into the second term, we note that for systems in which electron correlations are important, $\Psi_i^{N-1} = c_{\mathbf{k}} \Psi_i^N$ is not an eigenstate of the N-1 electron Hamiltonian. Equivalently, if electron-electron interactions are ignored, the N particle Hamiltonian is identical to the N-1 Hamiltonian and Ψ_i^{N-1} will be an eigenstate. In the former case, Ψ_i^{N-1} may have many projections onto the N-1 eigenstates $c_{m,i} = \left\langle \Psi_i^{N-1} \middle| \Psi_m^{N-1} \right\rangle$ that are non-zero. To obtain the full transition probability, we sum over all initial and final single particle states, as well as all N-1 eigenstates:

$$I(\mathbf{k}, E_{kin}) = \sum_{i,f,m} \left| M_{f,i}^{\mathbf{k}} \right|^2 |c_{i,m}|^2 \,\delta\left(E_{kin} + E_m^{N-1} - E_i^N - h\nu \right).$$
(2.32)

The quantity $\left< \Psi_i^{N-1} \middle| \Psi_m^{N-1} \right>$ can be related to the one-particle removal Green's function:

$$G^{-}(\mathbf{k},\omega) = \sum_{m} \frac{\left|\left\langle \Psi_{m}^{N-1} | c_{\mathbf{k}}^{-} | \Psi_{i}^{N} \right\rangle\right|^{2}}{\omega - E_{m}^{N-1} + E_{i}^{N} - i\eta}$$
(2.33)

Taking the limit $\eta \to 0^+$, this corresponds to the one-particle removal spec-

tral function as:

$$A^{-}(\mathbf{k},\omega) = -\frac{1}{\pi} \operatorname{Im} G^{-}(\mathbf{k},\omega)$$
$$= \sum_{m} \left| \left\langle \Psi_{m}^{N-1} \middle| c_{\mathbf{k}}^{-} \middle| \Psi_{i}^{N} \right\rangle \right|^{2} \delta\left(\omega - E_{m}^{N-1} + E_{i}^{N}\right)$$
$$= \sum_{m} |c_{i,m}|^{2} \delta\left(\omega - E_{m}^{N-1} + E_{i}^{N}\right), \quad (2.34)$$

in which we can see the right-hand side of Eq. 2.32 reappear. Note that in the case where electron-electron interactions are ignored, we can describe Ψ_m^{N-1} using a single eigenstate with $m = m_0$, and all other terms vanish. This means that the spectrum looks like a single delta function peak at energy ϵ_m . When electron-electron interactions are taken into account, the spectrum will have many peaks or a continuum of peaks as a broad hump. A famous example is the case of photoemission from molecular hydrogen, which produces an excited state of H_2^+ under photoemission. One observes a peak for each possible vibrational mode that overlaps with the ground state, minus one electron [87].

2.3.2 A photoemission experiment in practice

In this section we will discuss the parameters and considerations of a typical photoemission experiment. Experiments are normally performed using photon energies between 20 and 200 eV. In principle, the lower limit is set by the sample work function Φ , with an additional amount for the photoelectron to have non-zero velocity, so it can reach the analyzer. Although in practice, at such low energies, stray magnetic and electric fields tend to influence the measurements. Additionally, the aforementioned sudden approximation is likely invalid and the final state can no longer be modelled by a free electron. Although in theory there is no upper limit, the disadvantage of using higher photon energies is that the absolute energy and momentum resolution worsens linearly and quadratically, respectively. All data presented in this thesis are taken between 44 and 120 eV.

A challenge arising with these particular energies is that electron scat-

tering cross sections are very high and therefore the escape depth is only on the order of a few atomic spacings. This requires measurements to be done at ultra-high vacuum pressures ($< 5 \ 10^{-10}$ mbar) and samples to be prepared *in-situ*. This limits the technique to samples than can be prepared appropriately. This implies either cleaving of bulk crystals, *in-situ* growth like molecular beam epitaxy, evaporation or pulsed laser deposition, or some cleaning of a polished surface by sputtering and annealing. Meanwhile, in order to measure momentum, single crystals are needed so that the system is translationally symmetric. Samples studied in this thesis are all single crystalline, prepared by cleaving *in-situ*.

Since ARPES attempts to measure energies precisely, experiments are carried out at low temperatures to combat the broadening arising from k_BT . In practice, a cryostat is integrated into a movable sample stage, with liquid He providing cooling (displayed in gold in Fig. 2.7). Base temperature depends on the design of the system but is ordinarily between 4.2 and 20 K. While lower temperatures are better for optimizing energy resolution, the data presented in this thesis are taken at higher temperatures because of the insulating nature of Sr_2IrO_4 . Since electrons are removed from the material by the UV light, these need to be replenished or the sample will gain an electrostatic charge. This changes the energy of the photoemitted electrons and in some cases completely prevents photoemission. To mitigate this problem in Sr_2IrO_4 , most of the measurements in this thesis were performed at 150 K, at which temperature the resistivity is lower [17].

The UV light required for ARPES experiments can be generated in a multitude of ways. One strategy is to use a discharge lamp in conjunction with an inert gas, often He, which produces spectral lines at 21.1 and 40.8 eV. The disadvantage of using a discharge lamp is that the spot-size is typically quite large ($\sim 1 \text{ mm}^2$) and the energies are limited to the spectral lines of the gas used. Another strategy is to use a synchrotron light source, in which electrons are stored at highly relativistic energies in an accelerator ring. Devices with periodic arrays of magnets are inserted into this ring and the electrons generate light as they fly by. The advantage of using a synchrotron light source is that a large range of photon energies is available,

with a spot-size that is on the order of $\sim 100 \times 100 \ \mu$ m, with controllable, arbitrary polarization. However, in this case the user relies on allocated periods of "beamtime", which are highly competitive and limited. All of the work presented in this thesis was done at synchrotron light sources, although additional work using He-lamp ARPES was done for sample characterization and other initial experiments.

The electron analyzer used for ARPES experiments consists of two concentric hemispheres. A constant electric field is applied to an inner and outer shell, causing electrons with different energies to follow circular trajectories with different radii. Electrons enter the analyzer through an entrance slit, which allows a one-dimensional range of angles to be detected simultaneously. The energy separation in the hemisphere expands this onedimensional cut into a two-dimensional detector image. The electrons are incident on a phosphor screen and are subsequently detected by a camera. The full process of emission and dispersion in the hemisphere is depicted in Fig. 2.7, as well as the geometry of sample, analyzer and detector. Current ARPES chambers have an energy resolution on the order of 1 meV and an angular resolution better than 0.1° . Although such resolutions of $\sim 1 \text{ meV}$ are technically attainable at most of the experimental setups used in this thesis, the broad nature of the spectrum of Sr_2IrO_4 means that measurements presented here have been optimized towards counts, and are performed at an energy resolution of approximately 20 meV.

In Fig. 2.8 we show an example of a high quality ARPES dataset. This data was taken as a part of the commissioning of the Quantum Materials Spectroscopy Center (QMSC) endstation at the Canadian Light Source (CLS). The data shown were collected on Sr₂RuO₄, using 48 eV photons with horizontal polarization (indicated with a black arrow marked $\vec{\epsilon}$), at a sample temperature of 20 K. Sr₂RuO₄ has been studied using ARPES numerous times before [49, 88] and it is an excellent demonstration of what the requirements are to obtain a high quality dataset. This involves a high quality sample, with a freshly cleaved surface, a low vacuum pressure (6 10⁻¹¹ mbar), a small spot-size (150 μ m), and a high quality analyzer with a good angular resolution.



Figure 2.7: Schematic representation of an ARPES experiment. A (cutaway) hemispherical analyzer is shown with the trajectory of the electrons indicated. The one-dimensional entrance slit combined with the energy dispersion results in a two-dimensional image. The electrons are incident on a phosphor screen and are subsequently detected by a camera. The geometry is variable to access all possible take-off angles. Rather than moving the entire analyzer, the sample is rotated with the aid of a 6-axis manipulator. The manipulator can be rotated around its axis, the other two axes of rotation are internal. Light is incident from an angle next to the detector.



Figure 2.8: Example measurement of Sr_2RuO_4 , a dataset that was taken during commissioning time of the QMSC beamline at CLS. The data was taken at 20K, using 48 eV photons with linear horizontal polarization (indicated with a black arrow in panel (a)). The colour encodes the intensity of the photocurrent, with a linear scale indicated. (a) "Fermi surface map", a representation that plots the intensity recorded at many angles at the Fermi energy. The data here is integrated over 2 meV to improve statistics. (b) A single slice as measured. The data presented in (a) is recorded by measuring many of these individual slices at different manipulator angles. The curve traced out by the slit through k-space to record (b) is indicated in (a) as a thin dashed line.

The data is collected as a so-called Fermi-Surface mapping, in which the manipulator angles are changed sequentially and a spectrum $I(E, \theta)$ (Fig. 2.8(b)) is collected at each angle. These spectra can be put together to form a complete solid angle. After transforming the data into k-space using the expression in Eq. 2.24, the data can be plotted at constant energy in Fig. Fig. 2.8(a).

The many sharp bands that are visible correspond to the α , β and γ pockets of Sr₂RuO₄ and their folded replicas (α' , β' and γ') [49]. Furthermore, the two different surface octahedral rotations give rise to the doubled

bands, as explained in [88].

2.3.3 The photoemission dipole matrix element

The work in this thesis emphasizes on the simulation and modelling of the dipole matrix element introduced in Section 2.3.1. The purpose of this section is to explain the approach that is taken to calculate this quantity from tight binding and first principles calculations.

The goal is to calculate the photoemission matrix element arising from the dipole term in Fermi's golden rule in Eq. 2.28, which is given by [89]:

$$\left| M_{i,f}^k \right|^2 \propto \left| \left\langle \psi_f^k \left| \mathbf{r} \cdot \boldsymbol{\varepsilon} \right| \phi_i^k \right\rangle \right|^2, \qquad (2.35)$$

where ϕ_i^k is the initial state, ε is the light polarization vector, and ψ_f^k is the final state wavefunction. For the final state, a plane wave is used, which is an approximation that is valid if the kinetic energy is sufficiently high. The initial state is taken to be an eigenstate of a tight-binding Hamiltonian. It is insightful to first look at the symmetries of particular states and try to infer some information about the value of the matrix element in Eq. 2.35. Considering the illustration in Fig. 2.9, we can directly see that the dipole matrix element carries information about the symmetry of the initial state. The integrand, consisting of polarization, orbital, and plane wave like final state, needs to be an even function or it will vanish. Considering the plane spanned by the incoming light and the outgoing photoelectron, the free electron state is even, while for σ -polarization (as shown), the term $\mathbf{r} \cdot \boldsymbol{\varepsilon}$ is odd, which requires the initial state to be odd.

We can improve this simple picture by including the phases of the tight binding wavefunction and calculating the actual value of the matrix element. To do so for an arbitrary initial state ϕ_i^k , we expand it in terms of spherical harmonics:

$$\phi_{i}^{k} = R_{n,\ell} \sum_{m,\ell} C_{\ell,m}^{k} Y_{\ell}^{m}, \qquad (2.36)$$

where the phase and amplitude information is contained in $C_{\ell,m}^k$. Tight binding models in this thesis are in terms of cubic harmonics, which are



Figure 2.9: Illustration of the geometry used to calculate the photoemission matrixelement.

easily converted to spherical harmonics, making this a convenient basis to work in. Similarly, we write the final state in terms of spherical harmonics using the plane wave expansion:

$$\psi_f^k \propto e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{m=\ell} i^\ell j_\ell(kr) Y_\ell^m\left(\theta_{\mathbf{k}}, \phi_{\mathbf{k}}\right) \left(Y_\ell^m\left(\theta_{\mathbf{r}}, \phi_{\mathbf{r}}\right)\right)^*, \qquad (2.37)$$

where $j_{\ell}(kr)$ is the spherical Bessel function and the spherical harmonics are functions of the angles describing the **r** and **k** vectors. We can also write the polarization vector in terms of the $\ell = 1$ spherical harmonics, to obtain:

$$M_{\epsilon,\sigma} = \sum_{\substack{\ell_i,\ell_f,m_i\\m_{\varepsilon},m_f}} B_{n_i,\ell_i,\ell_f} \left(\int d\Omega_{\mathbf{r}} Y_{\ell_i}^{m_i} Y_1^{m_{\varepsilon}} Y_{\ell_f}^{m_f} \right) Y_{\ell_f}^{m_f} \left(\theta_{\mathbf{k}}, \phi_{\mathbf{k}} \right).$$
(2.38)

The product of three spherical harmonics can be found using the Clebsch-Gordan coefficients. The radial integrals are written as :

$$B_{n\ell} = \int dr r^3 R_{n_i,\ell_i}(r) j_{\ell_f}(r).$$
 (2.39)

These integrals can be calculated using some assumption for the initial state radial wavefunction. In this work, Slater type orbitals are most often used as implemented in the chinook package [90]. The argument of $j_{\ell}(kr)$ in Eq. 2.39 depends on the photon energy through k, as it increases with the free electron kinetic energy E_k , which causes the photoemission final state ratio to be photon energy dependent. Since selection rules, based on conservation of orbital angular momentum, only allow the final states of $\ell_f = \ell_i \pm 1$ like character, this implies that a model that only describes a single manifold of ℓ_i states, all but two terms in Eq. 2.38 vanish. A single parameter (i.e. the ratio $B_{n\ell_i-1}/B_{n\ell_i+1}$), in addition to an overall normalization factor suffices in such cases. The ratio can be kept as a model parameter, which can be adjusted to best match experimental data.

2.4 Spin-ARPES

The experimental results presented in Chapter 4 make use of an extension of ARPES: spin-resolved ARPES, in which, aside from energy and momentum, the spin of the photoelectron is also measured. The spin is measured after travel through the hemispherical analyzer. The electrons are redirected by electron lenses, away from the two-dimensional detector, to a separate spin detector.

2.4.1 A practical spin-ARPES experiment

Various strategies have been used for detecting the spin of electrons. The one used for this thesis is very low energy electron diffraction (VLEED) off magnetic targets [91–94]. This technique uses a magnetized film to scatter electrons, which follow different trajectories for the spin up and spin down channels. The targets for the spin-detectors used in this thesis are made of FeO films, which are magnetized prior to the experiment, using electromagnets. The magnetic easy axis for the films is in plane [91], therefore, one film is able to detect a total of four spin-directions (both up and down spin for two quantization axes). To measure the full three-dimensional spin-structure, two of such detectors are needed. The geometry of the experiment is such that a total of 8 spin channels can be measured $(x_{\uparrow}, x_{\downarrow}, z_{\uparrow}, z_{\downarrow}, y_{\uparrow}, y_{\downarrow}, z_{\uparrow}', z_{\downarrow}')$, of which two are redundant and can be used to check the consistency between the two detectors. Relevant parameters for these detectors are the

efficiency in which electrons are detected, and efficiency in which electron spins are separated. The former is captured in the "figure of merit" (FOM) [94]:

$$FOM = S^2 I / I_0,$$
 (2.40)

where I/I_0 is the fraction of detected photoelectrons and S is the Sherman function, which describes the efficiency with which the spin is separated. The Sherman function can be determined from:

$$\frac{I_{\uparrow} - I_{\downarrow}}{I_{\uparrow} + I_{\downarrow}} = PS, \qquad (2.41)$$

in which I_{σ} are the measured spin up and down currents, P is the actual polarization of the photoemitted states, and S is the Sherman function. Spin-resolved photoemission experiments are often complicated by low values for these parameters. As an example, a different strategy to observe spin is the so-called Mott detector, for which a typical value for the FoM is between 10^{-3} and 10^{-4} with a Sherman function of 0.068 [95]. For VLEED, these parameters are drastically improved to 10^{-2} and 0.5 respectively [94]. Nevertheless, the challenge of high statistics data persists and often spinresolved ARPES is limited to a single k-point and long acquisition times.

2.4.2 Circularly polarized spin ARPES

Naturally, spin-resolved ARPES is limited to those compounds that have spin-polarized electron states to photoemit from. This means that spin-ARPES is frequently used to study the spin-polarized surface states of topological insulators [96, 97] or Rashba states that arise on the surface due to strong spin-orbit coupling and the absence of inversion symmetry [98, 99]. Contrary to that, in the case where spin-orbit coupling is strong and inversion symmetry is not broken, Kramers degeneracy dictates that although states might be highly entangled with the spin degree of freedom, those states are not in fact spin-polarized. When there are no such spin-polarized states available to probe, it is possible to make use of the spin-orbital entanglement and circularly polarized light to preferentially excite one particular spin direction. In this section, we will discuss the theoretical and practical foundations of circularly polarized spin-ARPES (CPSA). The technique was first described in [100], after which it was successfully applied to Ca₂RuO₄ ([101]), Sr₂RuO₄ [21] and the iron superconductors ([23]). As this technique relies on the coupling of spin and orbital angular momentum to measure spin-polarization, it is particularly suited to use on systems with significant spin-orbit coupling, as for example the iridates. We will use the technique to understand spin-orbital entanglement in Sr_2IrO_4 in Chapter 4.

The Spin-Orbital Entanglement

Measuring spin, while limiting the orbital angular momentum states probed, captures the correlation between orbital and spin angular momentum. More quantitatively, performing this experiment corresponds precisely to measuring the z component of the $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ operator: $L_z S_z$.

We start by considering the photoemission matrix element as discussed in Section 2.3.3. Using circularly polarized light with positive helicity gives $\varepsilon^{\oplus} \cdot \mathbf{r} = \varepsilon_0 (x + iy) = \varepsilon_0 Y_1^1$. The matrix element then becomes:

$$M_{i,f}^{k} = \left\langle \psi_{f}^{k} \middle| \mathbf{r} \cdot \boldsymbol{\varepsilon} \middle| \phi_{i} \right\rangle = \varepsilon_{0} \sum_{\substack{\ell_{f} \\ m_{f}, m_{i}}} B_{n_{i},\ell_{i},\ell_{f}} \left\langle Y_{\ell_{f}}^{m_{f}} \middle| Y_{1}^{1} \middle| c_{\ell_{i}}^{m_{i}} Y_{\ell_{i}}^{m_{i}} \right\rangle Y_{l_{f}}^{m_{f}} \left(\theta_{k},\phi_{k}\right), \quad (2.42)$$

where B_{n_i,ℓ_i,ℓ_f} specifies the radial integral as defined in Eq. 2.39. At the Γ point, we can simplify this equation by using the fact that the spherical harmonic $Y_{l_f}^{m_f}(\theta_k, \phi_k)$ has nodes for all m_f except $m_f = 0$, where its value is 1. With the spherical harmonic arising from the polarization vector set to Y_1^1 , we only emit from a single initial state spherical harmonic. We can therefore simplify the expression in Eq. 2.42 to:

$$M_{i,f}^{k\sigma} = \varepsilon_0 \sum_{\ell_f} B_{n_i,\ell_i,\ell_f} \left\langle Y_{\ell_f}^0 \Big| Y_1^1 \Big| c_{\ell_i}^{m_i = -1,\sigma} Y_{\ell_i}^{-1} \right\rangle.$$
(2.43)

The effect of the spherical harmonic, arising from the polarization vec-
tor, is to raise the angular momentum of the initial state, meaning we can write the product as: $Y_1^1 Y_{\ell_i}^{-1} = \sum_{\ell_f} a_{\ell_i,\ell_f} c_{\ell_i}^{-1} L^+ Y_{\ell_f}^{-1}$, where a_{ℓ_i,ℓ_f} is a coefficient that describes the possible resulting angular momenta, determined by the Clebsch-Gordan coefficients arising from the product of two spherical harmonics. This allows one to write the matrix element as:

$$M_{i,f}^{k\sigma} = \varepsilon_0 \sum_{\ell_f} B_{n_i,\ell_i,\ell_f} a_{\ell_i,\ell_f} \left\langle Y_{\ell_f}^0 \left| L^+ \left| c_{\ell_i}^{m_i = -1,\sigma} Y_{\ell_f}^{-1} \right| \right\rangle \right.$$

$$= \varepsilon_0 \sum_{\ell_f} B_{n_i,\ell_i,\ell_f} a_{\ell_i,\ell_f} \left\langle Y_{\ell_f}^{-1} \left| L^- L^+ \left| c_{\ell_i}^{m_i = -1,\sigma} Y_{\ell_f}^{-1} \right| \right\rangle \right.$$

$$= \varepsilon_0 B_{n_i,\ell_i,\ell_f} a_{\ell_i,\ell_f} c_{\ell_i}^{m_i = -1,\sigma}. \quad (2.44)$$

This means that the measured photoemission intensity is:

$$I^{\oplus\sigma} = \varepsilon_0^2 \left(\sum_{\ell_f} B_{n_i,\ell_i,\ell_f} a_{\ell_i,\ell_f} \right)^2 \left| c_{\ell_i}^{m_i = -1,\sigma} \right|^2 = A \left| c_{\ell_i}^{-1,\sigma} \right|^2.$$
(2.45)

We can thus measure using $\sigma = \uparrow, \downarrow$ and $\varepsilon = \oplus, \ominus$ and construct:

$$I^{\ominus\uparrow} - I^{\oplus\uparrow} - I^{\ominus\downarrow} + I^{\oplus\downarrow} = A\left(\left|c^{1,\uparrow}\right|^2 - \left|c^{-1,\uparrow}\right|^2 - \left|c^{1,\downarrow}\right|^2 + \left|c^{-1,\downarrow}\right|^2\right) \quad (2.46)$$

Noting that in the basis of $|m_l = 1, \uparrow\rangle, |-1, \uparrow\rangle, |1, \downarrow\rangle, |-1, \downarrow\rangle$, we have:

$$L_z S_z = \frac{\hbar^2}{2} \begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 1 \end{pmatrix},$$
 (2.47)

we get for $\langle L_z S_z \rangle$:

$$\langle L_z S_z \rangle = \frac{\hbar^2}{2} \left(\left| c^{1,\uparrow} \right|^2 - \left| c^{-1,\uparrow} \right|^2 - \left| c^{1,\downarrow} \right|^2 + \left| c^{-1,\downarrow} \right|^2 \right),$$
 (2.48)

which is precisely the expression found in Eq. 2.46, aside from the prefactor. Note that the expression derived above is independent (up to the prefactor A) of the values for B_{n_i,ℓ_i,ℓ_f} . Since there is only a single term of m_{l_i} for each configuration, there are no interference terms and the sum in Eq. 2.45 can be evaluated separately. The only limiting case is when $B_{n_i,\ell_i,\ell_i+1} = -B_{n_i,\ell_i,\ell_i-1}$, in which case the photoemission signal is zero.

The Geometric Mean

This formulation of $\langle L_z S_z \rangle$ in terms of $I^{\varepsilon,\sigma}$ is unfortunately only valid if all factors B_{n_i,ℓ_i,ℓ_f} are the identical for both both polarizations ε^{\oplus} and ε^{\ominus} , which may not be the case in a system where there is circular dichroism. Moreover, if the sensitivity of the spin-detectors is not equal for up and down channels, the description also breaks down. By denoting the sensitivity of the detector of each spin detector as η^{σ} , and the factor related to the circular dichroism as α^{ε} , we can write the measured photoemission signal as:

$$\tilde{I}^{\varepsilon\sigma} = \alpha^{\varepsilon} \eta^{\sigma} I^{\varepsilon,\sigma} = \alpha^{\varepsilon} \eta^{\sigma} A \left| c_{\ell_i}^{m_i,\sigma} \right|^2, \qquad (2.49)$$

where $m_i = -1$ for ε^{\oplus} and 1 for ε^{\ominus} . Substituting the \tilde{I} into Eq. 2.46, the expectation value $\langle L_z S_z \rangle$ is no longer recovered as a result of the prefactors. We can instead take the geometric mean P which divides out the prefactors:

$$P = \frac{\sqrt{\tilde{I}^{\ominus\uparrow}\tilde{I}^{\ominus\downarrow}} - \sqrt{\tilde{I}^{\ominus\uparrow}\tilde{I}^{\ominus\downarrow}}}{\sqrt{\tilde{I}^{\ominus\uparrow}\tilde{I}^{\ominus\downarrow}} + \sqrt{\tilde{I}^{\ominus\uparrow}\tilde{I}^{\ominus\downarrow}}} = \frac{\sqrt{A\alpha^{\ominus}\eta^{\uparrow}|c^{1,\uparrow}|^{2}A\alpha^{\oplus}\eta^{\downarrow}|c^{-1,\downarrow}|^{2}} - \sqrt{A\alpha^{\oplus}\eta^{\uparrow}|c^{-1,\uparrow}|^{2}A\alpha^{\ominus}\eta^{\downarrow}|c^{1,\downarrow}|^{2}}}{\sqrt{A\alpha^{\ominus}\eta^{\uparrow}|c^{1,\uparrow}|^{2}A\alpha^{\oplus}\eta^{\downarrow}|c^{-1,\downarrow}|^{2}} + \sqrt{A\alpha^{\oplus}\eta^{\uparrow}|c^{-1,\uparrow}|^{2}A\alpha^{\ominus}\eta^{\downarrow}|c^{1,\downarrow}|^{2}}} = \frac{\sqrt{|c^{1,\uparrow}|^{2}|\alpha^{\oplus}\eta^{\downarrow}|c^{-1,\downarrow}|^{2}} - \sqrt{|c^{-1,\uparrow}|^{2}|c^{1,\downarrow}|^{2}}}{\sqrt{|c^{1,\uparrow}|^{2}|c^{-1,\downarrow}|^{2}} - \sqrt{|c^{-1,\uparrow}|^{2}|c^{1,\downarrow}|^{2}}}.$$
 (2.50)

In the case of Kramers degeneracy, we should have $|c^{m,\sigma}|^2 = |c^{-m,\bar{\sigma}}|^2$, and using the fact that the states are normalized $(\sum |c^{m,\sigma}|^2 = 1)$, we obtain:

$$P = \frac{\left|c^{1,\uparrow}\right|^{2} - \left|c^{1,\downarrow}\right|^{2}}{\left|c^{1,\uparrow}\right|^{2} + \left|c^{1,\downarrow}\right|^{2}} = \left|c^{1,\uparrow}\right|^{2} - \left|c^{1,\downarrow}\right|^{2} - \left|c^{-1,\uparrow}\right|^{2} + \left|c^{-1,\downarrow}\right|^{2} = \frac{2}{\hbar^{2}} \left\langle L_{z}S_{z} \right\rangle.$$
(2.51)

Using the geometric mean, we can thus extract the expectation value for $\langle L_z S_z \rangle$ without the need to know the exact detector sensitivities or circular dichroism effects. This method is therefore the sole method used in this thesis to present spin-polarized data.

So far, the only expectation value discussed is the one along the z direction. In principle, other components can be measured, such as $\langle L_z S_x \rangle$, as the detectors used have three separate spin-axes available to measure. While this is possible, it is used in this thesis only to demonstrate the robustness of the technique. As no terms in the spin-orbit coupling hamiltonian appear to actually couple momentum perpendicularly, the expectation value and measured spin-polarization should always be zero.

Furthermore, the calculated expectation values are only valid at the Γ -point. Despite this, the technique has been successfully applied away from Γ [23]. Later in this thesis, data away from the Γ -point will also be presented. The equations hold true as long as not too much weight comes from final states with $m_l \neq 0$. Following the k-dependent spherical harmonic in Eq. 2.38, these other components have a dependence $\propto (1 - \cos^2 \theta_k)$, where θ_k is the angle of the photoemitted electron and the surface normal. In particular, if the photon energy is large, this angle is small, even at larger momentum values at the edges of the Brillouin zone. However, in such cases it is recommended to properly model the matrix elements as implemented for example in chinook [90].

While it is possible to measure in-plane components like $\langle L_x S_x \rangle$, in practice, this is difficult as it would require measuring $m_l = 2, 0, -2$ coefficients, which have matrix elements identical zero for photoemission at normal emission. An experiment would therefore have to be off Γ , as close to the preferred spin-orbital axis to measure as possible.

Light Polarization

Until now, the calculations presented have assumed that the incident light is perfectly perpendicular to the surface. In the geometry of a realistic ARPES experiment (Fig. 2.7), the electron analyzer would be in the light path. Therefore, the incidence angle of the light is usually approximately 45° . Taking the direction of the sample surface normal to be $\hat{\mathbf{z}}$, we can write for the incoming light:

$$\boldsymbol{\varepsilon}^{\oplus} = \varepsilon_0 \left(\frac{1}{\sqrt{4}} \left(\hat{\mathbf{x}} - \hat{\mathbf{z}} \right) + i \hat{\mathbf{y}} \right).$$
 (2.52)

This can be converted into spherical harmonics that are used for the calculation as:

$$\boldsymbol{\varepsilon}^{\oplus} = \frac{1}{\sqrt{4}} Y_1^0 + \left(\frac{1}{\sqrt{4}} + \frac{1}{\sqrt{8}}\right) Y_1^1 + \left(\frac{1}{\sqrt{4}} - \frac{1}{\sqrt{8}}\right) Y_1^{-1}.$$
 (2.53)

This deviates from the ideal case where we only make excitations with Y_1^1 . However, at Γ , there are no available final state channels for Y_1^0 to scatter into, so that term can be safely be ignored. The Y_1^{-1} term meanwhile creates excitations of the opposite spin-orbital entanglement. Taking the squares of these coefficients, we get 0.73, and for 0.02 for Y_1^1 and Y_1^{-1} respectively. This means that this configuration leads to an opposite signal of just 3%, generating a net 6% of additional, unpolarized signal. This is far less than the Sherman function of 0.5 of the (high-efficiency) VLEED detectors discussed in Section 2.4, and can therefore be safely ignored.

Chapter 3

Spin-orbit Controlled Metal-Insulator Transition in Sr_2IrO_4

The transition of Sr_2IrO_4 into a metallic state is here reported, by making careful substitutions using Rh and Ru. Throughout this chapter we will argue that the transition is mediated by a reduction of the spin-orbit interaction. This is not only the first demonstration of a metal insulator transition driven by spin-orbit coupling, but also showcases the pivotal role spin-orbit plays in stabilizing the insulating phase of Sr_2IrO_4 . For correlated insulators, where electron-electron interactions (U) drive the localization of charge carriers, the metal-insulator transition (MIT) is described as either bandwidth controlled (BC) or filling controlled (FC) [6]. Where the former describes the modification of the kinetic energy terms versus the interaction terms, the latter brings a Mott system away from integer filling to induce a metallic state. Spin-orbit coupling is in this regard fundamentally different, as it does not change the respective scales of kinetic and interaction terms directly, but rather the entanglement of different orbitals in a multi-orbital system.

3.1 Introduction

As discussed in Chapter 1, the insulating phase in Sr_2IrO_4 was quite puzzling and it was proposed to be part of a new class of correlated insulators, in which spin-orbit coupling (SOC) is believed to fully entangle the Ir t_{2q} orbitals into a $j_{\text{eff}} = 3/2$ and 1/2 state. The bandwidth of the half-filled $j_{\rm eff} = 1/2$ doublet is then significantly reduced, allowing a modest U to induce a charge-localized phase [25, 27]. The insulating state has been believed to be stabilized by spin-orbit coupling for a while, but the evidence that was put forward has been debated. The existence of the $j_{\text{eff}} = 1/2$ state was demonstrated by resonant elastic x-ray scattering (REXS) [27], which shows a complete quenching of the ratio of the L_2 and L_3 absorption edge, indicative of a complete spin-orbital entanglement of the unoccupied state. It was later however shown that for systems with in-plane magnetic moments like Sr_2IrO_4 , the branching ratio is identically zero regardless of the spin-orbital entanglement [28]. This was later acknowledged by the authors of [27] in [29], where they perform a detailed study of the matrix elements for x-ray scattering. Meanwhile, different suggestions to explain the insulating state have emerged, such as a Slater insulator [26], in which the antiferromagnetic order breaks the translational symmetry of the lattice and opens a gap through band folding. Moreover, the results in [30] show that Sr_2IrO_4 is quite close to a quenching of the spin-orbital entanglement, further questioning the validity of the $j_{\text{eff}} = 1/2$ description. Here we provide evidence for the central role of spin-orbit coupling, by directly modifying its strength and showing that this causes a collapse of the insulating state.

The effect of spin-orbit coupling in the valence band is modified by making substitutions that replace Ir with Ru and Rh, both lighter, 4d elements, with substantially lower SOC. Rh substituted Sr₂IrO₄ has been studied previously and is known to drive the MIT. Previous studies have considered the role of SOC [102, 103], but a clear interpretation has been hindered by concurrently occurring changes to the filling [104–106]. We overcome this challenge by employing multiple substituents that introduce well defined changes to the signatures of SOC and carrier concentration in the electronic structure, as well as a new methodology that allows us to monitor SOC directly. Specifically, we study $\text{Sr}_2 \text{Ir}_{1-x} \text{T}_x O_4$ (T = Ru, Rh) by angle-resolved photoelectron spectroscopy (ARPES) combined with *ab-initio* and supercell tight-binding calculations. This allows us to distinguish relativistic and filling effects, thereby establishing conclusively the central role of SOC in stabilizing the insulating state of $\text{Sr}_2 \text{Ir} O_4$. Most importantly, we estimate the critical value for spin-orbit coupling in this system to be $\lambda_c = 0.42$ eV and provide the first demonstration of a spin-orbit-controlled MIT.

3.2 The MIT in Rh and Ru substituted Sr_2IrO_4

The familiar tools of chemical doping and pressure have provided straightforward access to both FC and BC MIT in conventional correlated insulators. In an effort to unveil the role of SOC in the insulating behaviour of Sr_2IrO_4 and whether it can indeed drive a MIT, we have attempted to controllably dilute SOC in the valence electronic structure by substituting Ir ($\lambda_{SOC} \sim$ 0.4 eV [20, 37, 107]) with Ru and Rh ($\lambda_{SOC} \sim 0.19$ eV [18, 21, 22]). While these substituents have similar values of λ_{SOC} and are both 4d ions with comparable values for U [108, 109] and ionic radii [110], they are otherwise distinct: Ru has one less electron than Rh and is therefore associated with a markedly larger impurity potential. We will show through supercell tight-binding model calculations that this leads to a pronounced contrast in the consequences of Rh and Ru substitution: the larger impurity potential associated with Ru precludes a significant reduction of the valence SOC. By comparison, Rh is electronically more compatible with Ir, facilitating a successful dilution of SOC. We measure this evolution directly, through orbital mixing imbued by SOC, manifest experimentally in the photoemission dipole matrix elements. To comprehend all aspects of the MIT observed here for both Rh and Ru substitution, we consider individually the effects of filling (Fig. 3.1), correlations/bandwidth (Fig. 3.2), and spin-orbit coupling (Fig. 3.6 and Fig. 3.7), ultimately concluding that the transition in $Sr_2Ir_{1-x}T_xO_4$ is a spin-orbit controlled MIT.

Having highlighted the three relevant aspects of the MIT, we begin our



Figure 3.1: Dependence of the MIT on Rh and Ru substitution. a-d ARPES spectra along $\Gamma - X$ for the pristine sample, $x_{Rh} = 0.22$, $x_{Ru} = 0.40$ and $x_{Ru} = 0.20$, respectively. e and f show Fermi surface maps for x = 0.22 Rh and x = 0.40 Ru. The sizes of the pockets are indicated with white lines. Fermi surface maps are integrated over 50 meV. All data taken at $h\nu = 64$ eV with temperatures between 120 K and 150 K for $x \leq 0.10$, and below 40 K otherwise.

disquisition by showcasing the changes that each substituent introduces to the electronic structure of Sr_2IrO_4 as measured by ARPES. We investigate samples with various nominal concentrations of Ru and Rh, for which details of growth and consistency are given in Section 3.A.1. Fig. 3.1a-d summarize ARPES spectra for x = 0, $x_{Rh} = 0.22$, and $x_{Ru} = 0.20, 0.40$. As reported previously [25], the pristine sample supports an energy gap, with a band maximum at X at a binding energy of around $E_b = 0.25$ eV. When substituting Rh, spectral weight appears at the Fermi level for concentrations $x \gtrsim 0.13$, signalling the formation of a metallic state. This observation is in line with previously reported ARPES [104–106]. This is exemplified by our $x_{Rh} = 0.22$ data, shown in Fig. 3.1b,e. At comparable values of x_{Ru} , the system remains insulating (cf. $x_{Ru} = 0.20$ in Fig. 3.1d), and only by going as high as $x_{Ru} = 0.40$ (Fig. 3.1c,f) do we find that the MIT has been traversed [111–113], consistent with transport measurements [112].

Within the metallic phase, the Fermi surface volume provides a direct measure of the hole doping introduced by the impurity atoms. We report a Brillouin zone coverage of $(16\pm 2)\%$ and $(46\pm 5)\%$ for Rh and Ru respectively, with the uncertainty arising from the ambiguity caused by the broad nature of the states. These surface areas correspond to a nominal doping of $0.16 \pm$ 0.02 holes (at $x_{Rh} = 0.22$) and 0.46 ± 0.05 holes (at $x_{Ru} = 0.40$), per formula unit. Note that there is no apparent transition from a small to a large Fermi surface as is observed in the cuprate superconductors [114–116] for the wide doping range we study, and the Fermi surface size n progresses with the doping p as n = p (due to there being two iridium atoms per unit cell). A possible reason for this may be found in the fact that whereas in the cuprates specific order such as antiferromagnetism is required to fold the bands, this distortion is already present in Sr_2IrO_4 through the staggered rotation of the octahedra. To within our level of certainty, each impurity atom then contributes approximately one hole carrier, with Ru contributing a slightly larger number than Rh. This observation runs contrary to the expectations for a FC transition: despite contributing at least as many holes as Rh, the MIT critical concentration required for Ru is roughly double that of Rh. This precludes a transition described in terms of filling, despite earlier reports to the contrary [104–106].

As the concentration of Ru increases, the octahedral distortions reduce slowly until a structural transition is observed at x > 0.5. The octahedral distortions in Sr₂IrO₄ cause hybridization between the d_{xy} and $d_{x^2-y^2}$ orbitals, which influences the overal bandwidth of the system. An explanation in terms of modification to the crystal structure however can be equally excluded, since changes to the TM-O bond length and octahedral distortions are minimal (a reduction from 12° to 10°) up to the concentrations



Figure 3.2: ARPES linewidth evolution with substitution. Energy distribution curves (EDC's) for Ru **a** and Rh **b** substituted samples, taken at the momentum with the leading edge closest to the Fermi energy. Photon energies and temperatures for the EDCs are the same as in Fig. 3.1 **c** Momentum distribution curve (MDC) curves for $x_{\rm Ru} = 0.40$ and $x_{\rm Rh} = 0.22$. **d** MDC fits for $x_{\rm Ru} = 0.40$ and $x_{\rm Rh} = 0.22$. MDC data shown in **c**,**d** were taken using $h\nu = 92$ eV at a temperature of 20 K.

used in our study [112]. The changes to bandwidth that are associated with such distortions are expected to be negligible, as the effect of the full 12° is to reduce the bandwidth by at most 4% [117]. Furthermore, a reduction of distortions would increase the bandwidth, opposite to our observations. Equally, recent studies regarding disorder in Mott systems point out that such effects could push the critical concentration to lower values [113, 118]. Both disorder and the progression of octahedral rotations would thus predict the opposite trend ($x_{c,Ru} < x_{c,Rh}$) to what we observe.

Looking beyond the disparate critical concentrations associated with Ru and Rh substitution, analysis of the ARPES spectral features allows for a more thorough comparison of these materials to be made. The selected energy distribution curves (EDCs) cut through the valence band maximum for each doping in Fig. 3.2a (Ru) and b (Rh), reflecting the evolution of each material across the MIT. This coincides with a definitive Fermi level crossing in the EDCs of Fig. 3.2a and b. By observing which samples are metallic and insulating in our experiments, we can infer x_c to be within the range set by highest insulating and lowest metallic concentration. This yields a range of possible critical concentrations as $x_{\rm Rh} = 0.13 \pm 0.03$ and $x_{\rm Ru} = 0.30 \pm 0.10$. These values are limited by the available samples, but match previous photo emission work on the Rh substituted compound [104–106]. Ru-substituted samples have not previously been studied by photoemission, as such no direct comparison to literature can be made. The values for the Ru doped samples do however agree with available transport data [112, 119]. As the interpretation of EDCs lineshape is non-trivial [120], we turn to an analysis of momentum distribution curves (MDCs) for a more quantitative analysis of the evolution of correlation effects. The MDC linewidth is directly related to the state lifetime, and by extension to both electronic interactions and disorder [86, 121, 122]. Two representative MDCs are shown in Fig. 3.2c for $x_{\rm Rh} = 0.22$ and $x_{\rm Ru} = 0.40$. Widths from these, and other MDCs along the dispersion, are summarized in Fig. 3.2d. As can be inferred by the comparison of data from 20 K and 150 K, correlations – rather than thermal broadening – are the limiting factor in determining the MDC linewidth. Consideration of both $x_{\rm Ru} = 0.40$ and $x_{\rm Rh} = 0.22$ reveal remarkably similar interaction effects in the two compounds, despite their significant differences in composition and disorder. In addition, while spectral broadening at high binding energies precludes a precise evaluation of the bandwidth, we estimate the latter to be constant to within 10% over the range of Rh/Ru concentrations considered.

3.3 Spin-orbit coupling

Through study of the Fermi surface sizes, and MDC widths, we have thus determined that while doping effects are comparable for Ru and Rh, similar correlated metallic phases are observed at very different concentrations. To rectify this apparent contradiction, one must consider the context of the present MIT: it has been proposed that the correlated insulating phase in Sr_2IrO_4 is stabilized by the strong spin-orbit coupling. This motivates consideration of the role SOC plays in the MIT for both Ru- and Rh- substituted compounds. The low-energy influence of SOC can be characterized by an effective value in the valence band, determined by the hybridization between atomic species as demonstrated in Refs. 123, 124. This effect could cause a reduction of SOC effects in the valence band as a function of (Ru,Rh) substitution. We find the reduction of SOC to be strongly dependent on the presence of an impurity potential, which limits hybridization of host and impurity states, ultimately curtailing the dilution of SOC effects (see Section 3.3.1). Various works report some form of electronic phase separation in the Ru doped compounds [125–127]. In particular in Ref. 126, Raman scattering shows the coexistence of multiple electronic states. Such electronic phase separation cannot be caused by structural phase separation, as Z-contrast (Z being the atomic number) scanning transmission electron microscopy (STEM) shows a homogeneous distribution of Ru dopants [119]. This suggests that electronically, the Ru ions form a separate manifold, away from the Ir bands. A SOC may therefore be more effective for Rh, providing a natural explanation for their disparate critical concentration in substituted Sr_2IrO_4 compounds. In the following sections we will quantify the influence of an impurity potential on the mixing of spin-orbit coupling in the valence band.

Firstly we will provide more quantitative evidence for the existence of the impurity potential. Using density functional theory (DFT), at x = 0.25substitution, in Fig. 3.3a we observe good overlap between the Rh and Ir projected density of states (DOS). This can be compared against the same scenario for Ru in Fig. 3.3b, where the substituent DOS is found to align poorly with Ir. Such an offset, observed most clearly through consideration of the centre of mass of the Ru-projected DOS, has been reported previously for similar substitutions (Co into Fe superconductors) [128, 129]. Calculating the band's centre of mass in terms of the projected densities of states for



Figure 3.3: In a and b, an analysis of the impurity potential of Rh and Ru in Sr_2IrO_4 is plotted, as calculated by density-functional theory. The grey background represents the total DOS, normalized by the number of TM sites. The black curves show the Ir projected DOS per Ir ion in the 25% substituted calculation, while the orange and green colored curves reflect the projected DOS per substituent ion for Rh and Ru respectively. The arrows indicate the centre of mass for the projected bands.

both, we find an impurity potential for Ru of 0.3 eV, which is close to the number found in [128, 129] (0.25 eV), and agrees with Wannier calculations (0.2 eV) performed on the same supercells. This establishes a reasonable starting point from which we can explore the influence of doping on SOC effects in more detail.

3.3.1 Spin-orbit mixing and the impurity potential

To illustrate how the impurity potential and spin-orbit coupling on two separate sites combine, we have distilled the phenomenon of mixing into a simple and more insightful model. We will demonstrate the sensitivity of hybridization to the impurity potential strength: strong hybridization produces mixed states that host an effective spin-orbit coupling derived from the atomic composition. The model used in this simple case contains only two atoms, with two orbitals (d_{xz} and d_{yz}) each, and only one-dimensional hopping along the z-direction. The atoms have different spin-orbit coupling ($\lambda_1 = 0.45$, $\lambda_2 = 0.19$), and atom 2 has an impurity potential ε , represented schematically in Fig. 3.4f. Since the Hamiltonian for spin-orbit coupling in the basis of d_{xz} and d_{yz} orbitals is degenerate in the spin degree of free-



Figure 3.4: Influence of the impurity potential on spin-orbit coupling in the valence band demonstrated in a 2-atom toy model. **a** Bandstructure for the system that is schematically depicted in **f**. The bands (1,2) and (3,4) are split by spin-orbit coupling, the splitting corresponds to the average value between the two atoms $\bar{\lambda}$. The dashed black line illustrates the bands in the absence of spin-orbit coupling. An arrow at Γ indicates the position at which the band energies are plotted in **c**. **b** The same bandstructure with an impurity potential of $\epsilon = 0.3$. The splittings are no longer the same size, and are k-dependent. **c** The band energies at Γ as a function of the impurity potential. The red and purple arrows correspond to the impurity potentials of panels **a** and **b**, the splitting for the upper and lower manifold are indicated. **d** The progression of the splittings Δ_A and Δ_B as a function of the impurity potential. **e** The orbital weight projected onto atom 1 (solid) and atom 2 (dashed) for each of the four bands. **g** The splitting of the lower manifold Δ_A (green) plotted together with λ_{eff} , calculated from the orbital weights (see text). **h** The splitting of the lower manifold Δ_A (green) plotted together with the analytic form discussed in the text.

dom, we only consider the spin up part of the Hamiltonian. This yields the Hamiltonian:

$$H = \begin{pmatrix} 0 & \frac{i\lambda_1}{2} & -2t\cos k & 0\\ \frac{-i\lambda_1}{2} & 0 & 0 & -2t\cos k\\ -2t\cos k & 0 & \varepsilon & \frac{i\lambda_2}{2}\\ 0 & -2t\cos k & \frac{-i\lambda_2}{2} & \varepsilon \end{pmatrix}.$$
 (3.1)

The band structure along from k = 0 to $k = \pi$ is presented in the presence (Fig. 3.4a) and absence (Fig. 3.4b) of an impurity potential of $\varepsilon = 0.3$. The band structure without spin-orbit coupling (black dashed line, both panels) is plotted for reference in Fig. 3.4a,b. As indicated by the purple contours, upon including SOC a 4-fold degeneracy is lifted, with a constant splitting along the dispersion. This splitting consistent with that expected for a pure crystal with $\overline{\lambda} = (\lambda_1 + \lambda_2)/2$.

Introducing a relative impurity potential of 0.3 eV between the two sites (Fig. 3.4b), the SOC-splitting persists, but is now momentum-dependent. Furthermore, the splitting between the lower (1,2) and upper (3,4) bands becomes inequivalent.

To investigate the evolution of this system as a function of impurity potential, we plot the eigenvalues at k = 0 for a range of ε in Fig. 3.4c. As indicated by the black dashed lines, the eigenvalues at k = 0 are defined largely by the onsite energies, with an avoided crossing due to kinetic terms in the Hamiltonian. Labelling the lower and upper bands as A and B, respectively, we plot their splittings, $\Delta_{A,B}$ vs ε in Fig. 3.4d. These splittings derive from spin-orbit coupling, but only in the limit of $|\varepsilon| >> t$ do $\Delta_{A,B} \to \lambda_{1,2}$. In the opposite limit ($|\varepsilon| >> 0$), both splittings converge to $\overline{\lambda}$ introduced previously. This asymptotic behaviour reflects the essential role of hybridization in mediating a mixing of spin-orbit coupling strengths in impurity-substituted systems.

To make this point more definitive, we include a comparison of orbital compositions on each of the four bands at k = 0 in Fig. 3.4e. In each case, for $\varepsilon \sim 0$, the eigenvectors are an equal mix of atom 1 (solid) and atom 2

(dashed). This even mixing changes rapidly with finite ε , saturating in the limit of large impurity potential. We attempt to relate the state composition for the lower two states to an effective spin-orbit coupling by calculating:

$$\lambda_{eff}(k) = \lambda_1 |\psi_{1,A}(k)|^2 + \lambda_2 |\psi_{2,A}(k)|^2.$$
(3.2)

This quantity is the average spin-orbit coupling on the lower band (A) weighted by the atom projected wavefunctions. It is plotted in Fig. 3.4g (white dashed line), and exactly traces the splitting (green curve) of the lower (A) state. This observation provides evidence for the idea that spin-orbit coupling in the valence band can be regarded as arising from a mixture between states of different atomic character, the mixture being influenced by hybridization, controlled by hopping and the impurity potential. A relevant scale for the process can be found in Fig. 3.4h, where the splitting is plotted as a function of the normalized $\varepsilon/4t$, as well as the function $\frac{x}{\sqrt{1+x^2}}$ (white dashed). The latter is the functional form of the orbital weight for a two-site model with an impurity potential and hopping, which is derived in Section 3.A.4.

We have thus shown that the effects of spin-orbit coupling as they occur in the valence band, are sensitive to the presence of different atomic species, subject to hybridization and impurity potential strength. This shows that it is possible to mix and tune spin-orbit coupling in the valence band by using the appropriate atomic species and controlling the hybridization through the impurity potential. It gives a direct handle on influencing spin-orbit coupling as a continuous parameter in an experimental scenario. It should be pointed out that the results of this model apply directly to other systems too, because the Hamiltonian presented does not assume any material specific properties.

3.3.2 Supercell calculations and band unfolding

The model presented in Section 3.3.1 to illustrate the mechanism of spinorbit mixing, can be made quantitative for the Ru/Rh iridates through consideration of impurity-substituted models. This is carried out through development of a supercell tight binding (TB) model. We expand the single iridium TB Hamiltonian derived in Section 3.A.3 to a 64 site supercell, randomly substituting a fraction x of sites with an impurity atom. A schematic of the generated model is given in Fig. 3.5a

For the sake of simplicity, the impurities are assumed to differ from Ir in only their λ_{SOC} (0.19 eV for both Ru and Rh, 0.45 for Ir), and onsite potential (0.0 eV for Rh and Ir, 0.25 ± 0.05 eV for Ru). Similarly, octahedral distortions and electron correlations are neglected to better illustrate the energy shift of the j_{eff} states. We have used the unfolding method [84, 85, 130, 131] (described in detail in Section 2.2) to project bands into the original Brillouin zone. This method makes use of the phase properties of Bloch waves to define a weight for each band representative of the band's projection onto the extended Brillouin zone. We average 200 possible permutations to reconstruct a stochastic representation of the doped system. The spectral function is found to have converged after averaging over 200 configurations, with no further appreciable changes observed for larger samplings. We observe a smooth evolution of effective SOC in this system, which depends strongly on the impurity potential.

Results of the calculations for the Rh substituted case are summarized in Fig. 3.5b-e. The splitting at $\mathbf{k} = \left(\frac{3\pi}{4a}, 0\right)$ (indicated with a red arrow) allows for direct estimation of the effective SOC. This k-point is chosen because later experimental results will be presented at this Brillouin zone location. Also indicated are the nominal values for 100% Ir (purple) and 100% Rh/Ru (vellow). Experimentally, such a straightforward extraction of SOC is not possible due to the dominant effects of linewidth which preclude detailed characterization of the level spacing. Furthermore, direct inference would require a more detailed analysis of the effect of correlations, as correlations enhance the splittings created by spin-orbit coupling, dependent on the crystal momentum [132, 133]. The calculated spectral functions indicate a monotonic reduction of this splitting as the substituent concentration is increased. Aside from the reduction of spin-orbit coupling, spectral broadening is observed at several points in the Brillouin zone. This broadening is caused by the disorder introduced by the Rh atoms, and is predominantly found in the places where the spin-orbit coupling alters the dispersion most.



Figure 3.5: Overview of the supercell calculations describing spinorbit coupling dilution. a Schematic overview of the supercell generation, indicating the extension of the orbital basis set over the larger unit cell. As indicated by the image colouring, a fraction of atoms is assigned reduced spin-orbit coupling and an impurity potential of $\varepsilon_i = 0.3$ (Ru) or $\varepsilon_i = 0$ (Rh). b-e Calculated averaged unfolded spectral function for Rh concentrations of x = 0.0, 0.1, 0.2 and 0.3. The high symmetry points are indicated in Fig. 3.9d. The arrows indicate the SOC induced splitting (red), with the associated splittings of the end limit compounds x = 0 (purple) and x = 1 (yellow) added for reference.



Figure 3.6: a Cuts (EDCs) for different concentrations of dopants at the position of the red arrow in Fig. 3.5 $[\mathbf{k} = (\frac{3\pi}{4a}, 0)]$. The substituted atoms have different SOC and on-site energy. We use $\lambda_{SOC} = 0.19 \text{ eV}$ and $\varepsilon_i = 0.0 \text{ eV}$ for Rh (black), while we use $\lambda_{SOC} = 0.19 \text{ eV}$ and $\varepsilon_i = 0.25 \pm 0.05 \text{ eV}$ for Ru (red). b Progression of the splitting between the outermost peaks for simulations in **a** for Rh (black markers) and Ru (red markers). For Rh, a linear interpolation is plotted between the end members of the phase diagram. For Ru, the resulting range of splitting for $\varepsilon_i = 0.25 \pm 0.05$ is indicated by red shaded rectangles. The critical concentrations obtained from our measurements are indicated by the black (Rh) and red (Ru) vertical lines. The blue shaded area indicates the inferred $\lambda_c = 0.42 \pm 0.01$.

Such disorder is much stronger in the calculated spectra for Ru doping.

We extract the effective value of SOC by fitting EDCs for each impurity concentration. The results are summarized in Fig. 3.6. The change in splitting is seen clearly in Fig. 3.6a, where we present a series of EDCs at $\mathbf{k} = (\frac{3\pi}{4a}, 0)$, for models with a non-zero on-site impurity potential (Ru, red), and those without (Rh, black). This doping dependence is summarized in Fig. 3.6b. The right vertical axis reflects the splitting observed at $\mathbf{k} = (\frac{3\pi}{4a}, 0)$, and the left the value of λ_{SOC} that would produce the corresponding splitting in a model without substitutions (i.e. for an overall uniform value of λ_{SOC}). This second axis serves to illustrate the *effective* spin-orbit coupling caused by substitution of Ir with Rh and Ru. From the progression in Fig. 3.6b it is evident that Rh should dilute SOC more

efficiently than Ru: the black markers trace the interpolation between the values of Ir and Rh, indicated by the grey line. Meanwhile the modelled impurity potential for Ru $(0.25\pm0.05 \text{ eV})$ prevents successful dilution of SOC. The results in Fig. 3.6b suggest that the different critical concentrations for the two substituents can be attributed to a common parameter: a value for spin-orbit coupling of $\lambda_c \sim 0.42 \pm 0.01$ (indicated as a blue shaded area in Fig. 3.6b) yields critical concentrations ($x_{\rm Rh} \sim 0.15$ and $x_{\rm Ru} \sim 0.3$) that fit well with our experimental observations. Theoretical results presented in Ref. 134 suggest that SOC in Sr₂IrO₄ is only marginally above the threshold for the insulating state, and that such a small change could drive the transition. The dilution of spin-orbit coupling is therefore found to provide a compelling theoretical picture of the transition.

3.4 Experimental observation of SOC

Having demonstrated this evolution of SOC via substitution and its ability to provide a natural explanation for the transition in $Sr_2Ir_{1-x}T_xO_4$, we aim to substantiate these predictions experimentally. To establish a convenient metric for SOC, we leverage the symmetry constraints of the photoemission matrix element. Dipole selection rules allow transitions from only certain orbitals: since d_{xz} (d_{yz}, d_{xy}) is even (odd) in the experimental scattering plane, states composed of this cubic harmonic are only observable with π - (σ) -polarization. As SOC mixes these orbitals into linear combinations prescribed by the j_{eff} construction [25], we quantify SOC by comparing the ratio of even/odd states at strategically chosen points in the Brillouin zone where these symmetry-based selection rules are most well defined. In the absence of SOC, the state along $\Gamma - X_x$ (defined in Fig. 3.7) in Sr₂IrO₄ would be of pure d_{xz} character: any photoemission from this state using σ -polarization must be due to the admixture of d_{yz} and d_{xy} introduced by SOC. More quantitatively, of interest here is the value of M_x^{σ} , the matrix element at the X_x point, which we normalize in our results through division by M_{y}^{σ} . A simulation of this quantity based on an *ab-initio* tight binding model for Sr_2IrO_4 with variable spin-orbit coupling is shown as a black solid



Figure 3.7: Observation of the reduction of SOC via the ARPES dipole matrix element. a-d Constant energy maps for different concentrations of x_{Rh} , using σ -polarized light. The constant energy maps are integrated over 150 meV to improve numerical accuracy, and taken at an energy such that the size of the pocket around X is the same for all concentrations. The relevant states used for the analysis are indicated using the red boxes, and their integrated values are shown within. All data are taken at 64 eV, with temperatures at 120 K for x = 0 and $x_{Ru} = 0.1$, 70 K for $x_{Rh} = 0.1$, and 20 K $x_{Rh} = 0.16$, all chosen to mitigate the effects of charging.



Figure 3.8: Inference of the value of spin-orbit coupling through modelling of the matrix element. Calculated ratio of matrix elements for a model of Sr_2IrO_4 (details in Section 3.A.3), plotted as a function of spin-orbit coupling (black curve). The coloured markers indicate the ratio of the experimental values shown in panels **a-d** of Fig. 3.7. The error bars are calculated from the standard deviation over the integrated range in energy. The top axis indicates the substitution required to produce the spin-orbit coupling value on the bottom axis, predicted by the supercell calculations in Fig. 3.6e.

line in Fig. 3.8. The model takes into account effects of experimental geometry as well as photon energy and polarization; for further details refer to Section 3.A.3. The curve shows a clear decrease of $M_x^{\sigma}/M_y^{\sigma}$ as a function of spin-orbit coupling, demonstrating the possibility for a direct measure of λ_{SOC} via ARPES. The model omits electron-electron interactions, which could in principle change the mixing of orbitals, and hence the observed SOC. However, since we measure the relative change to the pristine sample, our conclusions are robust against such an overall change.

Motivated by the supercell calculations, we investigate the progression of $M_x^{\sigma}/M_y^{\sigma}$ experimentally in a series of Rh and Ru substituted samples. In Fig. 3.7a-d we plot constant-energy contours for each of the concentrations, as recorded with σ -polarized light. To compare the different samples, we consider constant energy maps at the energy which places the state of interest at $k_x = \left(\frac{3\pi}{4a}, 0\right)$. We subtract a uniform background based on the average of the intensity in areas where no states are present. Then, integrating and dividing the ARPES intensity within the indicated regions of Fig. 3.7a-d yields the ratio $M_x^{\sigma}/M_y^{\sigma}$. We can proceed to make a quantitative connection with an effective spin-orbit coupling strength by plotting the experimental data points alongside the simulated curve in Fig. 3.8. The latter has been normalized to the experimental data for pristing Sr_2IrO_4 , allowing for an effective λ_{SOC} strength to be extracted for the Rh/Ru substituted samples. This analysis yields λ_{SOC} values of 0.443, 0.424, and 0.408 respectively. A connection to the supercell calculations can be made through these λ_{SOC} values: the associated impurity concentrations in Fig. 3.6e agree remarkably well with the actual experimental values, made explicit in the case of Rh with the top horizontal axis of Fig. 3.8. This confirms the premise of our supercell model and the sensitivity to the impurity potential for successful dilution of λ_{SOC} . In connection to the MIT, the $\lambda_c = 0.42 \pm 0.01$ eV at $x_{\rm Rh} = 0.15$ obtained from Fig. 3.6e is overlain in Fig. 3.8.

3.5 Conclusion

Generally speaking, λ_c is a function of filling, U, bandwidth, disorder, among others, and SOC represents but a single axis within a higher dimensional phase space. As filling, distortions, and disorder may be anticipated to expedite the metal-insulator transition in Ru-substituted samples, SOC seems alone capable of explaining the dichotomy in x_c observed for Ru and Rh. This indicates the critical role of SOC in the MIT of $\text{Sr}_2\text{Ir}_{1-x}\text{T}_x\text{O}_4$ for both Rh and Ru substitution.

The combination of SOC-sensitive techniques and the comparison of Ru and Rh substituted samples has put us in a unique position to comment on the role of SOC in the metal-insulator transition of Sr_2IrO_4 , demonstrating for the first time an SOC controlled-collapse of a correlated insulating phase.

Through doing so, as an important corollary to these results, our work conclusively establishes Sr_2IrO_4 as a relativistic Mott insulator.

Additionally, we note that the investigation into mixing spin-orbit coupling discussed in Section 3.3.1 was calculated for a generic two-site Hamiltonian. As such this mechanism pertains to other systems in which this type of physics appears, and has broad ranging implications for attempts to tune and tailor spin-orbit coupling. Controlling spin-orbit coupling is a material properties design challenge at which many attempts have been made, with varying success. This result not only sets the boundary conditions for successful dilution of spin-orbit coupling, it also explains what the controlling parameters are that influence the resultant spin-orbit coupling in mixed systems. It gives a direct explanation of the effects seen in systems such as $Ga_{1-x}Bi_xAs$, where Bi readily enhances the effects of SOC [135]. It also sheds light on attempts to drive a topological to trivial transition in topological insulators by reducing spin-orbit coupling through substitution [136– 140]. Moreover, the sensitivity of this phenomenon to an impurity potential has implications for ongoing efforts to enhance SOC effects in graphene and related systems through adatom deposition and other proximity-related techniques [123, 124, 141–143]. In particular, experimental results have been unable to observe the predicted enhancement of spin-orbit coupling so far. It is possible that an impurity potential, or small hopping parameter limits the hybridization between the adatom species and the graphene lattice, thus not effectively facilitating enhanced effects of spin-orbit coupling. In summary, this work has important implications for experiments that attempt to modify spin-orbit coupling, and should serve as a practical guide for future endeavours.

3.A Appendices

3.A.1 Methods

Single crystals of $Sr_2Ir_{1-x}Rh_xO_4$ were grown with nominal concentrations of $x_{Rh} = 0.0, 0.10, 0.16, 0.22$ and measured with electron probe microanalysis to be within 0.01 of their nominal concentration. Crystals of $Sr_2Ir_{1-x}Ru_xO_4$ were grown with nominal concentrations of $x_{Ru} = 0.10, 0.20, 0.40$. Quality of the Ru doped samples was assured by comparing magnetization measurements to available literature [112, 119]. Chemical homogeneity of the Ru doped samples was ensured using Z-contrast STEM. Measurements were carried out at the SIS beamline at the Swiss Lightsource (Rh substituted samples) and at the Merlin beamline at the Advanced Lightsource (Rh and Ru substituted samples). All measurements were done on freshly cleaved surfaces, where the pressure during measurement and cleaving was always lower than $3.3 \cdot 10^{-10}$ mbar. Measurements used for inference of spin-orbit coupling values were performed with 64 eV photons, using light polarized perpendicular to the analyzer slit direction (σ -polarization). The rotation axis of the manipulator for the acquisition of the Fermi surface was parallel to the slit direction. The sample was mounted such that the Ir-O bonds $(\Gamma - X)$ were aligned to this axis of rotation. Temperatures were chosen as low as possible while mitigating the effects of charging and are reported in the figure captions. A tight-binding model was constructed from a Wannier orbital calculation using the Wannier90 package [144]. The Wannier90 calculations were performed on results from density functional theory calculations done with the WIEN2K package [75, 145]. The DOS calculations presented in Fig. 3.6 were performed with the WIEN2K package. The supercell configuration assumed a single layer with 8 TM ions per unit cell. The presented results at x = 0.25 are similar to those found for x = 0.125 and x = 0.5.

3.A.2 Observation of SOC through the dipole transition matrix element

In the Section 3.4, we have demonstrated the ability to quantify spin-orbit coupling by taking advantage of the dipole selection rules associated with the photoemission process. To illustrate how the effects of SOC are manifest in polarization-dependent ARPES on Sr_2IrO_4 , it is instructive to consider a minimal tight-binding model consisting of a t_{2q} basis set with nearest neighbour hopping and spin-orbit coupling. Although too simple to capture the full detail of Sr_2IrO_4 , this model serves to highlight the general concept of this technique and its broad applicability beyond this particular set of materials. The calculations presented in the Fig. 3.8 use the more elaborate model described in Section 3.A.3. Suitable points in k-space are fixed by the symmetry of the lattice, as can be illustrated by the orbital-projected band structure plotted in Fig. 3.9 as a function of spin-orbit coupling. The dispersion of the model system is plotted for several values of λ_{SOC} in Fig. 3.9a-c. The colour scale encodes the expectation value of $\langle \mathbf{L} \cdot \mathbf{S} \rangle$. SOC can be seen to cause both an increase in the entanglement of spin and orbital angular momentum, as well as a splitting between the bands originating from d_{xz} and d_{yz} orbitals that eventually form the $j_{\text{eff}} = 3/2$ and 1/2 states. The fully entangled $j_{\text{eff}} = 3/2$ and 1/2 have $\langle \mathbf{L} \cdot \mathbf{S} \rangle = -1/2$ (red) and 1 (blue), respectively. Note that these values are the negative of the expectation value for $\ell = 1$, where j = 3/2 (1/2) yields $\langle \mathbf{L} \cdot \mathbf{S} \rangle = 1/2$ (-1), since the j_{eff} states are derived from $\ell = 2$ states. Any deviations from these numbers reflect the competition between SOC and kinetic terms.

The orbital mixing resulting from the entanglement of spin and orbital angular momentum can be seen in Fig. 3.9e-g, where the colour scale now reflects the orbital projection along the same k-space path as before. Negligible mixing is observed for $\lambda_{SOC} = 0.01$, becoming quite prominent by $\lambda_{SOC} = 0.4$ eV. As with the spin-orbital entanglement, except for extremely large values of SOC, the mixing is k-dependent as orbital angular momentum remains partially quenched. Directing our attention towards the $(\pi, 0)$ point on the edge of the Brillouin zone, we can further explore the evolution of the orbital character of the valence band. Although in the absence of



Figure 3.9: Orbital mixing between t_{2g} orbitals. **a-c** Bandstructures for λ_{SOC} 0.01, 0.1 and 0.4 eV along the k-path indicated in **d**; colour encodes the expectation value of $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ for each band. In all calculations the Fermi level was set by a total occupation of 5 electrons per site. **d** Fermi surface plots for λ_{SOC} 0.01 (left) and 0.4 eV (right), with band character colour encoded. **e-g** The same band structure as in **a-c**, where the colour now indicates the weight of d_{xy} , d_{xz} and d_{yz} for each state (the colour mapping is defined in the triangle in the top left). **h** The orbital composition of the state and matrix element ratio as a function of SOC, at the k-point indicated by a grey box in **d** and **g**. **i** The SOC induced splitting at Γ denoted by the grey double arrow in **g**.

SOC this state is of pure d_{xz} character, substantial admixture of d_{yz} and d_{xy} weight is observed in Fig. 3.9h for large SOC. Providing a connection to the experiment, the ratio of photoemission intensity between the $(\pi, 0)$ and $(0, \pi)$ points $(M_x^{\sigma}/M_y^{\sigma})$ is also plotted on the same axes. To within a global renormalization factor, this quantity is found to follow the ratio of d_{xz}/d_{yz} weight precisely, demonstrating the correspondence between this experimental signature and the orbital structure of the underlying electronic states. Consequently, $M_x^{\sigma}/M_y^{\sigma}$ provides an experimental measure of SOC in these states. This is particularly useful for the study of $\mathrm{Sr}_2\mathrm{Ir}_{1-x}\mathrm{T}_x\mathrm{O}_4$ (T = Ru,Rh) where we might expect the effective SOC to reduce with increasing substituent content.

We stress that this technique is not limited to this particular material, and could be used in other systems that are subject to spin-orbit coupling that causes mixing between even and odd orbitals, for example in other iridates [146, 147], ruthenates [14, 21] or the iron-based superconductors [23, 24]. Although the general principle of the idea is fully captured by this simple model, a better effort in predicting the intricacies of this ratio can be made by considering the full nature of the system, including its octahedral distortions and higher order hopping elements, as is done in the next section.

3.A.3 Tight binding and matrix element modelling

Qualitatively, the extent to which the matrix elements can be relied upon to convey information regarding orbital mixing is found to be independent of the details of a given model. For example, the Hamiltonians described in [148] as well as [44] have been tested, and found to be consistent with the intensity variations observed experimentally. To provide a quantitative connection to the experimental $M_x^{\sigma}/M_y^{\sigma}$ values, a more sophisticated model than that presented in Section 3.A.2 is required. We describe here the model used for matrix element calculations in Fig. 3.8, which relies on DFT and maximally localized Wannier functions to generate a tight-binding Hamilto-



Figure 3.10: Overview of the model used in this work. The high symmetry points are indicated in Fig. 3.9d. a Initial DFT calculation in the *I4/mmm* space group (black), overlaid on the calculated tight binding band structure as extracted from Wannier orbitals (grey). b Calculated band structure for the former Hamiltonian after it has been doubled, rotated, and stripped of out-of-plane hopping matrix elements (grey) c Calculated band structure for the rotated model to which atomic spinorbit coupling has been added (coloured). The experimental configuration is represented schematically in panel d.

nian [75, 144, 145]. DFT calculations were performed with the Wien2K package [75], under the generalized gradient approximation (GGA). To minimize the size of the basis set for Wannier down folding, octahedral distortions of Sr_2IrO_4 were suppressed at this stage, allowing for use of the I4/mmm space group. We used the lattice parameters reported in Ref. 16, and kept the Ir – O distance fixed to conserve overall bandwidth. Maximally localized Wannier functions for five Ir 5d orbitals were calculated using the Wien2Wannier [145] and Wannier90 packages [144]. The resulting tight-binding model was truncated beyond fifth nearest neighbour hopping integrals, with matrix elements smaller than 0.5 meV suppressed. The associated bandstructure is plotted in grey in Fig. 3.10a, and agrees well with the full DFT band structure (black curve). The quasi-two-dimensionality of the electronic structure has been strictly imposed through suppression of out-of-plane hopping terms. Staggered octahedral rotations of T=11.5 degrees can then be introduced as outlined in Ref. 148, recovering the true

I41/acd of both the pristine and substituted Sr₂IrO₄ lattice [16, 112]. The band structure in Fig. 3.10b reflects the effects of these distortions. Finally, spin-orbit coupling for the Ir *d*-orbitals has been added as:

$$\hat{H}_{SOC} = \lambda \ \hat{\mathbf{L}} \cdot \hat{\mathbf{S}},\tag{3.3}$$

resulting in the band structure plotted in Fig. 3.10c with the projection of $\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle$ indicated by the colourscale. While a $j_{\text{eff}} = 1/2$ ($\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = 1$) and $j_{\text{eff}} = 3/2$ ($\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = -1/2$) manifold can be defined, significant hybridization between the two persists due to the comparable energy scales of bandwidth and λ_{SOC} . To best match our experimental data we have set $\lambda_{SOC} = 0.45$, consistent with other reports [37, 107].

The tight-binding model defined here was used for the simulation of the ARPES matrix elements over a range of λ_{SOC} values, producing the black curve plotted in Fig. 3.8. The method uses the transition probability described by Fermi's golden rule [86, 121]:

$$\left| M_{i,f}^k \right|^2 \propto \left| \left\langle \phi_f^k \left| \mathbf{r} \cdot \boldsymbol{\varepsilon} \right| \psi_f^k \right\rangle \right|^2, \tag{3.4}$$

where ϕ_i^k is the initial state, derived from our tight binding model, ε is the light polarization vector, and ϕ_f^k is the final state wavefunction. The final state is assumed to be free-electron like, well justified by the high photon energies $h\nu \approx 50$ eV [86]. Fig. 3.10d illustrates the various components of the process. The matrix element can then be further calculated similar to the procedure outlined in 149. Matrix element calculations were performed using the chinook package [90].

3.A.4 Orbital weight for a two-site model with impurity potential

In Section 3.3.1 we discuss control of spin-orbit coupling dilution through the impurity potential. Here we derive the orbital weight for an eigenstate of a

two-site model, as controlled by hopping parameter t and impurity potential ϵ . We take for the Hamiltonian:

$$H = \begin{pmatrix} \epsilon & t \\ t & -\epsilon \end{pmatrix}, \tag{3.5}$$

which we normalize by the hopping strength t and write:

$$H = \begin{pmatrix} x & 1\\ 1 & -x \end{pmatrix}, \tag{3.6}$$

with $x = \epsilon/t$. The eigenvalues of this matrix are given by:

$$\lambda_{\pm} = \pm \sqrt{1 + x^2},\tag{3.7}$$

and eigenvectors:

$$\mathbf{v}_{\pm} = \frac{1}{\sqrt{A}} \begin{pmatrix} 1\\ \lambda_{\pm} - x \end{pmatrix}, \qquad (3.8)$$

with A the norm of the vector. We can now find the orbital weight as a function of the normalized impurity potential by taking the absolute value squared of one of the elements in the vector:

$$|v_{+,0}|^2 = \frac{1}{A} = \frac{1}{2 + 2x^2 - 2x\sqrt{1 + x^2}}.$$
(3.9)

We can rewrite this expression as:

$$|v_{+,0}|^2 = \frac{x + \sqrt{1 + x^2}}{2\sqrt{1 + x^2}} = \frac{1}{2} \left(\frac{x}{\sqrt{1 + x^2}} + 1\right), \qquad (3.10)$$

which corresponds to the functional form in the four-orbital model discussed in Section 3.3.1.

Chapter 4

Spin and k_z Resolved ARPES on Sr₂IrO₄

This chapter describes experiments studying the dispersion perpendicular (k_z) to the atomic layers and its effects on the spin-orbital entanglement. With these experiments we test validity of the $j_{\text{eff}} = 1/2$ model, and attempt to compare Sr_2IrO_4 to the superconducting cuprates, in particular La₂CuO₄. The two-dimensionality of the system will be investigated using photon energy dependent angle-resolved photoelectron spectroscopy (ARPES). Spin-ARPES will be used to investigate the spin-orbital entanglement in Sr_2IrO_4 , which should give a clear signature in light of the $j_{\text{eff}} = 1/2$ model. We ultimately find that the complex electronic structure in Sr_2IrO_4 cannot simply be explained as a two-dimensional pseudo-spin 1/2 insulator.

4.1 Introduction

Since the discovery of the cuprate superconductors [150], the physics community has put a lot of effort into finding other superconducting transitionmetal oxides (TMOs). The first successful attempt was the discovery of Sr_2RuO_4 [14], but many other compounds with similar properties had been suggested. Among them Sr_2IrO_4 [17], with the same structure as La_2CuO_4 and an antiferromagnetic ground state in the pristine "parent" compound.

A difference is that this system has a single hole in the t_{2g} manifold, rather than the e_g hole in the cuprates. Spin-orbit coupling has been suggested to play an important role in the insulating ground state of these materials, with t_{2q} orbitals possibly entangling into a filled $j_{\text{eff}} = 3/2$, and a half filled $j_{\text{eff}} = 1/2$ manifold [25]. It was quickly realized that this scenario brings Sr_2IrO_4 even closer to the quintessential cuprate superconductor: a (pseudo-)spin 1/2 Mott insulator on a square 2D lattice. Theoretical calculations predicted a superconducting state may exist in such a pseudo-spin 1/2 system when the system is electron doped [35], with more sophisticated analysis including all t_{2q} orbitals and strong spin-orbit coupling painting a similar picture [40, 41]. It was moreover found that the excitations of the pseudospins probed by resonant inelastic x-ray scattering (RIXS) are reminiscent of a Heisenberg model [37, 151], the expected low energy behaviour for a spin 1/2 Mott insulator [38, 39]. Promising observations were made in experiments: features reminiscent of doped Mott insulators, such as a particular gap shape and spatial distribution were found in scanning tunnelling microscopy (STM) [45], and a pseudogap was found in ARPES [44]. Stronger evidence was found using surface doped samples: using STM, a gap very reminiscent of those found in superconductors was observed [46], while in ARPES a d-wave gap was observed, a classic signature of the cuprate superconductors [47]. However, so far no signatures of bulk superconducting behaviour have been reported in the literature.

A possible explanation for the lack of superconductivity may be found in the multi-band nature of Sr₂IrO₄: the theoretical models predicting superconductivity are either done on a pseudo-spin 1/2 model [35], or a system in the strong spin-orbit coupling limit in which the $j_{\text{eff}} = 3/2$ states can be effectively projected out [40, 41]. Although spin-orbit coupling is large in this system (~ 0.45 eV [20, 37, 107]), it is still modest compared to the overall bandwidth of the t_{2g} bands [104–106]. Furthermore, it can be anticipated that the Ir t_{2g} bands have a more significant out-of-plane dispersion: not only are the 5d orbitals more extended than their 3 and 4d counterparts, the d_{xz} and d_{yz} bands have stronger π -like bonds between layers (as opposed to δ for the $d_{x^2-y^2}$ orbitals in cuprates). In this chapter, we will address these two arguments: the out-of-plane dispersion will be measured using photon energy dependent ARPES, and the spin-orbital entanglement will be measured using spin-ARPES. The observations indicate that the k_z dispersion in this compound is indeed significant. Moreover the highest unoccupied state can be found to be either of $j_{\text{eff}} = 1/2$ or $j_{\text{eff}} = 3/2$ character depending on k_z . We therefore conclude that the occupied states of Sr_2IrO_4 should be described by a three-dimensional multi-orbital Mott system, rather than a 2D, pseudo-spin 1/2 Mott insulator.

4.2 k_z dispersion in Sr₂IrO₄

In this section we will discuss the out-of-plane (k_z -axis) dispersion of Sr₂IrO₄, considering results from photon energy dependent ARPES experiments. We find that Sr₂IrO₄ has a significant inter-layer coupling, which will help to explain the results using spin-ARPES in Section 4.3, and has consequences for the description of Sr₂IrO₄ as a two-dimensional Mott insulator. It helps here to define exactly what is meant in this work by two-dimensionality. For such a multi-orbital system we require that no bands significantly change their character, or cross in energy as a function of the perpendicular momentum k_z . We will furthermore demonstrate that the electron removal spectrum of Sr₂IrO₄ is not the single-band spectrum that should be expected from a pure $j_{\text{eff}} = 1/2$ model.

4.2.1 Body centered tetragonal structure

In order to guide the reader through the various effects arising from the structure of Sr_2IrO_4 , this section presents a simple tight binding model in the same structure, to facilitate easy interpretation of the different effects. The structure of Sr_2IrO_4 is body centred tetragonal, which leads to the appearance of a few characteristic effects that will be discussed here.

In Sr_2IrO_4 , the IrO₄ octahedra are rotated around their z-axis by 11.5 deg in a checkerboard pattern. This implies that two separate iridium ions are needed to describe the unit cell of Sr_2IrO_4 . The symmetry reduces from the I4/mmm to the $I4_1/acd$ space group, with a c-axis stacking order ex-



Figure 4.1: Constant energy maps for a two-atom model in the body centred tetragonal structure. (a) Dispersion of the states along selected high symmetry points. (b,c) Constant energy contours at indicated energies. The locations of the cuts are indicated using coloured lines in (a).

panding the unit cell to four iridium atoms. To demonstrate the effects of folding, we calculate the dispersion for a structure with two iridium atoms. Although we describe two atoms per unit cell, no changes to the hopping integrals are made. The result is a dispersion that is mirrored along the zone anti-diagonal $((\pi, 0), (0, \pi))$, folding the bands at the $N(\pi, \pi)$ point to Γ and vice-versa.

The resulting dispersion is reminiscent of the band structure that is

frequently presented for Sr_2IrO_4 . Although this model neglects any changes to the band structure from the symmetry breaking, there is an important effect that can be clearly seen in Fig. 4.1(a). The bands originating from the N point $(\pi, \pi, 0)$, disperse with a different period due to the staggered nature of the reciprocal space BZ cells. This causes folded bands at Γ that disperse with this doubled periodicity, whereas in the unfolded band model no such bands were present. The dispersion from the X point $(\pi, 0, 0)$ to the X + Z point $(\pi, 0, \pi)$ is completely flat in this model only considering π hopping. Fig. 4.1(b-c) display cuts at constant energy (CE), effectively plotting contours at constant $k_y = 0$ and varying values of k_x and k_z , in the same way that data will be presented in the next section. The CE maps are shown for an identical k-range, with locations of relevant high-symmetry points indicated. The bands folded from the N point (b) show different periodicity from the original band at Γ (c). The reason is that whereas the original bands cut through the centres of the Brillouin zone (BZ) cells, the folded bands cut in between the staggered BZ cells, causing an apparent double periodicity. This is relevant since the interpretation of the electronic structure of Sr_2IrO_4 is such that the state at Γ arises from a folded band, which shows such double periodicity. Another feature arising due to the body centred tetragonal structure are the bands that "wave" in between the BZ cells visible in (c). Both these features are observed and will be discussed in Section 4.2.2.

4.2.2 Constant energy maps

As discussed in Section 2.3, assuming a free-electron-like final state, we can obtain the out-of-plane momentum using:

$$\frac{\hbar k_{\perp}^2}{2m} = E_k + V_0 - \frac{\hbar k_{\parallel}^2}{2m}.$$
(4.1)

The dependence of k_{\perp} on E_k implies we can measure the dispersion along k_z by changing the photon energy. This section will show the results from photon energy dependent measurements to highlight the k_z dispersion in


Figure 4.2: Overview of photon energy dependent results in Sr₂IrO₄. (a-d) Constant energy maps at E = -0.35 (a,b) and E = -0.55(c,d), using σ -polarized light (a,c) and π -polarized light. In (d) the faint elliptical pockets around Γ are highlighted by thin red lines on the right side of the centre. (e) Spectrum at $h\nu = 100$ eV (5.29 Å⁻¹). The red lines indicate the locations of the other data in this figure. (f) A series of MDCs from $h\nu = 60$ eV (4.18 Å⁻¹) to $h\nu = 100$ eV (5.29 Å⁻¹), with σ -polarization at E = -0.55 eV. The area encompassed is indicated by a red box in (c). 90

this system, in particular at the Γ point. Measurements presented in here were taken at the Advanced Lightsource at the Lawrence Berkeley National Laboratory at the Merlin endstation. Data are all collected at 150 K, to mitigate the effects of charging of the insulating Sr₂IrO₄ sample. Photon energy dependent measurements were done as the beamline specifications would allow, in this case from 50 eV to 120 eV, enabling the observation of almost two full reciprocal lattice cells. The Fermi level was corrected by taking measurements on electrically connected amorphous gold. For the inner potential, a value of $V_0 = 11$ eV was found by comparing the experimental data to the expected periodicity, in good agreement with the result in [152].

To provide a guide for the presentation of the acquired photon energy dependent data, we plot the band-structure of Sr_2IrO_4 in Fig. 4.2(e). The spectrum displays the valence band states at Γ and X. The red lines indicate the positions of cuts presented in other panels. We continue our overview of k_z -dependent effects by considering the constant energy cuts in Fig. 4.2. Figure 4.2(a) and (b) plot constant energy maps at $E_b = 0.35$, while (c) and (d) present maps at $E_b = 0.55$. Data for both σ - and π -polarization are shown ((a,c) and (b,d) respectively), with a clear difference in qualitative features between the two. Although it is challenging to find a clear periodic structure, the modulated intensity changes, especially those that repeat along k_z , are a clear sign of interlayer coupling. The intensity fluctuations arise due to the dipole matrix element (see Section 2.3.3), that varies as the composition of the initial state changes along the k_z direction. The photoemission matrix element is however also dependent on the final state (Section 2.3.3), and there can be a global change to these effects that may obfuscate the true periodic intensity fluctuations.

We now consider the dispersion of the X-states. To this end we show constant energy maps at higher energy, E = -0.35 ((a) and (b) in Fig. 4.2. An intensity pattern appears in these maps too, and furthermore, the perimeter of these states moves inward and outward going between the Γ and Z points. As discussed in the previous section, this is an effect that can be expected from the body centred crystal structure that Sr_2IrO_4 assumes. It causes a waving pattern between the different unit cells, which is discernible in Fig. 4.2.

A careful look at the state around Γ in Fig. 4.2(d) shows elliptical pockets that open and close with a periodicity twice that of the BZ. As discussed in Section 4.2.1, this is exactly the periodicity that a folded band in the body centred tetragonal (BCT) structure would yield. Continuing our discussion with the maps shown for σ -polarized light (I^{σ}), a careful inspection of Fig. 4.2(a) and (c) yields that there is also a pattern of nodes, but it is shifted with respect to the π -polarization (I^{π}) maps. The closing of the elliptical pockets is highlighted more clearly in Fig. 4.2(f), where a series of momentum distribution curves (MDCs) is plotted, in which the merging of two peaks can be clearly seen. The observation that this band is probed differently by different light polarizations indicates a k_z dependent symmetry change of the bands (I^{σ} probes d_{xz} , while I^{π} probes d_{yz} and d_{xy}). Moreover, as the dispersion is different for each polarization, this may be indicative that this state actually encompasses multiple, closely spaced bands, with different symmetries, a statement that will be explored in more detail in the next section.

4.2.3 Γ and X state dispersions.

We now turn to discussing cuts in k_z through the X and Γ points. These cuts allow better visualization of the amplitude of the oscillation in k_z . The results are presented in Fig. 4.3, where (a) and (c) show cuts through the Γ point, while (b) and (d) show cuts through the X point, both shown for I^{π} ((a) and (b)) and I^{π} ((c) and (d)) polarized light. Coloured markers are plotted at the peak maximum, extracted from fits these bands. We first turn our attention to X, which shows no significant periodic dispersion. This is in line with predictions from the model presented in Section 4.2.1, that shows negligible dispersion is expected to occur at the X point in the BCT structure when π -like hopping is dominant. Earlier photon energy dependent work on Sr₂IrO₄ shows a small dispersion of this state [152]. The amplitude of this oscillation is however small, and may be below our detectable limit. Meanwhile, (a) and (c) seem to show fluctuations that



Figure 4.3: Fits to k_z dispersion along the Γ and X point. (a-d) Spectra along the $\Gamma - Z$ (a,c) direction and the X (b,d) direction (indicated in Fig. 4.2 in panel (e)). Data are presented for π (a,b) and σ polarization. Peak maxima extracted from fits are plotted in green and purple for π and σ polarized light respectively. (e,f) EDC traces corresponding to the data presented in (c) and (d) respectively, including the fits to the peaks.



Figure 4.4: EDCs for σ and π polarizations at Γ (a) and X (b) at $h\nu = 60 \text{ eV} (k_z = 4.2 \text{ Å}^{-1}).$

are significantly larger, with a structure that appears to resemble the same periodicity also found in the constant energy maps in Fig. 4.2. The fits show that the peak positions change on the order of ~ 100 meV. No k_z dependent data at Γ was presented in [152] (this work concludes that k_z dispersion in these layered materials is negligible). The models in Section 4.2.1 however indicate that such k_z -dispersion would mostly arise at the Γ point, and not the X point, which is consistent with the data presented here. The dichotomy between the Γ and X point is highlighted in Fig. 4.3(e) and (f), which shows k_z dependent energy distribution curve (EDC)s. It is clear that whereas the state at the X point does not disperse in k_z significantly, the state at Γ does.

Interestingly, when comparing the two polarizations we find different peak maxima. This difference was alluded to in Section 4.2.2, and can be observed on careful inspection of Fig. 4.3(a) and (c). The difference becomes more evident when comparing the EDCs directly, as is done in Fig. 4.4. The data in Fig. 4.4 are taken at $h\nu = 60$ eV for both polarizations, at Γ (a) and X (b). While the peak positions of the EDCs at X line up well, those at Γ are approximately 100 meV apart. The peak maxima occurring at different energies for the polarizations, implies that this peak is comprised of more than one state with a small separation, with the individual states having different orbital symmetries. As the k_z dispersion moves these states relative to one another, different photon energies and polarizations give different results.

The observation of multiple of states the Γ point is seemingly at odds with a simple $j_{\text{eff}} = 1/2$ model, which predicts a single state throughout the Brillouin zone. Moreover, these data imply that the inter-layer coupling is strong enough to observe k_z -dispersion effects in photoemission, with an amplitude on the order of ~ 100 meV. In particular when states are close together like the states observed at Γ , this can have quite profound effects on these states (as for example demonstrated for Sr_2Ru_4 in Ref. 21). It turns out that this has strong consequences for their spin-orbital entanglement as will be discussed in the next section.

4.3 Circularly polarized spin-ARPES

We have used circularly polarized spin-ARPES (CPSA) to directly probe the entangled spin-orbital nature of the bands. This technique has been formerly used in [21, 23, 100, 101] and allows direct measurement of the various components of $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ by simultaneously selecting an orbital angular momentum using circular light and a spin using a spin detector. A full overview of the technique is given in Section 2.4.2, where we discuss the various matrix elements that give rise to the effect. In this section, we present data at various points in the Brillouin zone to investigate the spin-orbital entangled nature of the ground state, and test the validity $j_{\text{eff}} = 1/2$ scenario. Although data is presented all throughout the Brillouin zone, most attention is placed on results at normal emission ($\Gamma - Z$, depending on k_z), which are most easily interpreted, because the allowed final states are limited. The data presented are intended to demonstrate by direct experiment the entangled nature of the bands, and will lead to the conclusion that $\mathrm{Sr}_2\mathrm{IrO}_4$ cannot be simply described by an effective spin = 1/2 model.

Measurements in Section 4.3 were performed at the VESPA endstation [94] at the Elettra Sincrotrone Trieste. The endstation is equipped with a Scienta DA30 electron spectrometer with electrostatic deflectors. Using these deflectors it is possible to measure a $\sim 30^{\circ}$ solid angle without moving



Figure 4.5: k_z dependent tight binding model of Sr₂IrO₄. In (a) the colour encodes $\langle \mathbf{L} \cdot \mathbf{S} \rangle$, while in (b) the colour encodes $L_z S_z$. The bands that are referred to in the text are labelled in (b).

the sample. This way the date presented here was acquired without the need to rotate the sample. The spin was detected using a very low energy electron diffraction (VLEED) type detector (explained in detail in Section 2.4.1). All data were collected at 150 K to mitigate the effects of charging of the insulating Sr_2IrO_4 . The Fermi energy of the spin-detectors was measured using evaporated gold films, and the experimental energy resolution was measured to be 60 meV.

4.3.1 Interpretation of CPSA results for Sr₂IrO₄

To give a perspective to the resulting measurements, we briefly highlight the results that are expected from an *ab initio* tight binding model that includes interlayer hopping. The model contains the full rotated $I4_1/acd$ structure of Sr₂IrO₄ for the Ir t_{2g} orbitals. We use the Wannier Hamiltonian extracted from density functional theory (DFT) calculations as described in Section 3.A.3. Since we are interested in the k_z dispersion, we keep outof-plane hopping elements. We introduce distortions by rotating each atom from its local basis into the global basis by ± 12 degrees, in a checkerboard pattern within the layers, using the method described in [148]. The structure



Figure 4.6: High binding energy CPSA (green) measurements at Γ (a) and X (b). The sum of the photoemission signals is plotted in grey. The features in (a) are labelled in the way they are best represented by the bands in Fig. 4.5.

of the rotations is defined over 2 layers, giving a unit-cell size of 4 atoms, as defined in [16]. At this point, we project out the e_g orbitals to produce the final model. The calculated band structure is presented in Fig. 4.5 along various points in the BZ, with the expectation value for $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ (a) and $L_z S_z$ (b) for each state illustrated by the colour of the lines. A few things are important to note: firstly, the expectation value of $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ is highly k-dependent, in the case of $L_z S_z$ even changing sign for some of the bands. In particular, toward the X point the expectation of $L_z S_z$ reduces significantly, indicative of the itinerant nature of the Ir 5d orbitals, which was also pointed out in [153]. Secondly, the amplitude of the k_z dispersion for the bands labelled $j_{1/2}$ and $j_{3/2}$ is significant. Thirdly, the bands that are most likely observed in ARPES at Γ are the bands closest to E_F labelled $j'_{3/2}$. At odds with our findings in Section 4.2, these bands do not have significant k_z dispersion in this tight binding (TB) model.

Turning now to the experimental results obtained using CPSA, in Fig. 4.6 a dataset that was collected over a large binding energy range is presented. The CPSA is measured up to the oxygen states for the Γ (a) and X (b) point. The data presented here help to identify features from the simulations, and serve as an introduction for later results. In both panels, the CPSA signal (see Section 2.4.2) is plotted in green, and the sum of the four spin-polarization signals is plotted as the grey shaded area. The CPSA spectrum at the X point is flat and featureless within the indicated errors (the integrated signal can instead be observed to contain a significant amount of structure). This matches our initial expectation that spin-orbital entanglement is greatly reduced at X, and hopping terms dominate at that k-point in the Hamiltonian. Meanwhile at the Γ point there is a clear CPSA signal with a large number of peaks. Using the tight binding model presented in Fig. 4.6 it is possible to interpret the origin of these peaks. At this point it is good to reiterate the result from Section 2.4.2: at normal emission the sign of the CPSA is well defined, corresponding directly to $L_z S_z$. Therefore, any positive CPSA signal can be associated with a parallel spin-orbital entanglement, and vice-versa. Recalling the analysis in Section 1.4, a pure $j_{\rm eff} = 1/2$ state (dark blue in Fig. 4.5), should give rise to a positive peak, while pure $j_{\text{eff}} = 3/2$ states (dark red in Fig. 4.5) should show up negative. Even though in Fig. 4.5 full entanglement is not always reached, in the following we will refer to these states as $j_{3/2}$ -like and $j_{1/2}$ -like, as their CPSA signal still produces the sign of the expectation value for a fully entangled state.

Comparing the CPSA spectrum in Fig. 4.6(a) with the spin-orbital entanglement in Fig. 4.5(b) at the Γ point, we match up the positive and negative features in the CPSA with the blue and red bands respectively. Going from the high binding energy (large negative values) to lower binding energies, we identify a negative peak around E = -2 eV, followed by a strong positive at E = -1 eV, belonging to the unfolded bands labelled $j_{3/2}$ and $j_{1/2}$ in Fig. 4.5) respectively. The sharpest feature in the CPSA spectrum closest to E_F is observed to be positive. It seems most likely that this feature arises from folded band labelled $j'_{3/2}$ in Fig. 4.5(b), however, the red (negative) and white (zero) bands would give rise to a negative signal instead of a positive, hence the sharp upturn of the signal around E = -0.5 eV seems unexplained by *ab initio* band structure. The positive signal around E = -2.5 eV is also unexplained by the model presented in Fig. 4.5, but may arise from hybridization of the Ir states with the O band. Since this state is at higher binding energy we will not emphasize investigating its origin. From these CPSA measurements it is evident that the spin-orbital entanglement is strong, because a non-zero signal is measured all the way up to energies of ~ 3.5 eV. However, the variation of the CPSA signal at energies close to the Fermi energy indicates that a description in terms of a pseudo-spin 1/2 state may be challenged, as states vary drastically in a narrow region of energy.

4.3.2 k dependent CPSA

We continue our discussion of the data with spectra collected at various (k_x, k_y) points presented in Fig. 4.7, where CPSA traces are plotted for different k_x and k_y values. A schematic representation of the BZ with the various measurement points indicated is plotted in Fig. 4.7(e). The data display a reduction of the CPSA signal when moving away from normal emission, a property that is predicted by the TB simulation in Fig. 4.5. The yellow trace in Fig. 4.7(c,d) plots the CPSA signal measured in the *y*-axis channel, which effectively measures the L_zS_y term, which is zero as expected. Although CPSA has been successfully measured away from the Γ point [90], it should be pointed out that effects reducing the CPSA signal away from normal emission discussed in Section 2.4.2 may affect the signal. Nevertheless, such a drastic decrease of the CPSA signal throughout the Brillouin zone, highlights the change of the spin-orbital entanglement in reciprocal space.

4.3.3 k_z dependent CPSA

We now turn to a discussion of k_z dependent CPSA, which has as an advantage that all measurements can be done at normal emission, and the CPSA relates directly to the spin-orbital entanglement. The results are presented in Fig. 4.8, with an overview of the k_z position of the points studied by spin-ARPES displayed in panel (a), plotted over the photon energy dependent



Figure 4.7: k-dependent CPSA measurements using $h\nu = 64 \text{ eV}$. (a-d) CPSA measurements along k_x , measured at the points indicated in (e). The green curves represent the CPSA, with the grey shaded area the sum of the spin-signals. The yellow markers in (c) and (d) indicate the CPSA in the y channel. (f-h) CPSA measurements along the k_y direction (locations also indicated in (e)).

ARPES data previously presented in Fig. 4.2.

Photon energies were chosen such that they span most of the BZ, or as the beamline would allow. The data presented in Fig. 4.8(b) indicate the parallel signal $(\sqrt{I_{\uparrow}^{\oplus}I_{\downarrow}^{\oplus}})$ in blue and the antiparallel signal $(\sqrt{I_{\uparrow}^{\oplus}I_{\downarrow}^{\oplus}})$ in red. The CPSA signal can be found in panel (c) for the studied photon energies, with a grey line indicating the sum of the spin-polarization data. While the absolute changes to the parallel and anti-parallel signal are small, the progression of the CPSA signal is significant. The signal from the previously discussed $j_{3/2}$ (negative) and $j_{1/2}$ (positive) bands is present in all curves. The part of the spectrum at $E - E_F \gtrsim -0.5$ eV that appears as a positive peak in Fig. 4.6 at 64 eV can be seen to change sign as the photon energy decreases to 52 eV. The feature at E = -0.5 eV that causes this behaviour is precisely the feature that was observed to be dispersing in Section 4.2. It should be stressed that this is a significant result: the character of the spinorbital entanglement changes from parallel to anti-parallel through changing k_z , drastically changing the character of the states closest to E_F .

Sample Consistency

To show the consistency of the measurements in Fig. 4.8, we present in Fig. 4.9 a collection of different samples measured at different times all showing the same behaviour of both positive and negative $\langle \mathbf{L} \cdot \mathbf{S} \rangle$. These data provide convincing evidence that the results shown in this chapter are intrinsic sample properties, since the measurements can be repeated well within the signal uncertainty.

Considering the model presented in Fig. 4.5, such drastic dispersion and complete reversal of the spin-orbital entanglement is unexpected for these states: as such it seems that an *ab initio* derived model cannot explain these effects. It is possible that a a multiplet of states should be considered as in [154]. At this point it is also useful to point out that through the construction of the system in terms of j_{eff} states, hybridization between these spin-orbit states is possible through the original hopping elements, in both the in- and out-of-plane channels. As the j_{eff} orbitals are constructed



Figure 4.8: Photon energy dependent CPSA measurements. (a) Overview of of of the reciprocal space with green markers indicating the locations of the photon energy dependent measurements. The constant energy map is identical to the one in panel (c) of Fig. 4.2. (b) Plots of the parallel (blue) and anti-parallel (red) signal. (c) CPSA signal (green) plotted with the sum of the spin signals (grey).



Figure 4.9: CPSA repeatability. The two panels highlight the repeatability on different samples and beamtimes for two photon energies (64 eV in (a) and 51.7 eV in (b)). The different samples are S1 and S2, with S2 measured on a second occasion as S2-2.

from individual t_{2g} states that overlap on neighbouring sites, hybridization between the different j_{eff} states persists. This hybridization may play a role in the drastic changes that are observed upon changing k_z . Regardless of the precise origin of the change in sign of this state at -0.5 eV, the implication seems clear: the small but significant k_z dispersion in this system is strong enough to change the character of the highest electron removal state from aligned parallel to anti-parallel. This makes a description in terms of a pseudo-spin 1/2 model impossible, and signals that even a low energy model should consider excitations of the $j_{\text{eff}} = 3/2$ states too.

4.3.4 Slab Simulation of Sr₂IrO₄

In order to better understand the results from our CPSA measurements, we perform matrix element simulations using the chinook package [90].

To capture the effects arising from the k_z dependence, including possible photoelectron interference, we construct a slab model, in a similar way as described in Section 4.3.1. We use the same base Hamiltonian, but for the simulations in the following section, we keep the full 5-orbital 5*d* manifold for all the iridium atoms. We proceed to construct a slab along the c-axis of the crystal, consisting of 6 unit cells (12 atomic layers), resulting in a basis size of $12 \times 2 \times 10 = 240$ orbitals.

In order to simulate the gap, we have added an antiferromagnetic ordering through an S_z term, using the Hamiltonian:

$$H = \sum_{i,\nu,\sigma} dm_i S^z_{i,\nu}.$$
(4.2)

Here, *i* and ν are the atom and orbital index, $S_{i,\nu}^z$ the spin, m_i the magnetization, and *d* a parameter (related to the Coulomb interaction) that we set to d = 0.2 eV for an appropriate gap size. We set m_i according to $m_1 = m_2 = -m_3 = -m_4 = 1$, where atom 1 and atom 3 are in the same layer, and atom 2 and atom 4 are in the same layer, forming an antiferromagnet, with a checkerboard pattern.

The band structure for this system is presented in Fig. 4.10(b). Although all bands are flat along the $\Gamma - Z$ axis, the effective k_z dispersion for this slab model is captured by the series of bands at different binding energies formed by the inter-layer coupling. In the limit of an infinite sized crystal along the *c*-axis, the original dispersion would be recovered.

We proceed to calculate a simulated spectrum for various polarizations. As an example, the spectrum obtained using σ -polarization is shown in Fig. 4.10(a), which is in reasonable agreement with the experimental data presented in Fig. 4.2(e). Clearly visible are the hole like pockets centred at X, and the broad band around E = -1 eV.

What is not captured well in this simulation is the intensity of the folded band at Γ , around E = -0.5 eV, which appears more intense in experiments. Considering the discussion around unfolding in Section 2.2, for such a band to appear with high intensity in an experiment, there needs to be a significant potential to break the symmetry, in this model arising from rotations and antiferromagnetism. It is possible that the antiferromagnetism as it is treated in these simulations does not capture the full extent of symmetry breaking potential.

We continue to calculate the CPSA signal, by simulating $I^{\sigma,\epsilon}$ and taking



Figure 4.10: Slab model for Sr₂IrO₄ including AFM order. (a) Calculated ARPES spectrum using σ -polarization from the slab model band structure plotted in (b). (c) Calculated CPSA spectrum at Γ . The negative and positive peaks arise from the $j_{3/2}$ and $j_{1/2}$ like bands. (d) The CPSA spectrum calculated for the as a function of the out-of-plane momentum k_z .

the geometric mean as:

$$\frac{\sqrt{I^{\oplus,\downarrow}I^{\oplus,\uparrow}} - \sqrt{I^{\oplus,\downarrow}I^{\oplus,\uparrow}}}{\sqrt{I^{\oplus,\downarrow}I^{\oplus,\uparrow}} + \sqrt{I^{\oplus,\downarrow}I^{\oplus,\uparrow}} + \epsilon},\tag{4.3}$$

with ϵ a small constant to avoid zero-division, that we set as $0.01 \cdot \max(I^{\sigma,\epsilon})$, chosen to give the best agreement with experiments. The resulting CPSA curve at the Γ point is shown in Fig. 4.10(c), which can be see to match some of the aspects of the data presented in Fig. 4.8: the negative and positive signals belonging to the $j_{\text{eff}} = 3/2$ and $j_{\text{eff}} = 1/2$ states. A small peak close to E_F is also visible, a combination of the downturn arising from the folded $j_{\text{eff}} = 3/2$ band, with a positive signal from the $j_{\text{eff}} = 1/2$ above the Fermi energy, which is not seen in experiment. The image presented in Fig. 4.10(d) explores the k_z dependence of the CPSA signal for this slab model. While a change in k_z is clearly visible, Fig. 4.10 fails to reproduce the dramatic sign change seen in experiment.

In the rest of this section, we will investigate various properties that can influence the CPSA signal at Γ as a function of photon energy (and thereby k_z), to get in idea of the physical mechanism that could cause the switching of signal observed in Section 4.3.

Strength of Spin-Orbit Coupling

The first parameter we consider is spin-orbit coupling (SOC). Although SOC coupling is an atomic property with a nominal value ($\lambda_{\rm Ir} \sim 0.4$ eV [20]), actual observations seem to differ [44, 106, 148], which is possibly explained by the presence of the Coulomb interaction [132, 133], magnifying the Hamiltonian terms associated with SOC. We present simulations for $\lambda \in \{0.35, 0.45, 0.65\}$ eV in Fig. 4.11(a-c). Similar to the results presented in Fig. 4.10, the unfolded $j_{\rm eff}$ states are visible most clearly, with a small signal coming from the folded band close to E_b . This state is expected to give a negative (red) CPSA signal, but in panels b and c, the intensity from the unfolded $j_{\rm eff} = 1/2$ state overpowers this small signal. This negative (red) signal can be seen in panel a, where the spin-orbit coupling is smaller,



Figure 4.11: CPSA simulations for different values of λ_{SOC} , each as a function of k_z , as simulated for the antiferromagnetic slab model. The values for λ_{SOC} are indicated in each panel in the top right corner.

which results in the $j_{\text{eff}} = 1/2$ being further away from the folded $j_{\text{eff}} = 3/2$ band. These simulations demonstrate that a reasonable change of spin-orbit coupling is unable to reproduce a switch in sign as we find in our data.

The Mean Free Path

In order to investigate the possibility of photoelectron interference causing a rapid change in photoemission intensity dependent on k_z as seen for topological insulators in Ref. 96, we calculate the CPSA signal for various sizes of the mean free path. By modulating the intensity coming from layers using an exponential decay as is implemented in chinook we can investigate whether a particular value for the mean free path could explain the observed results. The results are presented in Fig. 4.12, where k_z dependent CPSA curves are plotted for various values of the mean free path. An interesting effect appears in these simulations: the amplitude of the k_z dispersion is dependent on the value of the mean free path in this slab model: when the value is so low that only a single layer is probed (e.g. 1 Å in (a)), the lack of probed coupling between layers, results in only a flat band being observed. The larger the mean free path, the more layers are probed and the stronger the apparent k_z dispersion (b,c). It is clear that aside from the observed



Figure 4.12: CPSA simulations for different values of the photoelectron mean free path. CPSA signal plotted as a function of k_z is presented for 1.0 (a), 4.8 (b) and 20.0 Å(c). (d) The dependence at Γ as a function of mean free path.

variation of the k_z dispersion, no big changes to the sign and magnitude of the CPSA signal occur, so we conclude that the mean free path can be ruled out as a source of observations presented in Fig. 4.8.

4.3.5 Magnitude of the k_z hopping terms.

Finally, we have modified the out-of-plane hopping elements to see if that could yield the desired result. To test that hypothesis, we rescaled all outof-plane hopping elements by a fixed factor and simulated the CPSA signal as a function of k_z . The results are presented in Fig. 4.13, where the effect is clearly visible: the dispersion of the states, seen as a shift of the peaks, is clearly enhanced at higher factors. While no changes in sign are observed for an enhancement of 2, for an enhancement of 4, the sign of the CPSA signal



Figure 4.13: CPSA simulations with enlarged k_z hopping elements. The hopping elements are multiplied by a factor 1 (a), 2 (b) or 4 (c).

changes at $k_z = \frac{\pi}{c}$. While this has so far been the only parameter that can be seen to change the sign as a function of k_z , there are two issues with this: an enhancement of 4 seems too large to be physically justifiable, as it would put the out-of-plane hopping at ~ 0.1 eV similar to the in-plane hopping (~ 0.3 eV). Furthermore, although a change in sign is observed, the peak itself does not change direction. It seems that this increased k_z hopping is in fact moving the $j_{\text{eff}} = 1/2$ state closer, thereby adding a background to the state closest to E_F .

4.4 Conclusion

The results presented both for photon energy dependent ARPES and CPSA measurements have a clear consequence. Firstly, from these data it is evident that Sr_2IrO_4 is certainly not two-dimensional, as interlayer coupling is strong enough to cause significant k_z dispersion likely caused by the extended character of the Ir 5*d* orbitals. Secondly, while spin-orbit coupling in Sr_2IrO_4 is undoubtedly very strong, the suggestion that a pseudo-spin 1/2 model is able to describe the ground state for this system is challenged by the reversal of spin-orbital entanglement that we observe. The photon energy dependent results suggest that there are multiple states in close proximity around the Γ -point, that move with respect to each other, dependent on k_z .

The CPSA data confirm this result, and adds that the spin-orbital entanglement changes from parallel to anti-parallel. To appropriately describe the occupied states of Sr₂IrO₄, it is therefore necessary to take into account the full, multi-orbital Mott physics as the bands are not separated well enough to fully project out the $j_{\rm eff} = 3/2$ states.

Chapter 5

Conclusion

This thesis has covered various topics relating to Sr_2IrO_4 and spin-orbit coupling. While most efforts were focussed specifically on Sr_2IrO_4 , these conclusions have further reaching effects. We readdress here the main questions of this thesis: firstly, the role of spin-orbit coupling in a correlated relativistic insulator such as Sr_2IrO_4 and secondly, whether Sr_2IrO_4 can be described by a pseudo-spin 1/2 model.

5.1 Spin-orbit controlled metal insulator transition in Sr_2IrO_4

With the suggestion of Sr_2IrO_4 as a relativistic Mott insulator [25], spin-orbit coupling was tentatively added to the canonical phase diagram describing correlated insulators [6]. However, while the insulating state in Sr_2IrO_4 has been believed to be stabilized by spin-orbit coupling, direct evidence has so far been lacking. In Chapter 3, a transition into a metallic state induced by a dilution of spin-orbit coupling was presented, establishing SOC as a fundamental parameter in the field of multi-orbital correlated insulators. Driving the metal-insulator transition in this material by SOC is not only the first demonstration of such a SOC controlled metal-insulator transition (MIT), but moreover provides direct evidence for the essential role of SOC in stabilizing the insulating state in Sr_2IrO_4 . In particular, we have substituted Ir in Sr_2IrO_4 with Ru and Rh to make well-defined changes to the effective value of spin-orbit coupling which drives the metal-insulator transition. Ru and Rh, having significantly lower spin-orbit coupling than Ir, both drive a MIT but at surprisingly different critical concentrations. It is found that the dilution of spin-orbit coupling, controlled by the impurity potential associated with the two different species, is what explains the dichotomy in critical concentrations. For Rh, no such impurity potential is present and spin-orbit coupling is reduced effectively. For Ru however, a potential of ~ 0.25 eV hinders such dilution of SOC and the rate of the transition is significantly retarded. ARPES measurements, interpreted using matrix element analysis confirm the predicted results: spin-orbit coupling is effectively reduced when Rh is substituted, but not for Ru.

A corollary to our results is the method with which spin-orbit coupling was observed. The entanglement of t_{2g} states by spin-orbit coupling mixes orbitals of different symmetries, causing a well-defined intensity change through the photoemission dipole matrix element. This method is not unique to Sr₂IrO₄ and may find applications in other t_{2g} systems where spin-orbit coupling is of importance.

Furthermore, our observation of impurity potential controlled SOC mixing is well explained by a simple two-site tight binding model without any specific considerations of electronic structure. The generic result is that the impurity potential controls hybridization between the sites, and the degree of hybridization controls the amount of spin-orbit coupling dilution. Since these results are obtained and explained on such a minimal model, with no specifically tuned crystal parameters, we expect these results to be valid generally for spin-orbitally coupled multi-species systems in which orbitals hybridize. These results are particularly helpful in elucidating pursuits to modify spin-orbit coupling by valence ion substitution. This strategy has been successful in GaAs using Bi substitution [135] for example. It may also clarify interpretation of attempts to enhance spin-orbit coupling in graphene through adatom deposition [123, 124, 141–143]. Although theory predicts large gap appearing at the Dirac cone of graphene when heavy elements are deposited [123, 124], experimentally such a gap is not observed [142]. It is possible that an impurity potential, or low hopping integrals prevent hybridization with the graphene lattice, and thereby preclude substantial enhancement of spin-orbit coupling. Furthermore it could help to enlighten the physics of attempts to drive a transition to a trivial state in topological insulators [136–140]. The results presented here about spin-orbit coupling set clear constraints on how to to think about these experiments, and make explicit suggestions on how to continue them. It not only shows how spin-orbit coupling can be successfully diluted, it also explains directly how to make use of the impurity potential and hybridization to fine-tune the obtained results.

5.2 Spin- and k_z -resolved photoemission on Sr_2IrO_4

Since the discovery of the cuprate superconductors [89, 150], an intense effort in the field has been made to observe superconductivity in other transition metal oxides. Sr_2IrO_4 appears to be a prime candidate: not only is the structure identical to that of La_2CuO_4 , it hosts an unexpected (Mott) insulating phase, with an antiferromagnetic ordering. Moreover, it was suggested that the ground state in Sr_2IrO_4 is pseudo-spin 1/2, because strong spin-orbit coupling could entangle the t_{2q} states into a filled $j_{\text{eff}} = 3/2$ and half-filled $j_{\rm eff} = 1/2$ state. The combination of these properties (two-dimensional, square transition-metal oxide lattice, half filled pseudo-spin 1/2 Mott insulator) are the quintessential ingredients attributed to high-temperature superconductivity. Yet, although some promising observations have been made [44–47], no signs of bulk-superconducting behaviour have been detected. In Chapter 4 the use of photon energy dependent ARPES has demonstrated that the k_z dispersion in this compound is significant (~ 100 meV) since in this energy window multiple states are observed, having distinct orbital symmetry for horizontally and vertically polarized light.

We furthermore study the spin-orbital entanglement directly by performing CPSA measurements. The results show that the spin-orbital entanglement is strong at energies throughout the Ir d manifold at normal emission. However, results also show that the spin-orbital entanglement reduces significantly away from normal emission toward the X-points, a feature that is explained by considering the increased itinerancy for those states. At normal emission, the state closest to E_F shows a complete reversal of the spin-orbital entanglement when changing k_z . This result agrees with the observations from photon energy dependent ARPES, and implies that Sr_2IrO_4 cannot simply be described by a $j_{\text{eff}} = 1/2$ model. Not only does the spinorbital entanglement change significantly with (k_x, k_y) , but the complete reversal of spin-orbital entanglement can only be explained if the $j_{\text{eff}} = 3/2$ are explicitly taken into account. These observations challenge the validity of the treatment of Sr_2IrO_4 as a pseudo-spin 1/2 model. The results presented here instead require that models constructed for Sr_2IrO_4 , take into account all three t_{2g} orbitals, and suggest that Sr_2IrO_4 should be considered a "relativistic multi-orbital Mott insulator", rather than a " $j_{\text{eff}} = 1/2$ Mott insulator".

Our results may furthermore shed light on the necessary ingredients for superconductivity in transition metal oxides: the studies suggesting superconductivity in Sr_2IrO_4 all take as a starting point either a pseudo-spin 1/2 model or strong ($\lambda > t$) spin-orbit coupling [35, 40, 41] limited to two dimensions. Our finding that Sr_2IrO_4 is not in fact spin 1/2, nor fully twodimensional suggests that those two properties are key pieces in the puzzle of high-temperature superconductivity.

5.3 Conclusion

This thesis has focussed on variations of a single compound with an extensive amount of work spent towards understanding the ground state of Sr_2IrO_4 and has therefore made significant strides in the understanding of relativistic correlated insulators. It has been shown that the ground state of Sr_2IrO_4 is strongly influenced by spin-orbit coupling, and that spin-orbit coupling should be considered as a fundamental parameter of multi-orbital Mott physics. However, it has also been clearly shown that SOC is not strong enough to describe Sr_2IrO_4 as a pseudo-spin 1/2 model, and it is important to consider the full manifold of t_{2g} orbitals. This has important consequences for the characterization of Sr_2IrO_4 as a model system for the superconducting cuprates and suggests that a system in which relative effects of spin-orbit coupling are stronger, may in fact be a more suitable candidate for observing superconductivity.

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Appendix A

Overview of expectation values spin-orbit entangled states

Here, tables are provided for frequently used states, including their representations in other relevant bases, as well as expectation values that are often referenced and used.

	state	Y_{ℓ}^m	L_z	S_z	J_z	$L_x S_x$	$L_z S_z$	$\mathbf{L}\cdot\mathbf{S}$
	$ 5/2,5/2\rangle$	$ 2,\uparrow angle$	2	$\frac{1}{2}$	$\frac{5}{2}$	0	1	1
j = 5/2	$ 5/2,3/2\rangle$	$\sqrt{\frac{4}{5}} \left 1, \uparrow \right\rangle + \sqrt{\frac{1}{5}} \left 2, \downarrow \right\rangle$	$\frac{12}{10}$	$\frac{3}{10}$	$\frac{3}{2}$	$\frac{4}{10}$	$\frac{2}{10}$	1
	$ 5/2,1/2\rangle$	$\sqrt{rac{6}{10}}\left 0,\uparrow ight angle+\sqrt{rac{4}{10}}\left 1,\downarrow ight angle$	$\frac{4}{10}$	$\frac{1}{10}$	$\frac{1}{2}$	$\frac{6}{10}$	$-\frac{2}{10}$	1
j = 3/2	3/2,3/2 angle	$\sqrt{rac{1}{5}}\left 1,\uparrow ight angle-\sqrt{rac{4}{5}}\left 2,\downarrow ight angle$	$\frac{18}{10}$	$-\frac{3}{10}$	$\frac{3}{2}$	$-\frac{4}{10}$	$-\frac{7}{10}$	$-\frac{3}{2}$
	$ 3/2,1/2\rangle$	$\sqrt{rac{4}{10}} \ket{0,\uparrow} - \sqrt{rac{6}{10}} \ket{1,\downarrow}$	$\frac{6}{10}$	$-\frac{1}{10}$	$\frac{1}{2}$	$-\frac{6}{10}$	$-\frac{3}{10}$	$-\frac{3}{2}$

Table A.1: Table of expectation values for the spin-orbit coupled $\ell = 2$ states.

	state	Y_{ℓ}^m	L_z	S_z	J_z	$L_x S_x$	$L_z S_z$	$\mathbf{L}\cdot\mathbf{S}$
j = 3/2	$ 3/2,3/2\rangle$	$ 1,\uparrow\rangle$	1	$\frac{1}{2}$	$\frac{3}{2}$	0	$\frac{3}{6}$	$\frac{1}{2}$
	$ 3/2,1/2\rangle$	$\sqrt{rac{2}{3}}\left 0,\uparrow ight angle+\sqrt{rac{1}{3}}\left 1,\downarrow ight angle$	$\frac{2}{6}$	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{2}{6}$	$-\frac{1}{6}$	$\frac{1}{2}$
j = 1/2	1/2,1/2 angle	$\sqrt{rac{1}{3}} \left 0, \uparrow ight angle - \sqrt{rac{2}{3}} \left 1, \downarrow ight angle$	$\frac{4}{6}$	$-\frac{1}{6}$	$\frac{1}{2}$	$-\frac{2}{6}$	$-\frac{2}{6}$	-1

Table A.2: Table of expectation values for the spin-orbit coupled $\ell = 1$ states.

	state	Y_{ℓ}^m	L_z	S_z	J_z	$L_x S_x$	$L_z S_z$	$\mathbf{L}\cdot\mathbf{S}$
jeff = 3/2	3/2,3/2 angle	$i \ket{2, -1, \uparrow}$	-1	$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$
	$ 3/2,1/2\rangle$	$\sqrt{rac{2}{3}}\left 0_{eff},\uparrow ight angle+i\sqrt{rac{1}{3}}\left 2,-1,\downarrow ight angle$	$-\frac{2}{6}$	$\frac{1}{6}$	$-\frac{1}{6}$	$-\frac{2}{6}$	$\frac{1}{6}$	$-\frac{1}{2}$
	$ 3/2, -1/2\rangle$ $ 3/2, -3/2\rangle$	$ \begin{array}{l} \sqrt{\frac{2}{3}} \left 0_{eff}, \downarrow \right\rangle - i \sqrt{\frac{1}{3}} \left 2, 1, \downarrow \right\rangle \\ - i \left 2, 1, \downarrow \right\rangle \end{array} $	$\frac{2}{6}$ 1	$-\frac{1}{6} -\frac{1}{2}$	$\frac{\frac{1}{6}}{\frac{1}{2}}$	$-\frac{2}{6}$ 0	$-\frac{\frac{1}{6}}{-\frac{1}{2}}$	$-\frac{1}{2} \\ -\frac{1}{2}$
jeff = 1/2	$ 1/2, 1/2\rangle$ $ 1/2, -1/2\rangle$	$\begin{array}{l} \sqrt{\frac{1}{3}} \left 0_{eff}, \uparrow \right\rangle - i \sqrt{\frac{2}{3}} \left 2, -1, \downarrow \right\rangle \\ \sqrt{\frac{1}{3}} \left 0_{eff}, \downarrow \right\rangle + i \sqrt{\frac{2}{3}} \left 2, 1, \uparrow \right\rangle \end{array}$	$-\frac{4}{6}$ $\frac{4}{6}$	$-\frac{1}{6}$ $\frac{1}{6}$	$-\frac{5}{6}$ $\frac{5}{6}$	$\frac{\frac{2}{6}}{\frac{2}{6}}$	$\frac{2}{6}$ $\frac{2}{6}$	1 1

Table A.3: Table of expectation values for the spin-orbit coupled t_{2g} ($\ell_{\text{eff}} = 1$) states.

	t_{2g} construction
jeff = 3/2	$\frac{1}{\sqrt{2}} \left(d_{yz},\uparrow\rangle + i d_{xz},\uparrow\rangle \right) \\ \frac{1}{\sqrt{6}} \left(d_{yz},\downarrow\rangle + i d_{xz},\downarrow\rangle - 2 d_{xy},\uparrow\rangle \right) \\ \frac{1}{\sqrt{6}} \left(- d_{yz},\uparrow\rangle + i d_{xz},\uparrow\rangle - 2 d_{xy},\downarrow\rangle \right) \\ \frac{1}{\sqrt{2}} \left(- d_{yz},\downarrow\rangle + i d_{xz},\downarrow\rangle \right)$
jeff = 1/2	$\frac{1}{\sqrt{3}} \left(d_{yz},\downarrow\rangle + i d_{xz},\downarrow\rangle + d_{xy},\uparrow\rangle \right) \\ \frac{1}{\sqrt{3}} \left(- d_{yz},\uparrow\rangle + i d_{xz},\uparrow\rangle + d_{xy},\downarrow\rangle \right)$

Table A.4: Construction of the j_{eff} states in terms of the t_{2g} orbitals.

	state	Y_ℓ^m	L_z	S_z	J_z	$L_x S_x$	$L_z S_z$	$\mathbf{L}\cdot\mathbf{S}$	t_{2g}
j^+	$\begin{array}{c} j^+,\uparrow\rangle \\ j^+,\downarrow\rangle \end{array}$	$\begin{array}{l} 2,1,\uparrow\rangle \\ 2,-1,\downarrow\rangle \end{array}$	1 -1	$-\frac{\frac{1}{2}}{\frac{1}{2}}$	$-\frac{3}{2}$	0 0	$\frac{\frac{1}{2}}{\frac{1}{2}}$	$\frac{\frac{1}{2}}{\frac{1}{2}}$	$\frac{\frac{1}{\sqrt{2}}\left(\left d_{xz},\uparrow\right\rangle+i\left d_{yz},\uparrow\right\rangle\right)}{\frac{1}{\sqrt{2}}\left(\left d_{xz},\downarrow\right\rangle-i\left d_{yz},\downarrow\right\rangle\right)}$
<i>j</i> ⁻	$ j^-,\uparrow angle\ j^-,\downarrow angle$	$\begin{array}{l} 2,1,\downarrow\rangle \\ 2,-1,\uparrow\rangle \end{array}$	1 -1	$-\frac{1}{2}$ $\frac{1}{2}$	$-\frac{\frac{1}{2}}{-\frac{1}{2}}$	0 0	$-\frac{1}{2}$ $-\frac{1}{2}$	$-\frac{1}{2}$ $-\frac{1}{2}$	$ \begin{array}{l} \frac{1}{\sqrt{2}} \left(\left d_{xz}, \downarrow \right\rangle + i \left d_{yz}, \downarrow \right\rangle \right) \\ \frac{1}{\sqrt{2}} \left(\left d_{xz}, \uparrow \right\rangle - i \left d_{yz}, \uparrow \right\rangle \right) \end{array} $

Table A.5: Table of expectation values for the spin-orbit coupled d_{xz} and d_{yz} states.